

Supporting Information

Efficient Organic Solar Cells Processed from Halogen-Free Solvent Based on Benzo[1,2-b:4,5-b']difuran Terpolymers

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Experimental Section

Materials: All chemicals and solvents were purchased from commercials and used directly without further purification except mention. PBDF4F, PBDF4F-Th2 and PBDF4F-Th5 were synthesized according to reported literature.^{1,2} IT-4F was purchased from Derthon Optoelectronic Materials Science Technology Co LTD.

Device Fabrication and Characterization

Device Fabrication: The BDF based devices were fabricated with inverted device structure of ITO/ZnO/active layer (120nm)/MoO_x/Ag. Indium tin oxide (ITO) covered glasses were cleaned by an ultrasonication treatment in detergent, ultrapure water, ethanol, acetone, and ethanol every 30 min, and then dried with air blow. For active layer of BDF based donor blend with IT-4F in a weight ratio of 1:1.5 in halogen solvent (CB) or non-halogen solvent (*o*-XY) and maintain a concentration of 20 mg/mL with different additives inside. These precursors were stirred in nitrogen-filled glove box for 8h. Then spin-coated on ZnO layer. After annealing at 130 °C for 2min, hole transport layer MoO_x(1.5nm) and electrode Ag(100nm) were formed via vacuum evaporation.

The LBL devices were fabricated with inverted device structure of ITO/ZnO/PBDF4F-Th2(or PBDF4F-Th5)/IT-4F/MoO_x/Ag. The BDF based donor polymers dissolved in *o*-XY with a concentration of 7.5 mg/mL, and spin coating at 1800r for 40s, then annealed at 130°C for 2 min. IT-4F was dissolved in THF at a concentration of 10.5 mg/mL, spin coating at 1800 rpm for 40s. The hole transport layer MoO_x(1.5nm) and electrode Ag(100nm) were formed via vacuum evaporation.

Measurement: All the measurements were carried out under ambient condition. The current-voltage (J-V) characteristics of the devices were measured on a Keithley 2400 Source Measure Unit. The power conversion efficiency (PCE) was measured under an illumination of AM 1.5G (100 mW/cm²) using a 7IS0503A (SOFN Instruments Co. Ltd.) solar simulator. The EQE was measured by 7-SCSpec (SOFN Instruments Co. Ltd.) which light intensity at each wavelength was calibrated with a standard single-crystal Si photovoltaic cell. The morphologies of the polymer/acceptor were investigated by AFM (Dimension Fastscan) in contacting under normal air conditions at room temperature with 2 μ m scanner.

Figures and Tables

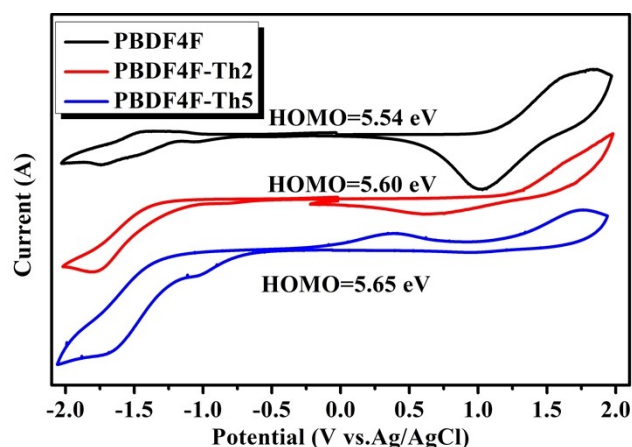


Fig. S1. Cyclic voltammograms of the PBDF4F, PBDF4F-Th2 and PBDF4F-Th5 films on glassy carbon electrodes in 0.1 mol L⁻¹ Bu₄NPF₆ of acetonitrile solution at a scan rate of 40 mV/s.

