Supplementary Information (SI) for Journal of Materials Chemistry C.

Supporting Information

Non-Halogen Solvent Processed All-Polymer Organic Solar Cells with Improved Vertical Phase Morphology

Xinrui Li [a], LuYe Cao [b], Xiaoyang Du [b,], Jianchuan Liu [a], Hui Lin [b], Caijun Zheng [b], Silu Tao [b,*].*

[a] *School of Electrical Engineering and Electronic Information, Xihua University, Chengdu 610039, China*

[b] *School of Optoelectronic Science and Engineering, University of Electronic Science and Technology of China (UESTC), Chengdu 610054, China*

**Corresponding author: Silu Tao Email addresses: silutao@uestc.edu.cn*
Xiaoyang Du Email addresses: xiaoyangdu@uestc.edu.cn

1. Experimental Section

Materials: PM1, PBDB-TF and PDIN were purchased from Solarmer Materials Inc. PYF-T-o was purchased from Shenzhen Yirou Photovoltaic Technology Co. Hole transport material PEDOT: PSS was purchased from Xi'an p-OLED Technology Corp. Other related materials and solvents were bought from Alfa Chemical Inc. or Sigma-Aldrich Corp and used directly.

Device fabrication: All devices in this paper adopted a conventional structure that Indium Tin Oxide (ITO)/PEDOT: PSS/Active Layer/PDIN/Ag. The glass substrates with ITO were sonicated in ethanol, acetone and ethanol solvent for 30mins respectively, then blown dry with nitrogen and put into UV ozone treatment for 15mins. The PEDOT: PSS was soon coated onto the substrates (4000rpm, 30s) and annealed at 150°C for 15 mins in the air atmosphere. Afterward, the substrates coated with PEDOT: PSS were transferred to the glove box. For BHJ-type devices, the active layer of PM1: PYF-T-o (1:1.2) or PM1: PBDB-TF: PYF-T-o (0.97: 0.03: 1.2) was prepared by dissolving materials in o-xylene (O-XY) solution at a total concentration of 17.5 mg/mL with 1% v/v CN and spin coated at 1500 rpm for 59 s to form. For LbL-type devices, PM1 or PM1: PBDB-TF (0.97: 0.03) was first dissolved in O-XY solvent at a concentration of 9.5 mg/ml and then spin-coated to form the donor layer, the spin-coating time is 60s, the spin rate is 1200 rpm and the volume of the solution is 30μL. PYF-T-o was also dissolved in O-XY solvent at a concentration of 9 mg/ml with 1% v/v CN and then was spin-coated onto the donor layer. The spin-coating time for depositing the PYF-T-o layer is 60s, the spin rate is 2500 rpm and the volume of PYF-T-o solution is 16μL. Next, an extra pre-annealing at 100 °C for 5 mins was performed for BHJ-type and LbL-type devices. PDIN was dissolved in methanol (2 mg mL^{-1}) with 0.3% acetic acid. And the prepared PDIN solution was spin-coated onto the active layer at 5000 rpm for 30 s. Finally, 100 nm silver (Ag) electrode was deposited by vacuum vapor deposition under vacuum conditions of $5*10^{-4}$ Pa.

Measurement Method: Hitachi U-3010 ultraviolet-photoluminescence spectroscopy is used to measure the absorption spectrum of films. The current density versus voltage (J-V) curves are measured adopting Newport Oriel-Sol3A to simulate AM 1.5G sunlight and processing with Keithley 2400 source meter. The external quantum efficiency (EQE) is obtained by the QEX10 quantum 16 Efficiency Measurement System. The mobility of hole (μ_h) and electron (μ_e) for devices are calculated by space charge limiting current (SCLC) method. The structures of ITO/ PEDOT: PSS/ Active layer/ MoO_3/ Ag and ITO/ ZnO/ Active layer/ PDIN/ Ag are adopted to fabricate hole-only and electron-only devices, respectively. Transient photocurrent (TPC) and Transient photovoltage (TPV) were measured by PD-RS system and then the obtained TPC and TPV curves were fitted by Graphic User Interface measurement software. Morphology of blended films are conducted though atomic force microscope (AFM, Dimension Icon) and transmission electron microscope (TEM, Talos F200S G2), respectively. The contact angle (CA) test is obtained from a German kruss DSA100 measurement. Film-depth-dependent light absorption spectra (FLAS) is conducted by a home-made setup. Low-pressure (less than 20Pa) oxygen plasma was used for the incremental etching of the film.

