Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

This journal is © The Royal Society of Chemistry 2018

Electronic Supplementary information (ESI):

Design of Asymmetric Benzodithiophene based Wide Band-gap Conjugated Polymers toward Efficient Polymer Solar Cells Promoted by Low Boiling Point Additive

Yonghai Li,‡[a] Linrui Duan,‡[a] Deyu Liu,‡[a,d] Weichao Chen,[a,b]* Xichang Bao,[a] Hongyu Zhen,[c] Huizhou Liu[a]* and Renqiang Yang[a]*

[a] *CAS Key Laboratory of Bio-based Materials, Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, Qingdao 266101, China.*

**E-mail: liuhz@qibebt.ac.cn, yangrq@qibebt.ac.cn.*

[b] *College of Textiles & Clothing, Qingdao University, Qingdao 266071, China. *E-mail: chenwc@qdu.edu.cn.*

[c] *College of Chemistry and Materials Science and Engineering, Fujian Key Laboratory of Polymer Materials, Fujian Normal University, Fuzhou 350007, China.*

[d] *University of Chinese Academy of Sciences, Beijing 100049, China.*

‡ Yonghai Li, Linrui Duan and Deyu Liu contributed equally to this work.

1. Materials Characterization Techniques

^{1}H NMR and ^{13}C NMR spectra of intermediates were collected on a Bruker AVANCE-III 600 Spectrometer at 298 K as solutions in $CDCl_3$. Gel permeation chromatography (GPC) was performed with trichlorobenzene (TCB) as eluent at 150 °C and polystyrene was used as the standard. Elemental analysis was performed on a Heraus CHN-Rapid elemental analyzer. TGA measurement was performed using a SDT Q600 V20.9 Build 20 at a heating rate of 10 ^{o}C min^{-1} under a nitrogen atmosphere. UV-vis absorption spectra were measured from a Hitachi U-4100 spectrophotometer with dilute solutions in *o*-DCB and solid state films of the polymers (or polymer/acceptor blends) at room temperature. Cyclic voltammetry (CV) measurements were performed on a CHI660D electrochemical workstation, equipped with a three-electrode cell consisting of a platinum working electrode, a saturated calomel electrode (SCE) as reference electrode and a platinum wire counter electrode. CV measurements were carried out in anhydrous acetonitrile containing 0.1 M *n*-Bu_4NPF_6 as a supporting electrolyte under an argon atmosphere at a scan rate of 100 mV s^{-1} assuming that the absolute energy level of Fc/Fc^{+} was -4.80 eV. Thin films were deposited from *o*-DCB solution onto the working electrodes. Density functional theory (DFT) calculations were confirmed by the Gaussian 09 program at the B3LYP/6-31G(d,p) level. XRD measurements were carried out in reflection mode at room temperature. Atomic force microscopy (AFM) images were obtained using Agilent 5400 scanning probe microscope in tapping-mode with MikroMasch NSC-15 AFM tips. Transmission electron microscopy (TEM) images were obtained by using a HITACHI H-7650 electron microscope with an acceleration voltage of 100kV.

2. Device Fabrication and Evaluations

Photovoltaic devices were fabricated with a conventional device structure of ITO/PEDOT:PSS/polymer : acceptor/PFN/Al. The patterned ITO glass (sheet resistance = 15 Ω/square) was pre-cleaned in an ultrasonic bath of acetone and isopropyl alcohol and treated in an ultraviolet-ozone chamber (PREEN II-862) for 6 min. Then a thin layer (about 30 nm) of PEDOT:PSS was spin-coated onto the ITO glass at 4000 rpm and baked at 150 ^{o}C for 15 min.

Solutions of polymer/acceptor in *o*-DCB (~12 mg/mL, total concentration) were stirred overnight and warmed to 90 °C for 30 mins before spin-coating on the PEDOT:PSS layer to form the active layer about 100-120 nm. The thickness of the active layer was measured using a Veeco Dektak 150 profilometer. Then PFN solution (in CH_3OH) was spin-coating as electron transfer layer. Finally, Al (100 nm) metal electrode was thermal evaporated under about 4×10^{-4} Pa and the device area was 0.1 cm^2 defined by shadow mask.

