

## Supporting information

### **Dithienobenzoxadiazole based wide bandgap donor polymers with strong aggregation property enable efficient as-cast non-fullerene polymer solar cells processed by non-halogenated solvent**

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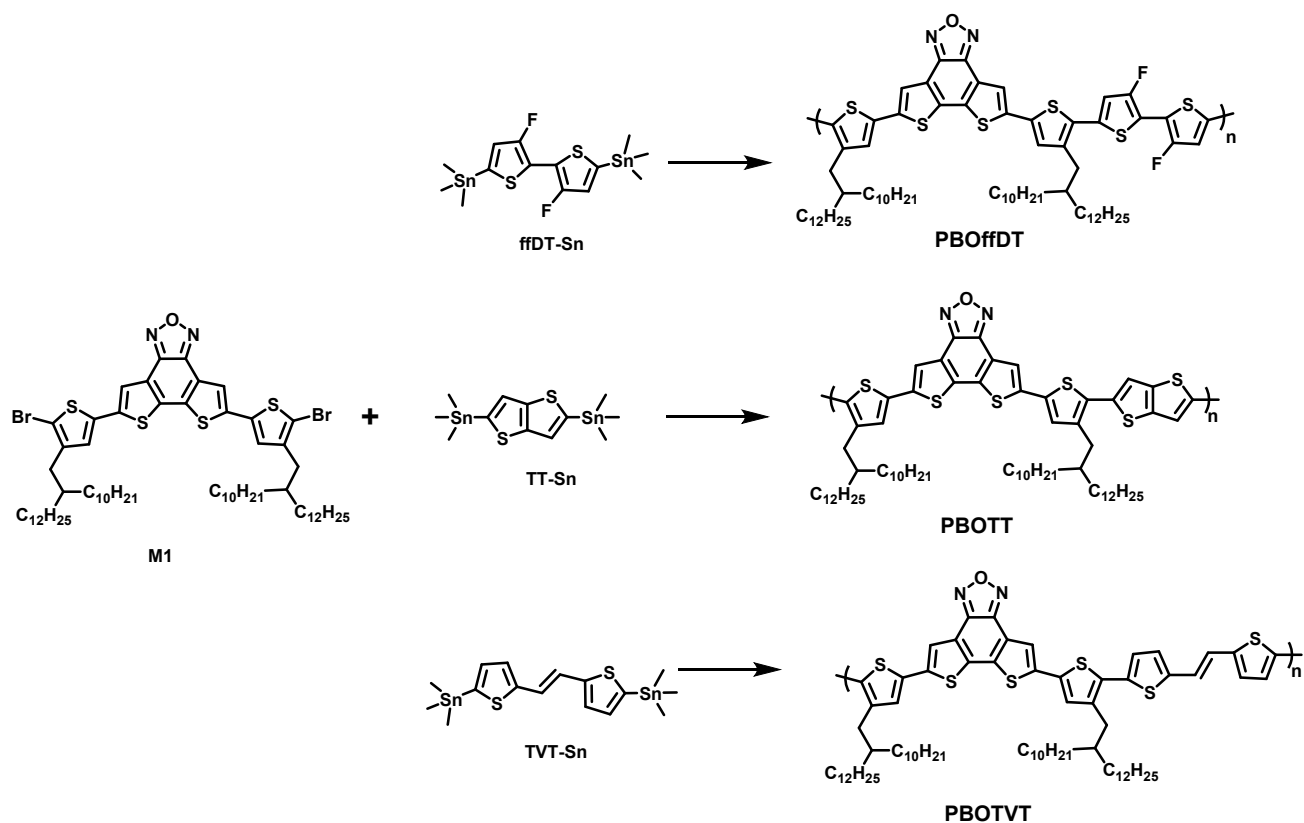
## EXPERIMENTAL SECTION

### General Information

<sup>1</sup>H NMR spectra were recorded on a Bruker AV 500 or 400 spectrometer with tetramethylsilane (TMS) as the internal reference. Mass spectrometry (MALDI-TOF) was performed on a Autoflex III smart bean. Elemental analyses were performed on a Vario EL elemental analysis instrument (Elementar Co.). UV-vis absorption spectra were recorded on an UV-3600 (Shimadzu Co.) spectrophotometer. Cyclic voltammetry was carried out on a CHI660A electrochemical work station with platinum electrodes at a scan rate of 50 mV/s against an Ag/Ag<sup>+</sup> reference electrode with a nitrogen-saturated solution of 0.1 M tetrabutylammonium hexafluorophosphate (Bu<sub>4</sub>NPF<sub>6</sub>) in acetonitrile. Potentials were referenced to the ferrocenium/ferrocene couple by using ferrocene as an internal standard. The deposition of a copolymer on the electrode was done by the evaporation of a dilute chlorobenzene solution. Thermogravimetric analysis (TGA) was performed on Netzsch TG 209 in nitrogen, with a heating rate of 20 °C min<sup>-1</sup>.

