Supporting Information should be included here (for submission only; for publication, please provide Supporting Information as a separate PDF file).

A Polymer Design Strategy toward Green Solvent Processed Efficient Non-fullerene Polymer Solar Cells

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Materials

Compound 1, 2a, 2b, the polymer PBDB-T and the acceptor IT-M was purchased from Solarmer Materials, Inc. All of the other materials are commercial available and the reagents were used as received.

4,8-bis(5-(2-butyloctyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene (3a):

n-butyl lithium (2.5M, 10 mL) was added dropwise to a solution of compound 2a (6.25g, 24 mmol) in THF under argon protection at 0 ^oC. The mixture was then heated up to 50 ^oC and stirred for 40 min. Subsequently, the reactant was cooled to room temperature and compound 1 (1.55g, 7 mmol) was added into the mixture in one portion. The reaction mixture was then stirred at 50 ^oC for another 1 h. After cooling the reaction to 0 ^oC, a mixture of $SnCl_2·2H_2O$ (11.3g, 50 mmol) in 10% HCl (24 mL) was added and the reaction was stirred at room temperature overnight. The mixture was poured into ice water and extracted with diethyl ether twice. The organic phases were combined and then concentrated to obtain the crude product 3a. Column chromatography was used to purify the compound and the pure 3a was obtained as light yellow liquid with a yield of 63%.

^1H NMR (300MHz, $CDCl_3$): δ 7.65-7.63 (d, 2H), 7.46-7.44 (d, 2H), 7.30 (d, 2H), 6.89 (d, 2H), 2.87-2.85 (d, 4H), 1.73 (s, 2H), 1.36 (m, 32H), 0.92-0.90 (m, 12H)

4,8-bis(5-(2-butyloctyl)benzo[b]thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene (3b)

The synthetic procedure for compound 3b is similar with compound 3a.

^1H NMR (400MHz, $CDCl_3$): δ 7.84 (d, 2H), 7.71 (d, 2H), 7.68 (s, 2H), 7.66 (s, 2H), 7.51 (d, 2H), 7.26-7.23 (dd, 2H), 2.71-2.69 (d, 4H), 1.73 (m, 2H), 1.38-1.25 (m, 32H), 0.93-0.87 (m, 12H)

(4,8-bis(5-(2-butyloctyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane)

(4a)

In a two neck round bottom flask, compound 3a (1.2g, 1.74 mmol) was dissolved into 30 mL of THF with argon protection, the solution was cooled to -78 ^{o}C by using liquid nitrogen-acetone bath and then n-butyl lithium (2.5M, 1.5 mL) was added into the flask dropwise. The mixture was then stirred for 1 h. Subsequently, chlorotrimethylstannane (1.0M, 4.5 mL) was added by syringe in one portion and the reaction was stirred for another 1 h at ambient temperature. The mixture was poured into water and extracted by diethyl ether. The product was concentrated and used in polymerization without any purification procedure.

^{1}H NMR (300MHz, $CDCl_3$): δ 7.68 (s, 2H), 7.31 (d, 2H), 6.90 (d, 2H), 2.88-2.86 (d, 4H), 1.74 (m, 2H), 1.35-1.30 (m, 32H), 0.92-0.89 (m, 12H), 0.40 (t, 18H)

(4,8-bis(5-(2-butyloctyl)benzo[b]thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) (4b)

The synthetic route for compound 4b is similar with compound 4a, but the final monomer was purified by crystallization and obtained as yellow solid with a yield of 70%.

^{1}H NMR (300MHz, $CDCl_3$): δ 7.85-7.83 (d, 2H), 7.74 (t, 2H), 7.70 (s, 2H), 7.67 (s, 2H), 7.25-7.22 (dd, 2H), 2.72-2.70 (d, 4H), 1.73 (m, 2H), 1.39-1.29 (m, 32H), 0.94-0.87 (m, 12H), 0.39 (t, 18H)

Polymerization process

The polymers were obtained by Stille coupling polymerization as follows: The BDT monomer (0.5 mmol) and BDD monomer (0.5 mmol) was mixed in 10 mL of toluene. After being purged with argon for 5 min, $Pd(PPh_3)_4$ (25 mg) was added as the catalyst in one portion, and the mixture was then purged with argon for another 20 min. The reaction was stirred at 110 ^{o}C for 17 h and subsequently cooled to room temperature. The polymer was precipitated from 50 mL of methanol and then collected after filtration. The polymer was purified through column chromatography by using hot chloroform as the eluent, and then precipitated from methanol again. The polymer was collected and dried in vacuum oven, and then obtained as dark purple solid with a yield of ~60%.

