

## Electronic Supplementary Information

### High Voltage All Polymer Solar Cells with a Polymer Acceptor based on NDI and Benzotriazole

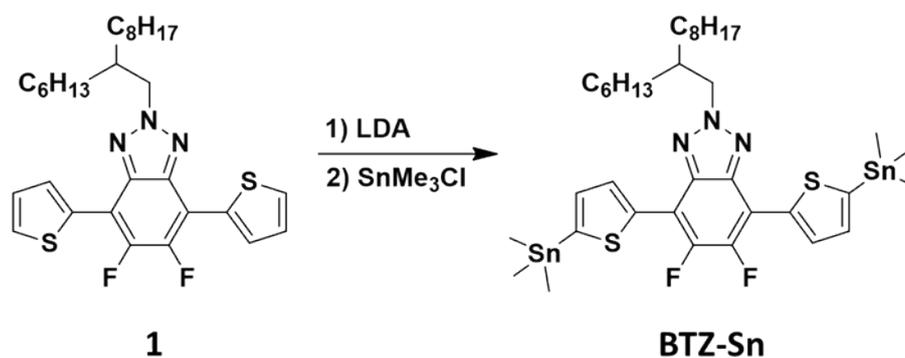
*Qing Ma<sup>a,d</sup>, Xiaonan Xue<sup>b</sup>, Lian Zhong<sup>a,d</sup>, Indunil Angunawela<sup>c</sup>, Shanshan Chen<sup>e</sup>, Harald Ade,<sup>c\*</sup>Lijun Huo,<sup>b\*</sup>Zhanjun Zhang,<sup>a\*</sup>and Yongfang Li<sup>a,d\*</sup>* *a School of Chemical Science, University of Chinese Academy of Sciences Beijing 100049, China b School of Chemistry, Beihang University, Beijing 100191, P. R. China c Department of Physics and Organic and Carbon Electronics Lab North Carolina State University Raleigh, NC 27695, USA d Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China e MOE Key Laboratory of Low-grade Energy Utilization Technologies and Systems, CQU-NUS Renewable Energy Materials & Devices Joint Laboratory, School of Energy & Power Engineering, Chongqing University, Chongqing 400044, China*

#### Experimental Section

**Materials:** All chemicals and solvents were purchased from J&K, Alfa Aesar and TCI Chemical Co. PBDB-T was purchased from Solarmer Materials, Inc. PDINO were obtained according to our previous reported methods. N2200 was prepared according to the procedure reported in literature. The PDI and  $M_n$  of PBDB-T/ N2200 are listed in Table S4.

**Synthesis:** Synthesis of 4,7-bis(2-trimethylstannylthien-5-yl)-5,6-difluoro-2,1,3benzotriazole (BTz-Sn). The synthetic route of BTz-Sn is shown in Scheme S1. A solution of compound 1 (0.54 g, 1 mmol) in dry THF (12 mL) under argon was cooled down to -78 °C. Then LDA (1.25 mL, 2M in THF, 2.5 mmol) was added dropwise. The dark green solution was stirred at -78 °C for 1 h, following which a 1 M solution of trimethyltin chloride in hexane (3 mL, 1M in THF, 3 mmol) was added. The reaction mixture was then allowed to warm to room temperature and stirred overnight. Water was

added to quench the reaction. The mixture solution was extracted with diethyl ether (50 M × 3). Solvent was evaporated under reduced pressure and the product was purified by recrystallization. Yield: 460 mg, (53%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.44 (d, J = 3.5 Hz, 2H), 7.35 (d, J = 3.5 Hz, 2H), 4.76 (d, J = 6.4 Hz, 2H), 2.32 (dt, J = 12.0, 6.1 Hz, 1H), 1.48 – 1.23 (m, 24H), 0.90 (dd, J = 7.0, 5.6 Hz, 6H), 0.57 – 0.40 (m, 18H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 148.21, 145.70, 141.25, 137.88, 135.34, 130.85, 109.82, 59.93, 39.10, 31.91, 31.85, 31.54, 29.91, 29.61, 29.57, 29.34, 26.36, 26.32, 22.69, 22.67, 14.12, 14.09, -8.24. MS (EI) m/z: calcd for C<sub>36</sub>H<sub>55</sub>N<sub>3</sub>S<sub>2</sub>F<sub>2</sub>Sn<sub>2</sub>, 869; found, 869. Elemental analysis calcd (%) for (C<sub>36</sub>H<sub>55</sub>N<sub>3</sub>S<sub>2</sub>F<sub>2</sub>Sn<sub>2</sub>): C, 49.74; H, 6.38; found: C, 49.72; H, 6.39.