### Synthesis

All reagents and solvents, unless otherwise specified, were obtained from Aldrich, Acros, and TCI Chemical Co. and were used as received. All manipulations involving air-sensitive reagents were performed under an atmosphere of dry argon. Monomer 1 and (E)-1,2-bis(5-(trimethylstannyl)thiophen-2-yl)ethene (TVT-Sn) were synthesized according to previous report. (3,3'-difluoro-[2,2'-bithiophene]-5,5'-diyl)bis(trimethylstannane) (ffDT-Sn), 2,5-bis(trimethylstannyl)thieno[3,2-b]thiophene (TT-Sn) were purchased from Derthon Optoelectronic Materials Science Technology Co LTD. The IT-4Cl acceptor was purchased from Solarmer Materials Inc.



**Scheme S1.** Synthesis routes of polymer PBOffDT, PBOTT and PBOTVT

### Synthesis of polymer PBOffDT

In a 50 mL two-neck flask containing M1(368.2 mg, 0.3 mmol) and ffDT-Sn (158.4 mg, 0.3 mmol), Pd<sub>2</sub>(dba)<sub>3</sub>(9 mg) and P(*o*-Tol)<sub>3</sub>(18 mg), 10 mL anhydrous *o*-xylene was added. The mixture was purged with argon for 30 min. The mixture was heated to 140 °C for 72h. After the solution was cooled to 80 °C and precipitated in methanol. The precipitate was collected and subjected to soxhlet extraction with acetone, ethyl acetate, *n*-hexane, dichloromethane, chloroform, chlorobenzene. The chlorobenzene fraction was concentrated and precipitated in methanol. The precipitate was dry over vacuum and black solid was obtained (276 mg, 71%). High temperature GPC measurement (at 140 °C and 1,2,4-trichlorobenzene as the eluent) was performed to characterize the molecular weights of the polymer PBOffDT. HT-GPC:  $M_n = 50.8$  kg/mol;  $M_w/M_n = 1.62$

### **Synthesis of polymer PBOTT**

The synthesis process of PBOTT was similar with PBOffDT by replacing ffDT-Sn with TT-Sn. And PBOTT was obtained from the CF fraction (285 mg, 77%). HT-GPC:  $M_n = 38.1$  kg/mol;  $M_w/M_n = 2.19$

### **Synthesis of polymer PBOTT**

The synthesis process of PBOTT was similar with PBOffDT by replacing ffDT-Sn with TVT-Sn. And PBOTVT was obtained from the CF fraction (289 mg, 75%). HT-GPC:  $M_n = 41.7$  kg/mol;  $M_w/M_n = 1.75$

### **Fabrication and Characterization of Organic Solar Cells (OSCs).**

The device structure was ITO/ZnO/D:A /MoO<sub>3</sub>/Al. Patterned indium tin oxide (ITO)-coated glass with a sheet resistance of 15–20 ohm/square was cleaned by a surfactant scrub and then underwent a wet-cleaning process inside an ultrasonic bath that began with deionized water, followed by acetone and 2-propanol. A solution-processed zinc oxide (ZnO) interlayer of 30 nm was prepared according to a recent report. The substrates were then transferred into a nitrogen-filled glove box. Active layer solutions with different donor concentrations were prepared in 1,3,5-TMB. Warm solutions (90 °C) were then spin-coated onto the substrates. A 10 nm MoO<sub>3</sub> layer and a 100 nm Al layer were subsequently evaporated through a shadow mask to define the active area of the devices (5.8 mm<sup>2</sup>) and form the top anode.