PBDB-T-BO. Elemental analysis calcd (%) for $C_{76}H_{94}O_2S_8$: C 70.43, H 7.31; found: C 70.29, H 7.47

PBDB-BzT. Elemental analysis calcd (%) for $C_{84}H_{96}O_2S_8$: C 72.26, H 7.07; found: C 71.73, H 7.18

Fabrication of the PSC Devices

All devices were fabricated with the device structure of ITO/PEDOT: PSS/Active layer/PFN-Br/Al. TheITO-coated glass substrates were thoroughly cleaned by deionized water, acetone, and isopropanol twicesuccessively at first. After the substrates were dried at 150 ˚C for 15 minutes, thin layers of PEDOT (30 nm) were spin-coated on them and then annealed at 150 ˚C for 15 minutes in the air.The materialsPBDB-T:IT-M, PBDB-T-BO:IT-M andPBDB-BzT:IT-Mwere dissolved in CB or THF with the total concentration of 10 mg/mL or 8mg/mLand stirred at 25 ˚C for 5 hours. Subsequently, the mixture were spin coated on PEDOT modified glasssubstrates at 3000 rpm to the optimal film thickness of ca. 100 nm. The active layers were then thermalannealed at 100 ˚C for 10 minutes. Finally, 10 nm thick PFN-Br film and 100 nm thick Al layer were depositedsequentially to complete the device. The J-V measurement was performed via solar simulator (SS-F5-3A) along with AM 1.5G spectra whose intensity was calibrated by the certified standard silicon solar cell (SRC-2020, Enlitech) at 100 mW cm^{-2}. The external quantum efficiency (EQE) data were obtained by using the solar-cell spectral-response measurement system (QE-R, Enlitech)

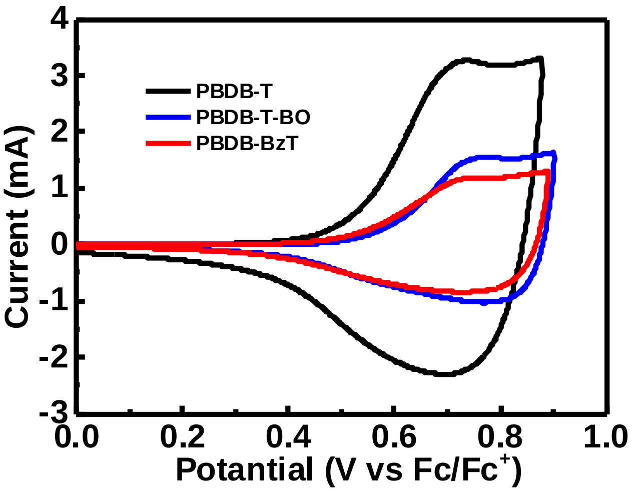

Figure S1. CV curves of PBDB-T, PBDB-T-BO and PBDB-BzTwitha scan rate of 20 mVs^{-1}(calibrated byFc/Fc$^+$redox couple).