**Scheme S1.** Synthetic route of monomer BTZ-Sn

**Polymerization for LA03:** 0.15 mmol of the monomers of NDI2OD-2Br (141.3mg) and BTz-Sn (130.6mg), respectively, were put into a three-neck flask. Then 15 ml argon purged toluene was added under the protection of argon. And then 5 mg of Pd(dba)<sub>2</sub> and 8 mg of o-methyl triphenylphosphine was added. After another flushing with argon for 20 min, the reactant was heated to reflux for 18 h. Then the reaction system was cooled to room temperature, and the polymer was precipitated by adding 50 ml methanol, and filtered through a Soxhlet thimble, then subjected to Soxhlet extraction with methanol, hexane, and chloroform. The polymer was recovered as solid from the chloroform fraction by rotary evaporation. The solid was dried under vacuum for 1 day.

Yield: 78 mg, (66%).  $M_n$ : 92 KDa, PDI: 1.9.

**Measurements:**  $^1\text{H}$  NMR spectra were measured on a Bruker DMX-400 spectrometer with d-chloroform as the solvent and trimethylsilane as the internal reference. TGA was conducted under a nitrogen flow rate of  $100\text{ mL min}^{-1}$  on a Perkin-Elmer TGA-7 thermogravimetric analyzer at a heating rate of  $20\text{ }^\circ\text{C min}^{-1}$ . The UV-visible absorption spectra were measured on a Hitachi U-3010 UV-vis spectrophotometer.

The electrochemical cyclic voltammetry was carried out on a Zahner IM6e Electrochemical Workstation, in an acetonitrile solution of  $0.1\text{ mol L}^{-1}$   $n\text{-Bu}_4\text{NPF}_6$  at a potential scan rate of  $100\text{ mV s}^{-1}$ . The sample film on Pt plate was used as working electrode, a platinum wire was used as counter electrode and Ag/AgCl was used as reference electrode.

The thickness of the thin films was measured by a profilometry (Ambios Tech.XP-2). The surface morphology of thin films was measured by atomic force microscope (AFM, Bruker-ICON2-SYS) in the tapping mode. The bulk morphology of thin films was measured by transmission electron microscopy (TEM, JEM-2100F).

**SCLC Measurements:** Hole and electron mobilities were measured using the SCLC model, With ITO/PEDOT:PSS/active layer/Au for hole-only devices and ITO/ZnO/active layer /PDINO/Al for electron-only devices. The SCLC mobilities were calculated by Mott-Gurney equation:  $J = (9/8)\epsilon_r\epsilon_0\mu(V^2/L^3)$ . where J is the current density,  $\epsilon_r$  is the dielectric permittivity of the active layer,  $\epsilon_0$  is the vacuum permittivity, L is the thickness of the active layer,  $\mu$  is the mobility.  $V = V_{\text{app}} - V_{\text{bi}}$ , where  $V_{\text{app}}$  is the applied voltage,  $V_{\text{bi}}$  is the offset voltage ( $V_{\text{bi}}$  is 0 V here). The mobility can be calculated from the slope of the  $J^{0.5} \sim V$  curves.