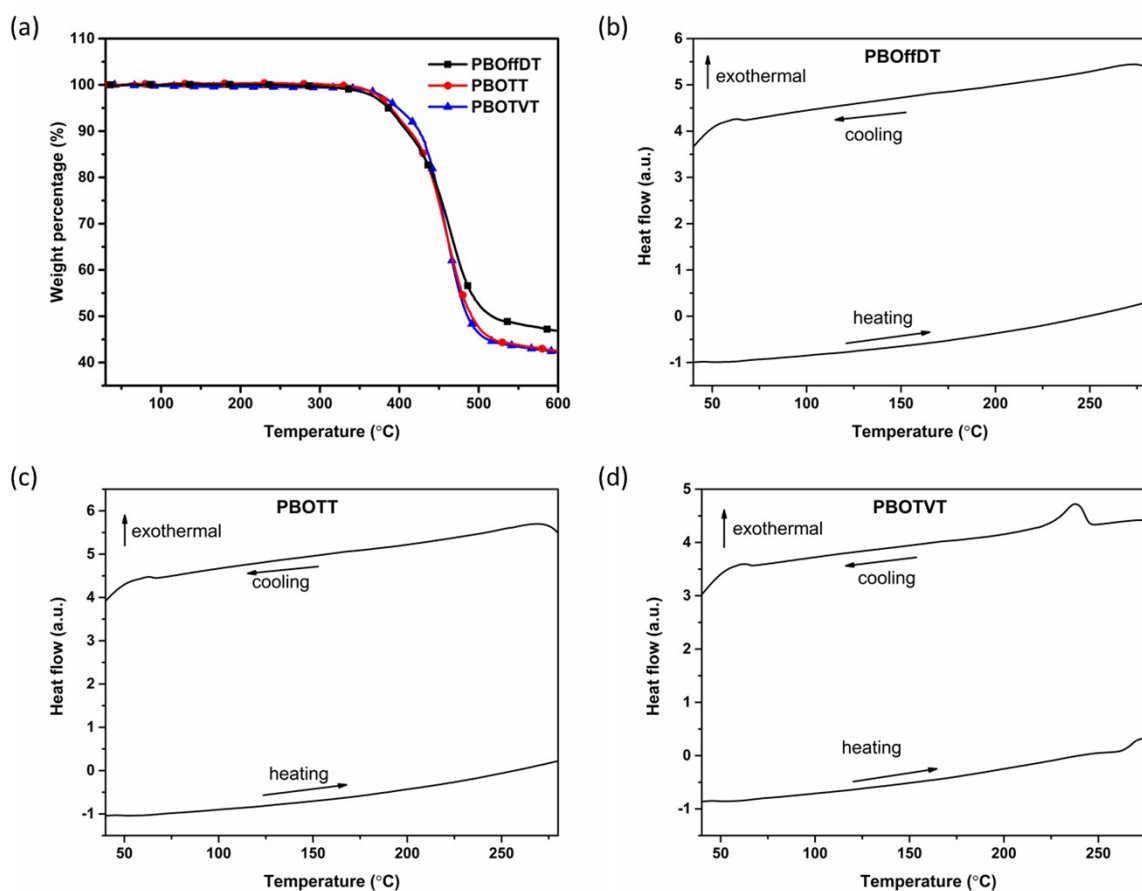
The PCE was determined from  $J-V$  curve measurements (using a Keithley 2400 sourcemeter) under a 1 sun, AM 1.5G spectrum from a solar simulator (SAN-EI-XES-40S3; 1000 W m<sup>-2</sup>). Masks made using laser beam cutting technology to have a well-defined area of 5.8 mm<sup>2</sup> were attached to define the effective area for accurate measurement. The solar simulator illumination intensity was determined using a monocrystal silicon reference cell (Enlitech-SRC-2020) calibrated by the National Renewable Energy Laboratory (NREL). Theoretical  $J_{sc}$  values obtained by integrating the product of the EQE (QE-R3011) with the AM 1.5G solar spectrum agreed with the measured value to within 5%.