2. **Supplementary Figure Section**

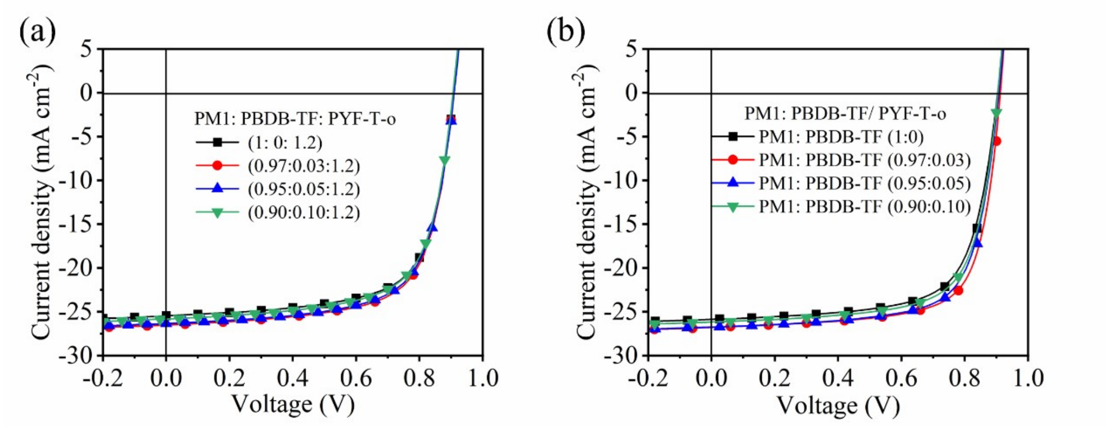

Fig. S1 J-V curves of (a) PM1: PYF-T-o-based BHJ PSCs with different weight ratios of PBDB-TF and (b) bilayer PSCs based on PM1/ PYF-T-o system with different weight ratios of PBDB-TF in PM1.

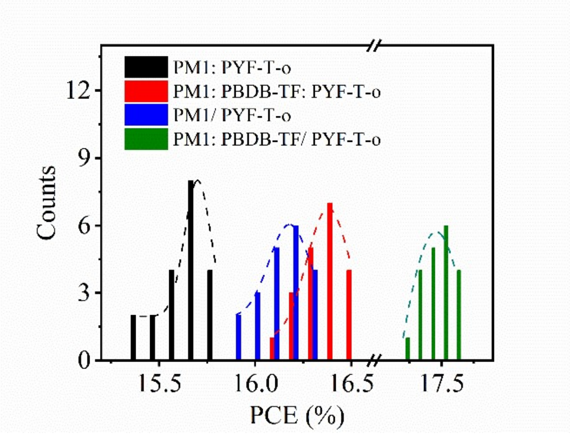

Fig. S2 Efficiency histograms of PM1: PYF-T-o-based BHJ PSCs and bilayer PSCs based on PM1/ PYF-T-o system with or without 3% PBDB-TF.

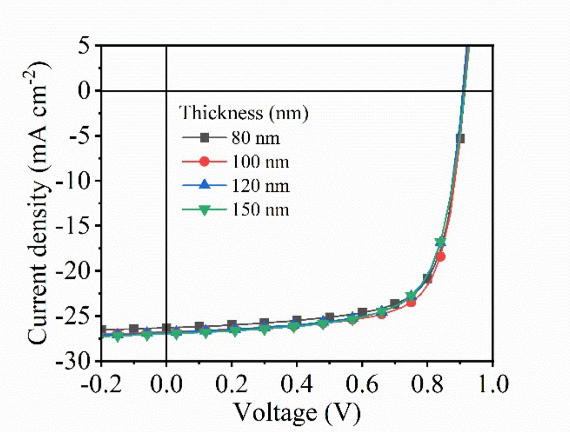

Fig. S3 J-V curves of PM1: 3%PBDB-TF/ PYF-T-o-based bilayer PSCs with different active layer thickness.