**GIWAXS Characterization:** Grazing-incidence wide-angle X-ray scattering (GIWAXS) measurements were conducted at Advanced Light Source (ALS), Lawrence Berkeley National Laboratory, Berkeley, CA at the beamline 7.3.3. Data was acquired at the critical angle (0.130) of the film with a hard X-ray energy of 10 keV. X-ray irradiation time was 10-30 s, dependent on the saturation level of the detector. Beam center was calibrated using AgBr powder and the sample-to-detector distance was about

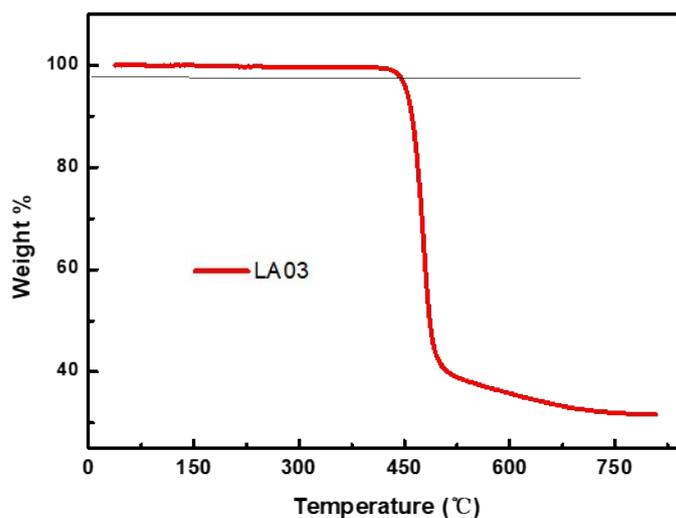
330 nm. The  $\pi$ - $\pi$  coherence lengths ( $L$ ) are estimated based on the Scherrer Equation ( $L=2\pi K/\text{FWHM}$ ), where  $K$  is the shape factor (here we use 0.9), and FWHM is the full width at half maximum of the (010) diffraction peaks.

**Resonant soft X-ray scattering (RSoXS):** Resonant soft X-ray scattering was performed at beamline 11.0.1.2 Advanced Light Source, LBNL. Thin film samples were spin-casted on top of the PEDOT: PSS covered Si wafers under exactly the same condition as those for the fabrication of solar cell devices. Then BHJ thin films were floated and transferred onto silicon nitride membrane windows. The scattering was done in transmission mode and signals were collected in vacuum using Princeton Instrument PI-MTE CCD camera. The RSoXS profiles are Lorentz corrected (assuming 3D unisotropy) and thickness normalized.

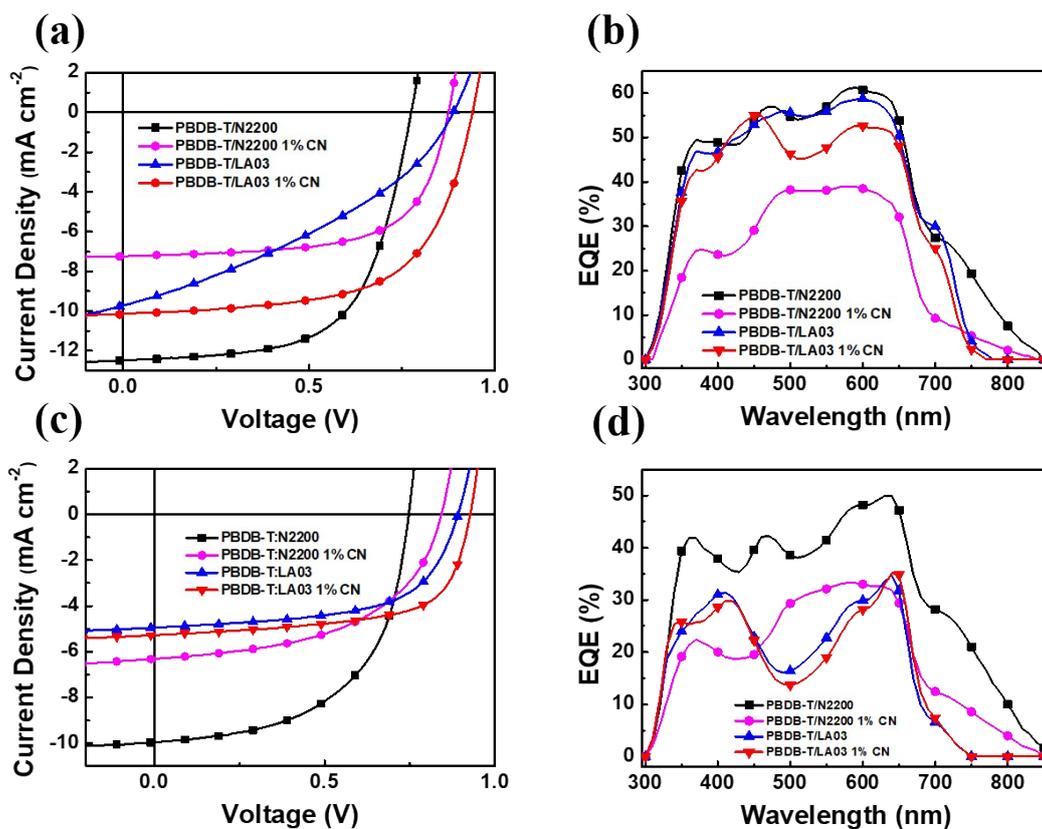
**Fabrication of all-PSCs :** The all-PSCs were fabricated with traditional device structure of ITO /PEDOT: PSS/Active layer/PDINO/Al. The ITO-coated glass substrates were cleaned by ultrasonic treatment in deionized water, acetone, and isopropanol for 15 min, dried under a nitrogen stream, and subsequent ultraviolet-ozone treatment for 20 min. A thin layer of PEDOT: PSS was prepared on precleaned ITO glass through spin-coating a PEDOT: PSS aqueous solution (Baytron P VP AI 4083 from H. C. Starck) at 4200 rpm and dried subsequently at 150 °C for 20 min in air. Then the device was transferred to a nitrogen glove box, where the active blend layer of PBDB-T:Polymer acceptor (LA03 or N2200) was spin-coated from its chloroform solution onto the PEDOT: PSS layer at 3000 rpm. After spin-coating, the active layers were annealed at 150 °C for 5 min for the devices with TA treatment. The electron transport layer PDINO at a concentration of 1.0 mg mL<sup>-1</sup>. Finally, cathode metal Al was deposited at a pressure of  $5.0 \times 10^{-5}$  Pa. The active layer effective area of the devices was 4.6 mm<sup>2</sup>.