## Space-Charge Limited Current (SCLC) Measurement.

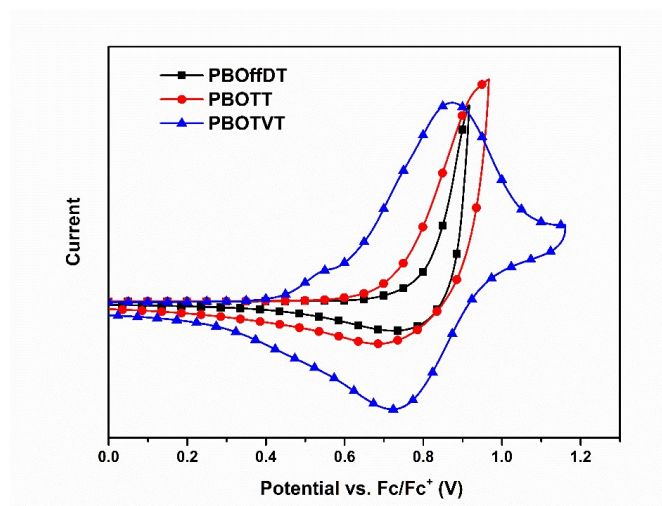
Hole-only and electron-only devices were fabricated to measure the hole and electron mobilities of active layers using the space charge limited current (SCLC) method with hole-only device of ITO/PEDOT:PSS/Active layer/MoO<sub>3</sub>/Al and electron-only device of ITO/ZnO/Active layer/PFN-Br/Al. The mobilities ( $\mu$ ) were determined by fitting the dark current to the model of a single carrier SCLC, described by the equation:

$$J = \frac{9}{8} \epsilon_0 \epsilon_r \mu \frac{V^2}{d^3}$$

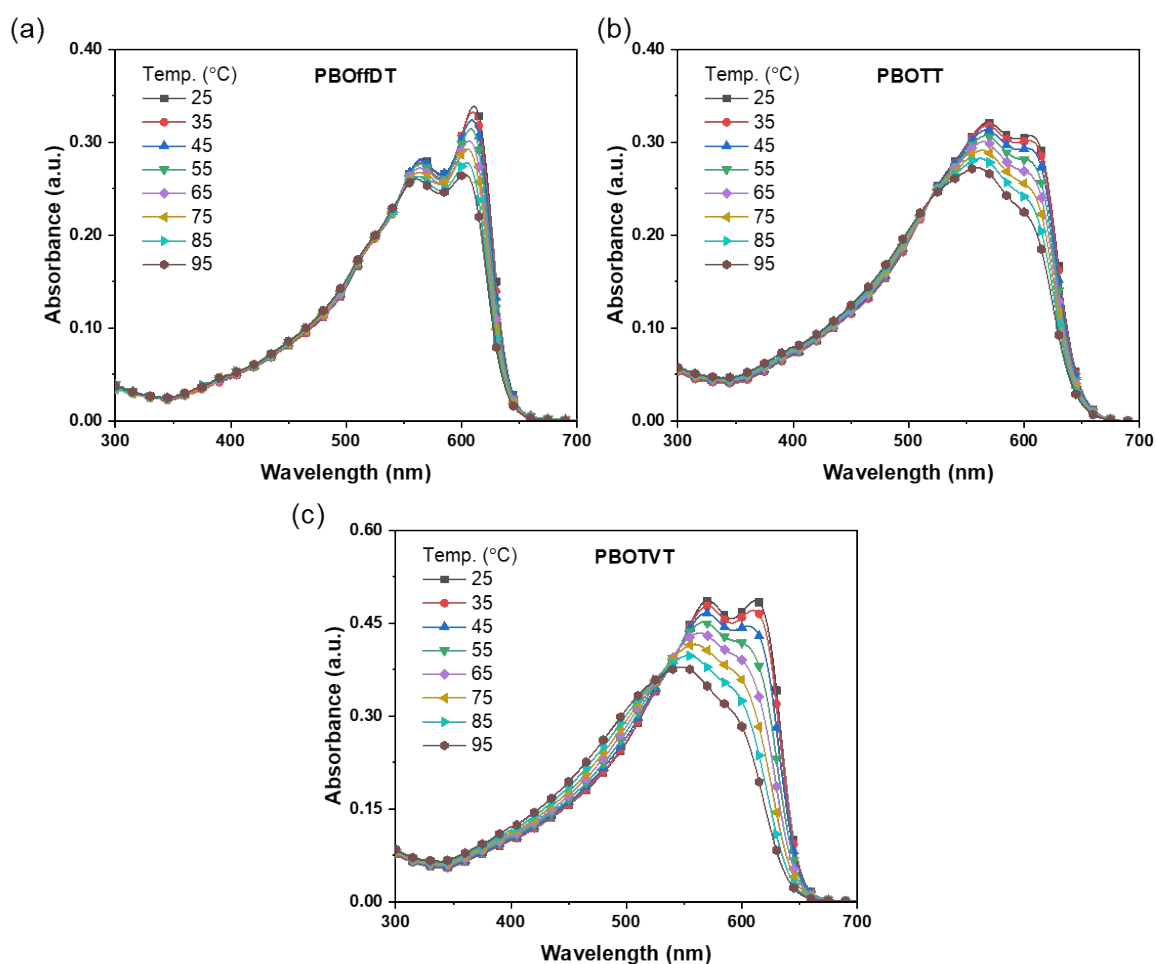
where  $J$  is the current,  $E$  is the effective electric field,  $\epsilon_0$  is the permittivity of free space,  $\epsilon_r$  is the material relative permittivity,  $d$  is the thickness of the active layer, and  $V$  is the effective voltage. The effective voltage can be obtained by subtracting the built-in voltage ( $V_{bi}$ ) and the voltage drop ( $V_s$ ) from the substrate's series resistance from the applied voltage ( $V_{appl}$ ),  $V = V_{appl} - V_{bi} - V_s$ . The mobility can be calculated from the slope of the  $J^{1/2} \sim V$  curves.