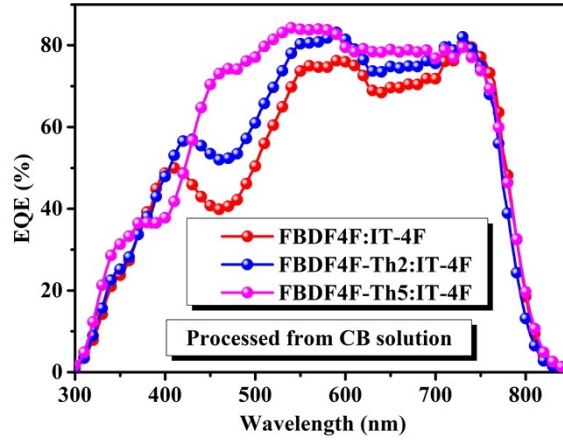


Fig. S2 EQE spectra of PBDF4F, PBDF4F-Th2 and PBDF4F-Th5 devices processed from *o*-XY solution.

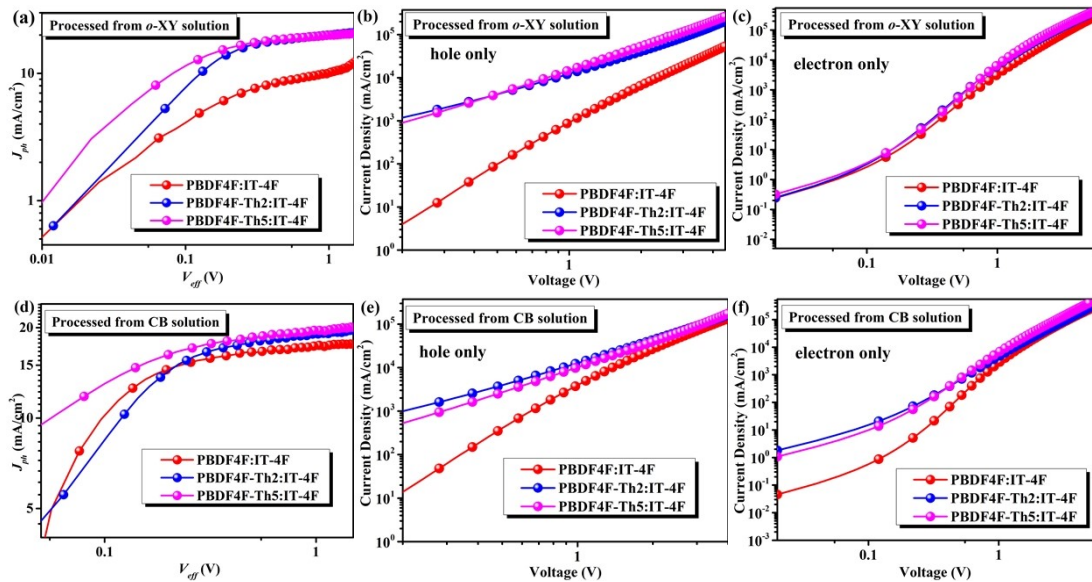


Fig. S3. (a, d) J_{ph} - V_{eff} characteristics, (b, e) the hole only devices and (c, f) the electron only devices of non-halogen solvent prepared PBDF4F:IT-4F, PBDF4F-Th2:IT-4F and PBDF4F-Th5:IT-4F based devices.