**Characterization of all-PSCs:** The current density-voltage ( $J$ - $V$ ) characteristics of the all-PSCs were measured on a computer-controlled Keithley 2450 Source-Measure Unit under AM 1.5G solar illumination at 100 mW cm<sup>-2</sup> using a Newport solar simulator. The EQE spectra of the devices were measured by Solar Cell Spectral Response

Measurement System QE-R3-011 (Enli Technology Co., Ltd., Taiwan).

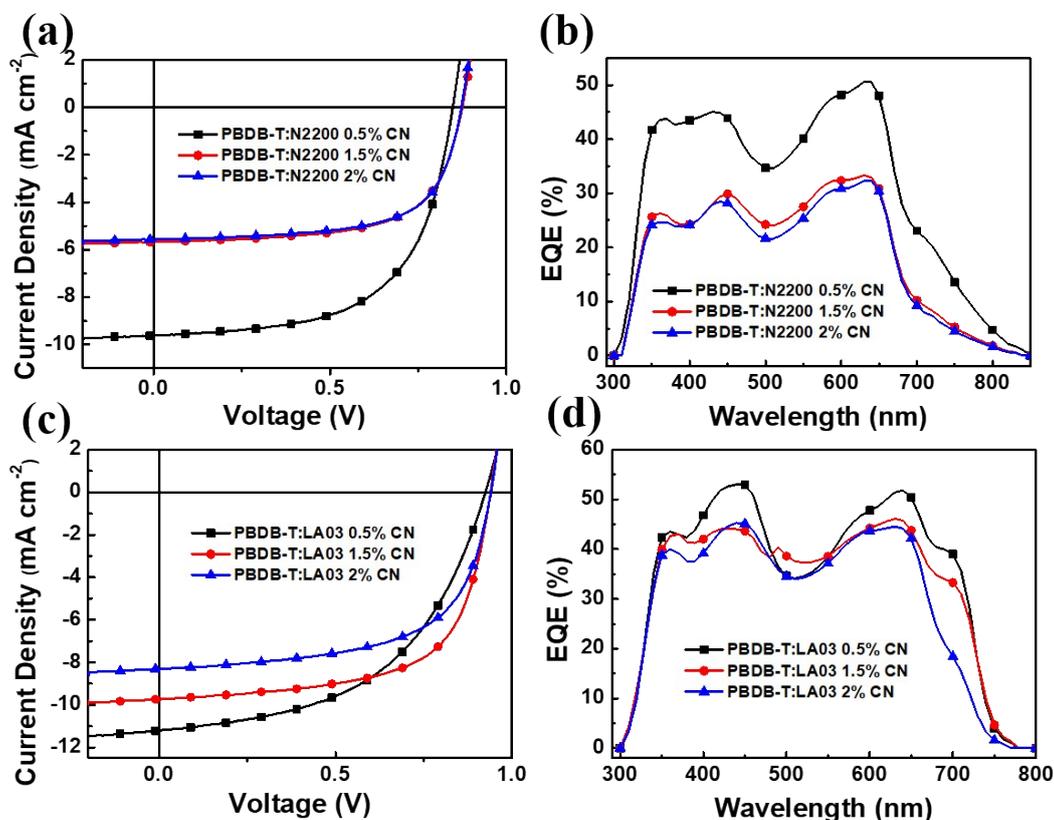


**Figure S1.** TGA plot of LA03 with a heating rate of 20°C/min under the inert atmosphere.

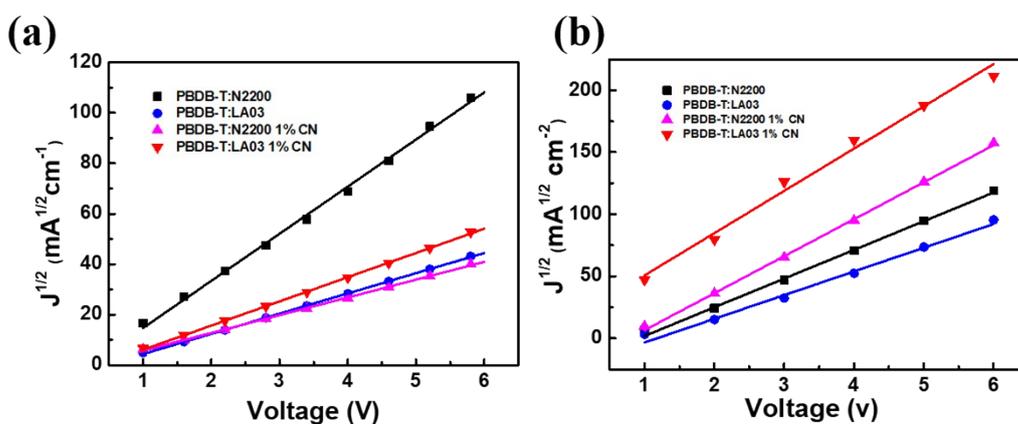


**Fig. S2.** (a)  $J-V$  curves of the all-PSCs with D/A weight ratio of 3:1 under the illumination of AM1.5G, 100 mW/cm<sup>2</sup>, (b) EQE spectra of the corresponding all-PSCs with D/A weight ratio of 3:1. (c)  $J-V$  curves of the all-PSCs with D/A weight ratio of

1:1 under the illumination of AM1.5G, 100 mW/cm<sup>2</sup>, (d) EQE spectra of the corresponding all-PSCs with D/A weight ratio of 1:1.



**Fig. S3.** (a),(c)  $J$ - $V$  curves of the all-PSCs(PBDB-T:N2200/LA03) with different volume percentage of CN additive under the illumination of AM1.5G, 100 mW/cm<sup>2</sup>, (b),(d) EQE spectra of the corresponding all-PSCs(PBDB-T:N2200/LA03) with different volume percentage of CN additive.



**Fig. S4.** (a) Current-Voltage plots of the all-PSCs for the measurement of electron mobility, (b) Current-Voltage plots of the all-PSCs for the measurement of hole mobility.