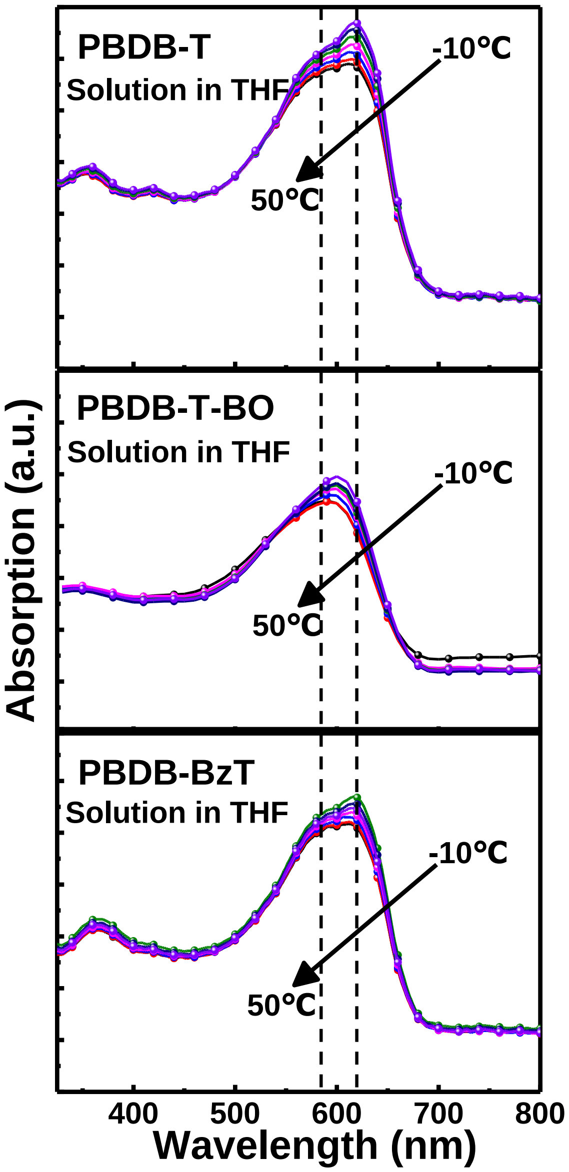

Figure S2. Temperature-dependent absorption spectra of the three polymers in THFasthe temperature reduced from 50 to -10 ^{o}Cwith a 10 ^{o}C interval

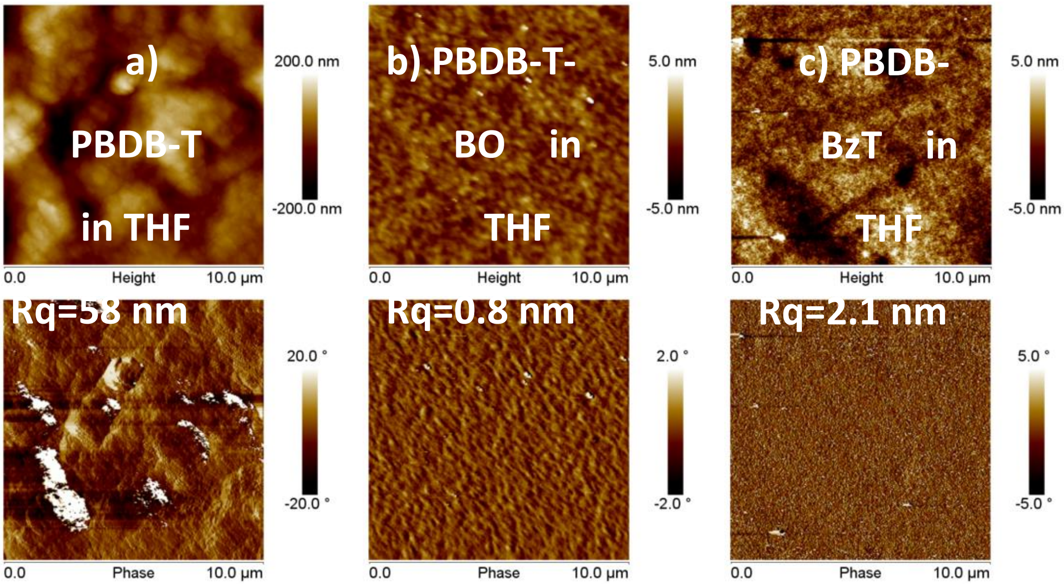

Figure S3. AFM with different concentrations of the three polymers in THF solution(PBDB-T for 3mg/mL, PBDB-T-BO for 30 mg/mL, PBDB-BzT for 20 mg/mL)