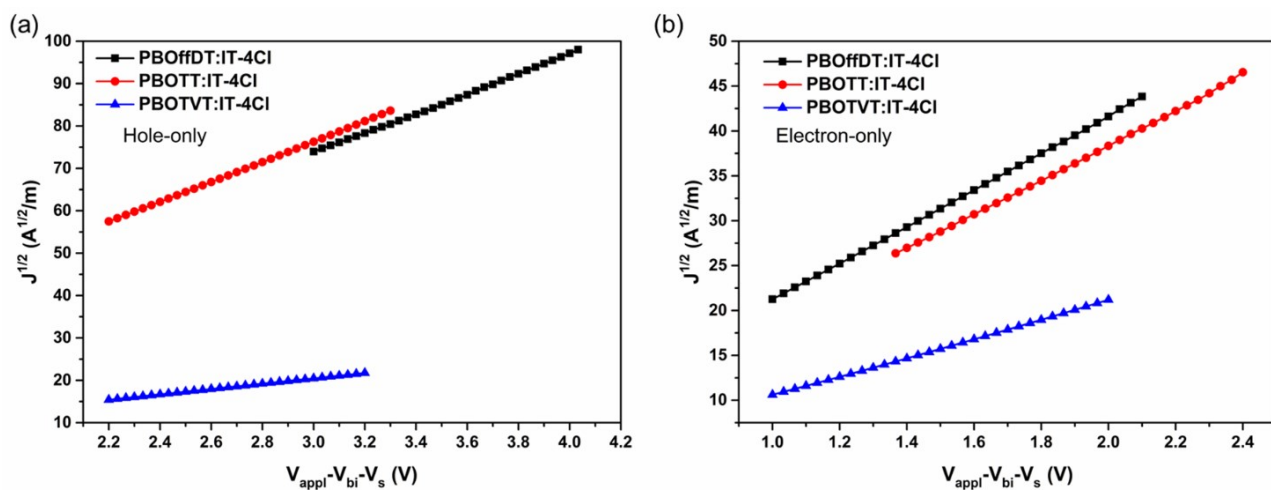
**Figure S1.** (a) TGA curves of polymers; DSC curves of (b) PBOffDT; (c) PBOTT and (d) PBOTVT



**Figure S2.** The CV curves of PBOffDT, PBOTT and PBOTVT



**Figure S3.** Temperature dependent UV-vis absorption spectra of (a) PBOffDT, (b) PBOTT and (c) PBOTVT in 1,3,5-TMB diluted solution.



**Figure S4.** The  $J^{1/2}$ - $V$  curves based on PBOffDT, PBOTT and PBOTVT blend films (a) hole-only devices; (b) electron-only devices

**Table S1.** Photovoltaic parameters of the polymer:IT-4Cl (1:1) based devices using CB as process solvent under AM1.5G condition, 100 mW/cm<sup>2</sup>

Polymer	$V_{oc}$ (V)	$J_{sc}$ (mA/cm <sup>2</sup> )	FF (%)	PCE (%)
PBOffDT	0.86	15.68	65.5	8.24
PBOTT	0.76	14.89	60.7	6.89
PBOTVT	0.73	8.67	48.9	3.09