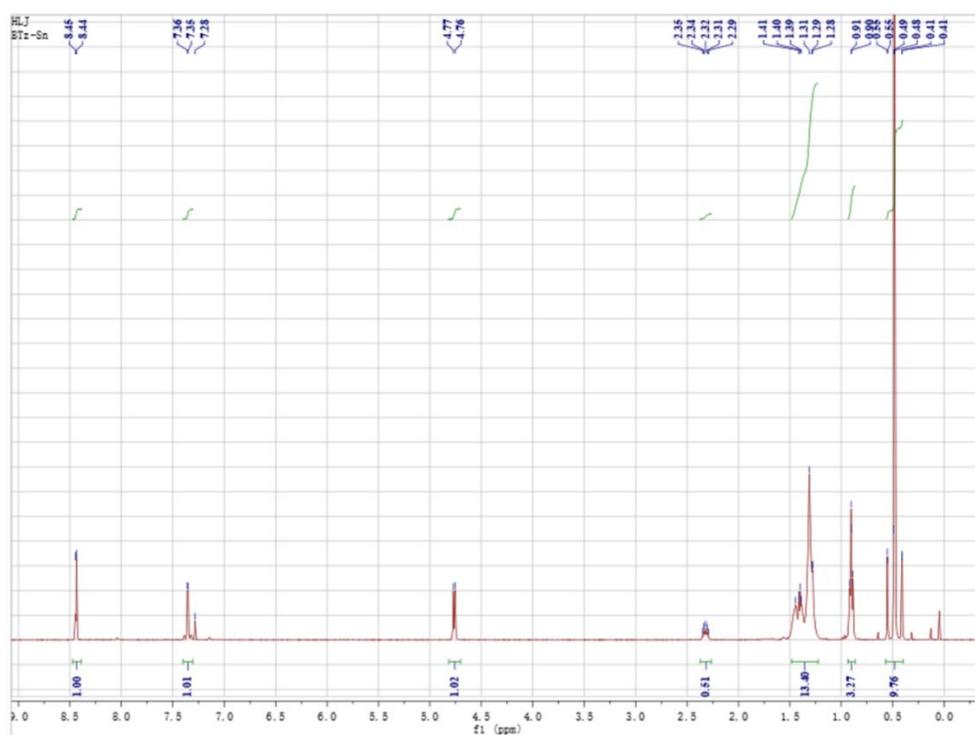


Fig. S5.  $^1\text{H}$  NMR spectrum of compound BTz-Sn.