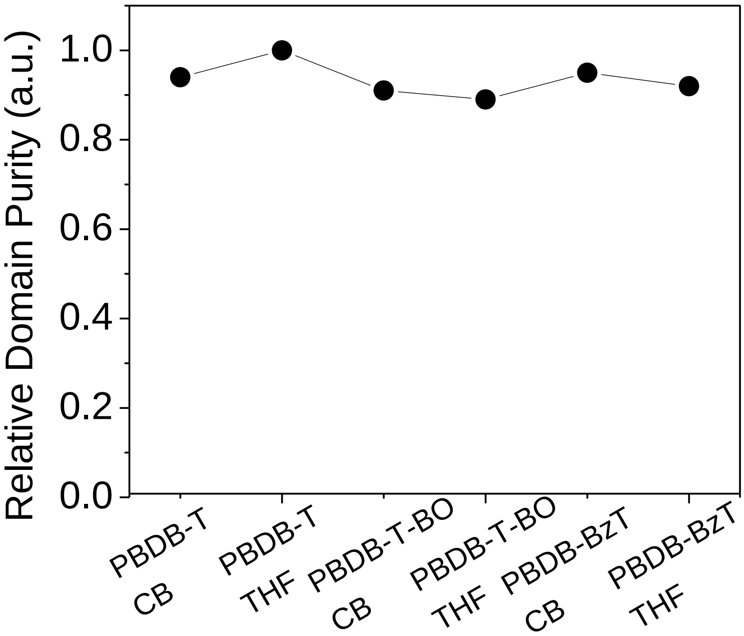

Figure S4. Plot of relative purity (ISI$^{1/2}$) values of different blend films.

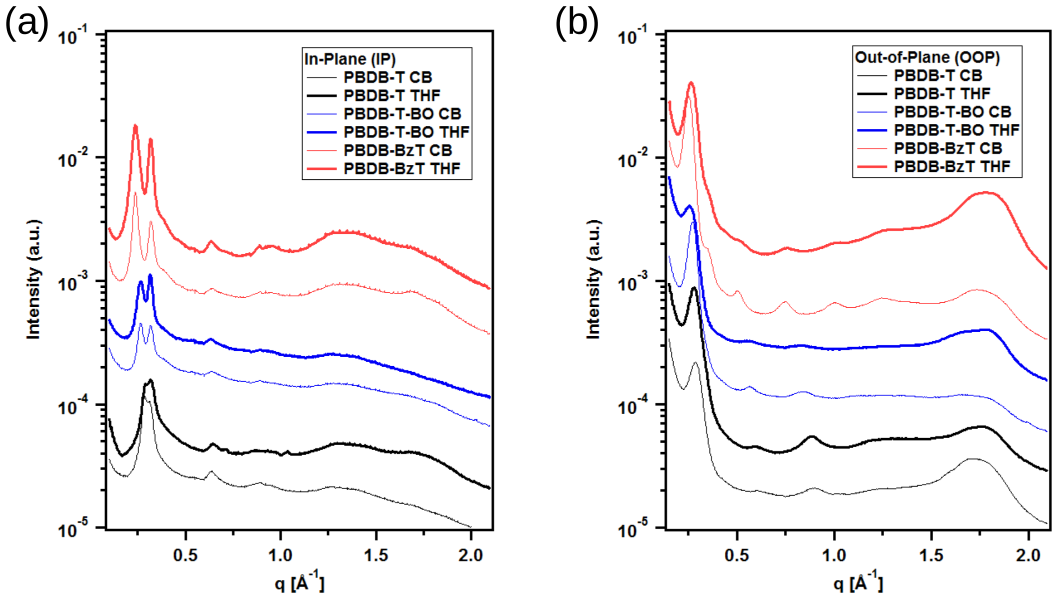

Figure S5. 1D in-plan and out-of-plane line-cut profiles of the blended films processed from different solvents.