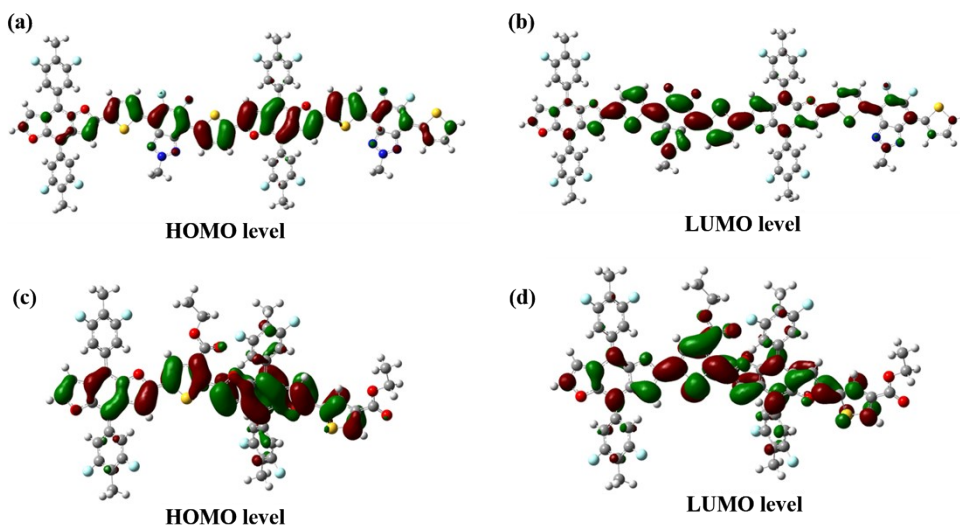


Fig. S4 The DFT calculations of PBDF4F (a, b) and PBDF-Th2 (c, d).

As there is only small amount of Th units in the terpolymers PBDF4F-Th2 and PBDF4F-Th5, it means the Th units are also randomly located in the polymer main chain, therefore it is hard to make the DFT calculations of PBDF4F-Th2 and PBDF4F-Th5 directly. Instead, we have made the DFT calculations of PBDF4F and PBDF-Th2, which are the polymer with 0% and 100% of Th2 unit, respectively. As it can see from Figure S4, the HOMO levels of PBDF4F and PBDF-Th2 are delocalized over the BDF and acceptor units, whereas the LUMO levels of PBDF4F and PBDF-Th2 are mainly localized on the acceptors unit with partially delocalization on the BDF unit. The terpolymers PBDF4F-Th2 and PBDF4F-Th5 should also have similar HOMO and LUMO delocalizations.

Table S1. The value of excitation dissociation, charge collection, and hole and electron mobilities.

Active layer	Solvent	P_{diss} (%)	P_{coll} (%)	μ_h ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)	μ_e ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)	μ_h/μ_e
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PBDF4F:IT-4F	<i>o</i> -XY	43.45	30.65	1.91×10^{-5}	6.0×10^{-5}	3.14
	CB	89.88	75.67	5.0×10^{-5}	7.0×10^{-5}	1.4
PBDF4F-Th2:IT-4F	<i>o</i> -XY	87.89	72.54	8.34×10^{-5}	1.10×10^{-4}	1.32
	CB	89.99	75.68	8.47×10^{-5}	1.0×10^{-4}	1.18
PBDF4F-Th5:IT-4F	<i>o</i> -XY	90.03	73.32	1.07×10^{-4}	1.17×10^{-4}	1.03
	CB	91.76	76.68	8.72×10^{-5}	1.12×10^{-4}	1.28

Table S2. Photovoltaic parameters of the BDF based polymer donor:IT-4F acceptor devices prepared with halogen solvent.

Active layer	solvent	RMS
PBDF4F:IT-4F	<i>o</i> -XY	8.82
	CB	5.59
PBDF4F-Th2:IT-4F	<i>o</i> -XY	5.71
	CB	5.60
PBDF4F-Th5:IT-4F	<i>o</i> -XY	3.77
	CB	4.20

Table S3. The contact angles (θ) and surface tension (γ) of pure film and interaction parameters (χ) between polymer and IT-4F.

Film	θ_{water} ($^{\circ}$)	$\theta_{glycerol}$ ($^{\circ}$)	γ (mNm^{-1})	χ
PBDF4F	107.68	96.35	18.75	1.35
PBDF4F-Th2	108.12	88.31	21.98	0.65
PBDF4F-Th5	109.10	85.97	35.38	0.21
IT-4F	100.29	80.82	30.19	-

Reference

1. E. He, Z. Zheng, Y. Lu, F. Guo, S. Gao, X. Pang, G. T. Mola, L. Zhao and Y. Zhang, *J. Mater. Chem. A*, 2020, **8**, 11381-11390.
2. E. He, Z. Zheng, Y. Lu, F. Guo, S. Gao, G. T. Mola, L. Zhao and Y. Zhang, *J. Mater. Chem. C*, 2021, **9**, 13617-13624.