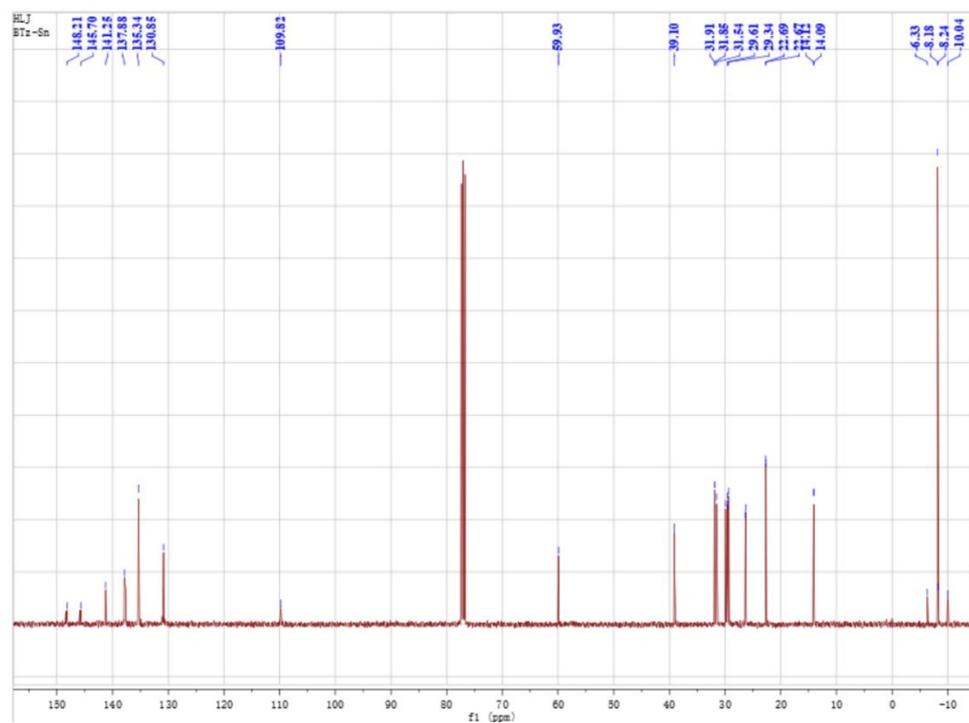
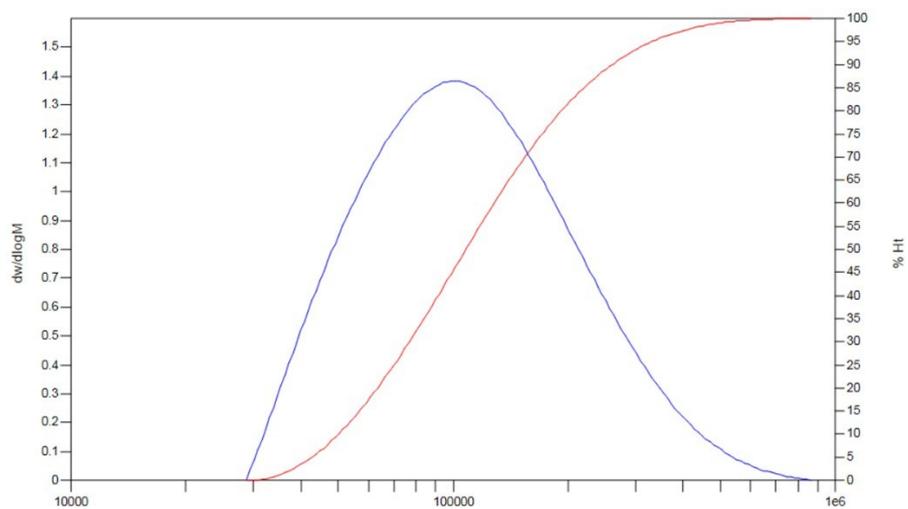
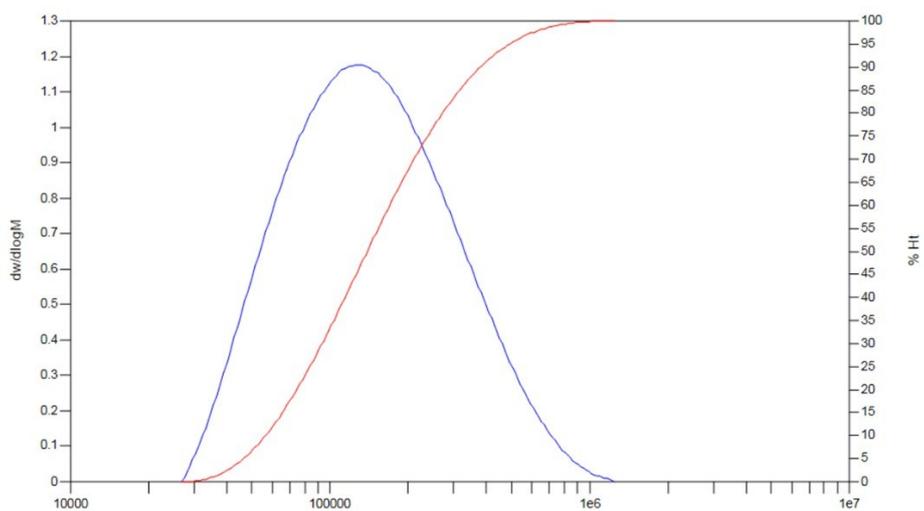