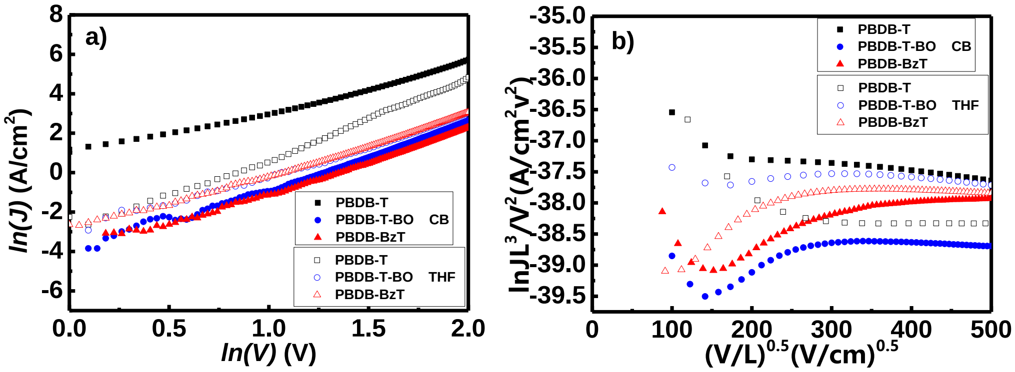

Figure S6. The electon mobility(a) and hole mobility(b)of PBDB-T:IT-M, PBDB-T-BO:IT-M and PBDB-BzT:IT-M fabricated with CB and THF measured by SCLC method.

Table S1 The data of charge mobilities for PBDB-T:ITM, PBDB-T-BO:ITM and PBDB-BzT:ITM fabricated with CB and THF measured by SCLC method.

		CB	THF
PBDB-T:IT-M	μ_{hole}(cm^2/Vs)	2.69×10^{-4}	7.7×10^{-5}
	μ_{elec}(cm^2/Vs)	3.79×10^{-4}	7.39×10^{-5}
PBDB-T-BO:IT-M	μ_{hole}(cm^2/Vs)	5.77×10^{-5}	1.7×10^{-4}
	μ_{elec}(cm^2/Vs)	3.04×10^{-5}	1.7×10^{-4}
PBDB-BzT:IT-M	μ_{hole}(cm^2/Vs)	1.07×10^{-4}	1.68×10^{-4}
	μ_{elec}(cm^2/Vs)	1.26×10^{-4}	1.22×10^{-4}

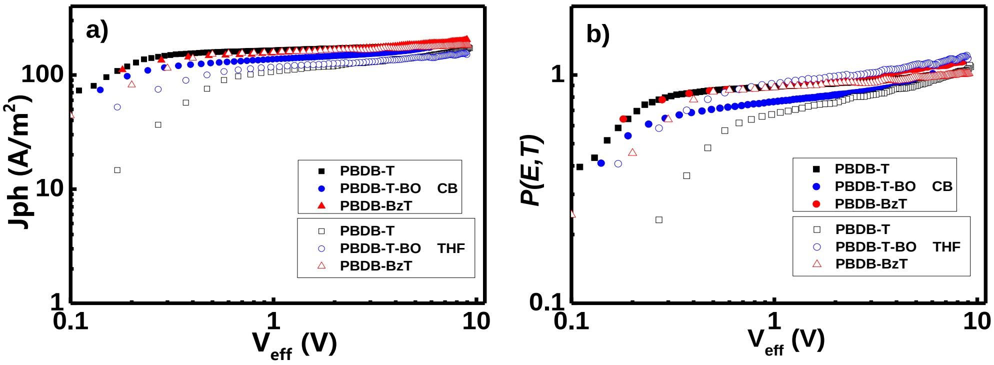

Figure S7. Photocurrent density (J_{ph})(a) and exciton dissociation probability [P(E,T)](b) versus effective bias (V_{eff}) characterizations

Table S2 The data of themaximum exciton generation rates (G_{max}) and exciton dissociation probability [P(E,T)] of PBDB-T:IT-M, PBDB-T-BO:IT-M and PBDB-BzT:IT-M fabricated with CB and THF. Table S2 The data of themaximum exciton generation rates (G_{max}) and exciton dissociation probability [P(E,T)] of PBDB-T:IT-M, PBDB-T-BO:IT-M and PBDB-BzT:IT-M fabricated with CB and THF.

		CB	THF
PBDB-T:IT-M	G_{max}/m^{-3}s^{-1}	1.13×10^{28}	8×10^{27}
	P(E,T) /%	88.9	70
PBDB-T-BO:IT-M	G_{max}/ m^{-3}s^{-1}	8.2×10^{27}	1.08×10^{28}
	P(E,T) /%	70.3	88
PBDB-BzT:IT-M	G_{max}/m^{-3}s^{-1}	1.12×10^{28}	1.15×10^{28}
	P(E,T) /%	76.7	89.2