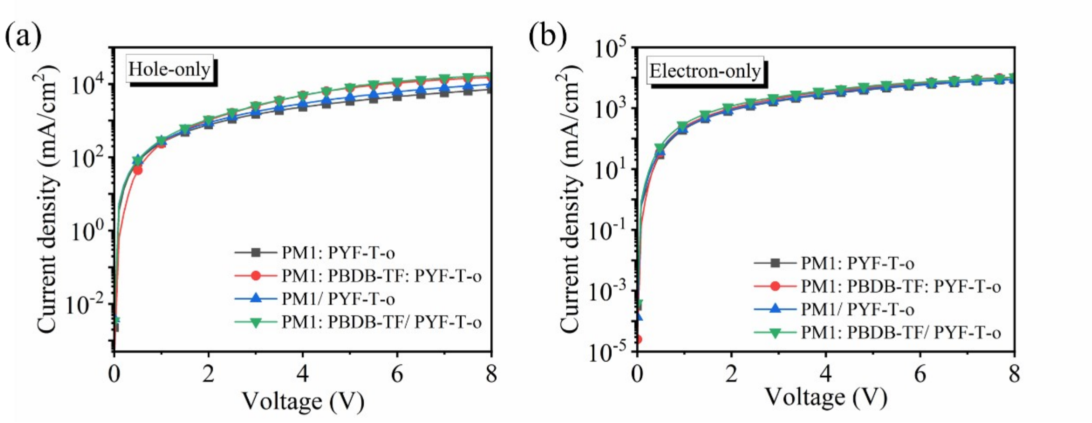

Fig. S4 (a) Hole mobilities and (b) electron mobilities of BHJ and bilayer devices.

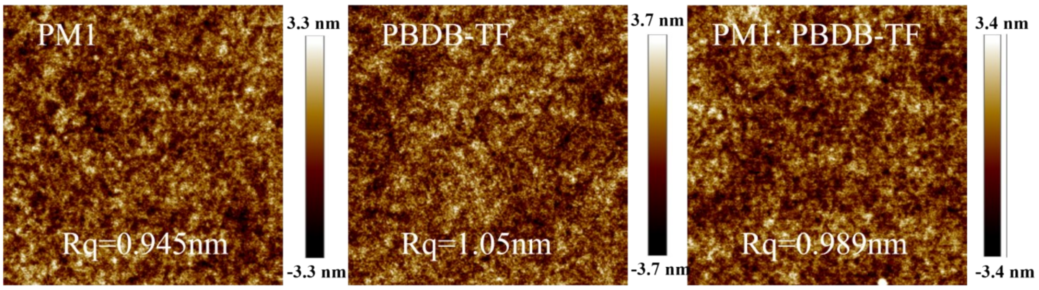

Fig. S5 AFM images for neat PM1, PBDB-TF and blended film of PM1: PBDB-TF.

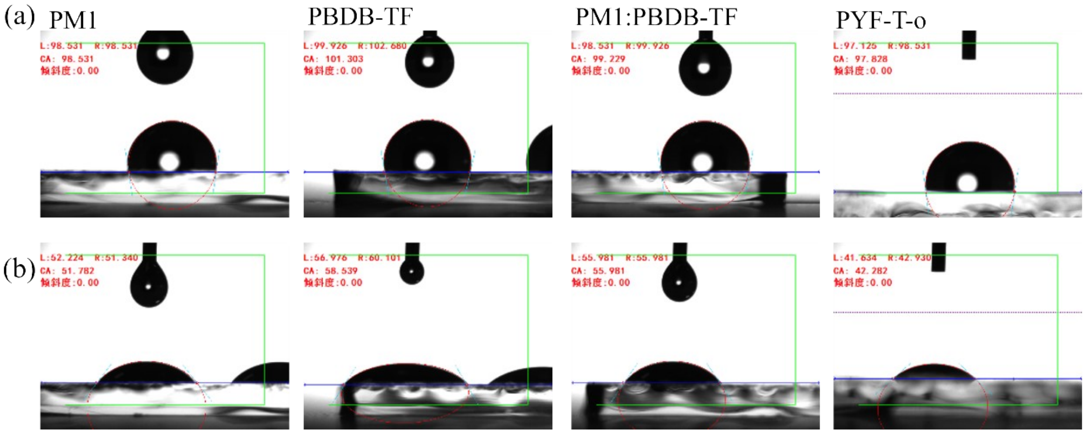

Fig. S6 Contact angles of (a) water (H_2O) and (b) diiodomethane (CH_2I_2) droplets of PM1, PBDB-TF, PM1: PBDB-TF and PYF-T-o films.

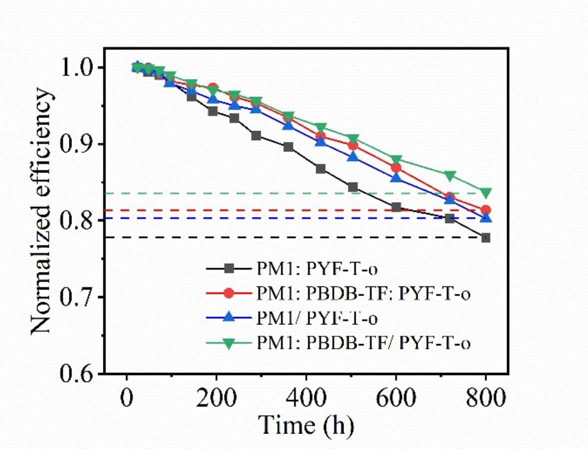

Fig. S7 The stability curves of BHJ devices and bilayer devices with or without 3%PBDB-TF.