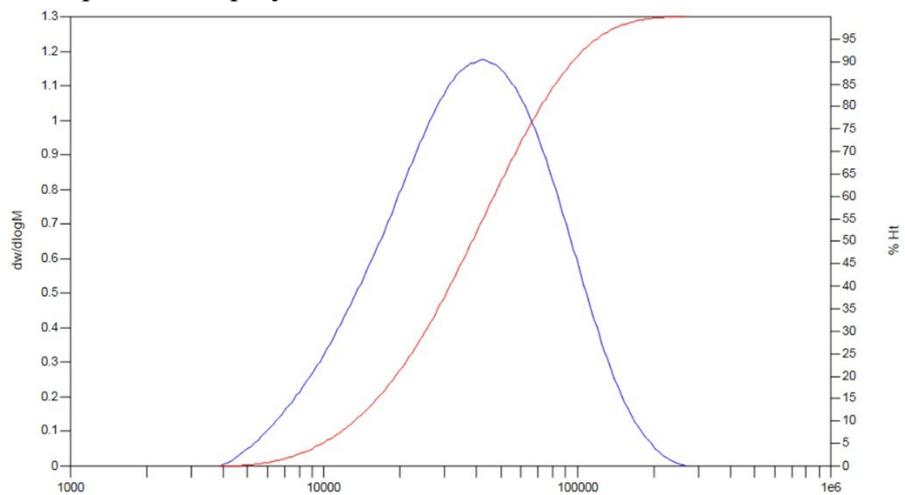
Fig. S6.  $^{13}\text{C}$  NMR spectrum of compound BTz-Sn.



**Fig. S7.** GPC spectrum of polymer LA03.



**Fig. S8.** GPC spectrum of polymer N2200.



**Fig. S9.** GPC spectrum of polymer PBDB-T.

**Table S1.** The PDI and  $M_n$  of Polymers.

Polymer	PDI	$M_n$ (KDa)
PBDB-T	1.73	27.21
N2200	1.65	111.26

**Table S2.** Summary of the photovoltaic performance parameters of the all-PSCs based PBDB-T: Polymer acceptors with different D/A weight ratios under the illumination of AM 1.5G, 100 mWcm<sup>-2</sup>

Polymer acceptor	D/A weight Ratio	CN (%v/v)	$V_{oc}$ [V]	$J_{sc}$ [mA/cm <sup>2</sup> ]	FF (%)	$PCE_{max}$ ( $PCE_{avg}$ )	$J_{scb}$ [mA/cm <sup>2</sup> ]
N2200	3:1	/	0.776	12.26	61.90	5.89(5.71)	12.05
		1	0.875	7.23	64.76	4.10(3.88)	6.82
	1:1	/	0.747	9.95	56.31	4.18(4.11)	9.96
		1	0.816	6.21	52.01	2.64(2.51)	6.03
LA03	1:1	/	0.891	4.95	59.80	2.64(2.59)	4.88
		1	0.927	5.26	64.64	3.15(2.87)	4.68
	3:1	/	0.89	10.45	37.31	3.48(3.55)	11.04
		1	0.939	10.14	62.03	5.91(5.70)	9.95

a) Average PCE from 20 devices.

b) Integrated  $J_{sc}$  values from EQE spectra.

**Table S3.** Summary of the photovoltaic performance parameters of the all-PSCs based PBDB-T: Polymer acceptors with different volume percentage of CN additive under the illumination of AM 1.5G, 100 mWcm<sup>-2</sup>

Polymer:	CN (%v/v)	$V_{oc}$ [v]	$J_{sc}$ [mA•cm <sup>2</sup> ]	FF (%)	$PCE_{max}$ ( $PCE_{avg}$ )	$J_{scb}$ [mA•cm <sup>2</sup> ]
PBDB-T	0.5	0.848	9.62	60.14	4.91(4.78)	9.28
	1.5	0.874	5.74	63.05	3.22(3.17)	5.68
	2		5.56	65.73	3.19(3.14)	5.47
LA03		0.872				
	0.5	0.924	11.20	50.88	5.44(5.27)	11.34
	1.5	0.934	9.73	63.79	5.83(5.81)	9.88
	2	0.940	8.30	60.88	4.76(4.74)	8.20

a) Average PCE from 20 devices.

b) Integrated  $J_{sc}$  values from EQE

spectra.

**Table S4.** The hole ( $\mu_h$ )/electron mobilities ( $\mu_e$ ) of the blend active layers of PBDBT:polymer acceptors.

Polymer acceptor	CN (% <i>, v/v</i> )	Thickness (nm)	$\mu_h$ $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$	$\mu_e$ $10^{-5}\text{cm}^2\text{V}^{-1}\text{s}^{-1}$	$\mu_e/\mu_h$
N2200	/	125	$1.69 \times 10^{-4}$	9.41	1.79
	1	125	$3.02 \times 10^{-5}$	1.34	0.44
LA03	/	125	$6.23 \times 10^{-5}$	1.96	0.31
	1	125	$4.28 \times 10^{-5}$	3.89	0.9