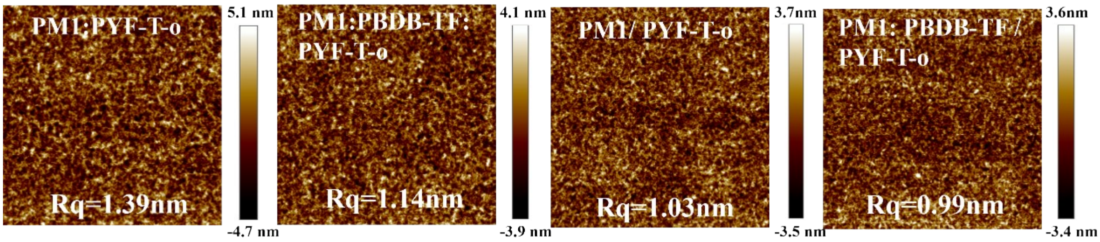

Fig. S8 AFM image of the films placed for 10 days.

3. Supplementary Table Section

Table S1. Photovoltaic parameters of PM1: PYF-T-o-based BHJ PSCs with or without different weight ratios of PBDB-TF.

PM1: PBDB-TF: PYF-T-o weight ratio	V_{OC} (V)	J_{SC} (mAcm^{-2})	FF (%)	PCE (%)
1: 0: 1.2	0.91	25.44	68.44	15.83 (15.68)
0.97: 0.03: 1.2	0.91	26.47	68.68	16.52 (16.41)
0.95: 0.05: 1.2	0.91	26.31	68.20	16.32 (16.10)
0.90: 0.10: 1.2	0.90	25.80	68.05	15.90 (15.71)

Table S2. Photovoltaic parameters of PM1/ PYF-T-o-based bilayer PSCs with or without different weight ratios of PBDB-TF in donor solution.

Bilayer devices	V_{OC} (V)	J_{SC} (mAcm^{-2})	FF (%)	PCE (%)
PM1: PBDB-TF (1: 0) /PYF-T-o	0.91	25.85	69.72	16.32 (16.15)
PM1: PBDB-TF (0.97:0.03) /PYF-T-o	0.91	26.76	72.31	17.66 (17.48)
PM1: PBDB-TF (0.95:0.05) /PYF-T-o	0.91	26.73	71.21	17.30 (17.09)
PM1: PBDB-TF (0.90:0.10) /PYF-T-o	0.90	26.15	70.30	16.64 (16.45)

Table S3. Photovoltaic parameters of PM1: 3%PBDB-TF/ PYF-T-o-based bilayer PSCs with different active layer thickness.

Devices	Thickness (nm)	V_{OC} (V)	J_{SC} (mAcm^{-2})	FF (%)	PCE (%)
PM1: PBDB-TF/ PYF-T-o	80	0.91	26.29	71.09	17.09 (16.81)
	100	0.91	26.76	72.31	17.66 (17.48)
	120	0.91	26.82	70.36	17.14 (16.96)
	150	0.91	26.96	69.21	17.05 (16.71)

Table S4. Summary of charge mobilities of PM1: PYF-T-o-based BHJ devices and PM1/ PYF-T-o-based bilayer PSCs with or without 3% PBDB-TF.

Devices	μ_h	μ_e	μ_h /μ_e
PM1: PYF-T-o	4.19×10^{-4}cm^{2}V^{-1}s^{-1}	2.91×10^{-4}cm^{2}V^{-1}s^{-1}	1.44
PM1: PBDB-TF: PYF-T-o	4.42×10^{-4}cm^{2}V^{-1}s^{-1}	3.39×10^{-4}cm^{2}V^{-1}s^{-1}	1.30
PM1/ PYF-T-o	4.31×10^{-4}cm^{2}V^{-1}s^{-1}	3.03×10^{-4}cm^{2}V^{-1}s^{-1}	1.42
PM1: PBDB-TF/ PYF-T-o	4.58×10^{-4}cm^{2}V^{-1}s^{-1}	4.20×10^{-4}cm^{2}V^{-1}s^{-1}	1.09

Table S5. The contact angle and the surface energy (γ) for PM1, PBDB-TF, PM1: PBDB-TF, PYF-T-o films as well as the interaction parameters (χ) between the materials.

Material	θ water (°)	θ diiodomethane (°)	γ (mN m^{-1})	$X_{D\text{-}A}$
PM1	98.531	51.782	33.60	0.171
PBDB-TF	101.303	58.539	29.72	0.574
PM1: PBDB-TF	99.229	55.981	31.30	0.378
PYF-T-o	97.828	42.282	38.56	/