The current density–voltage (*J*–*V*) characteristics were recorded with a Keithley 2400 source measurement unit under simulated 100 mW cm^{-2} irradiation from a Newport solar simulator. The external quantum efficiencies (EQEs) were analysed using a certified Newport incident photon conversion efficiency (IPCE) measurement system. The hole mobility and electron mobility were measured by space-charge-limited current (SCLC) method with a device configuration of ITO/PEDOT:PSS/active layer/MoO_3/Al and ITO/ZnO/active layer/PFN/Al structure, respectively. The SCLC is described by the Mott–Gurney law:

$$J = 9\varepsilon\mu V^2/(8L^3)$$

where ε represents the dielectric constant of the metal, and μ is the carrier mobility, V is the voltage drop across the device and L is the thickness of the active layer.

3. TGA measurments

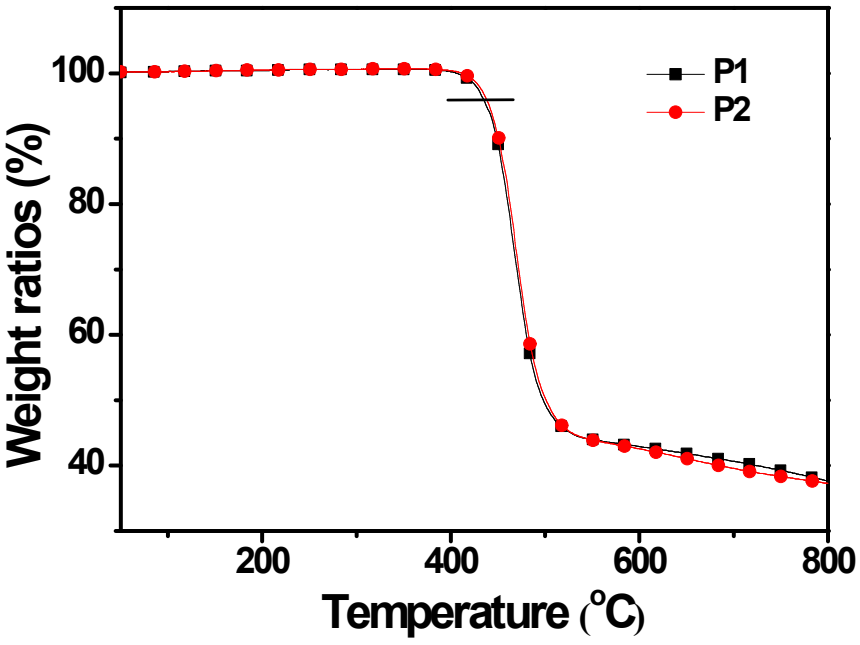

Fig. S1 TGA curves of P1 and P2 with a heating rate of 10 °C/min in N_2.

4. Electrochemical properties

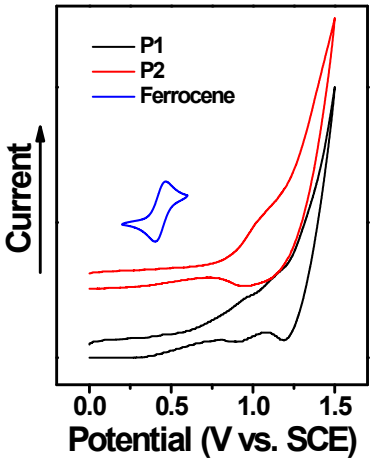

Fig. S2 Ferrocene calibrated cyclic voltammograms of P1 and P2 on Pt electrodes in 0.1 M Bu_4NPF_6-CH_3CN solution at a scan rate of 100 mV s^{-1}.

5. Calculated frontier energy levels

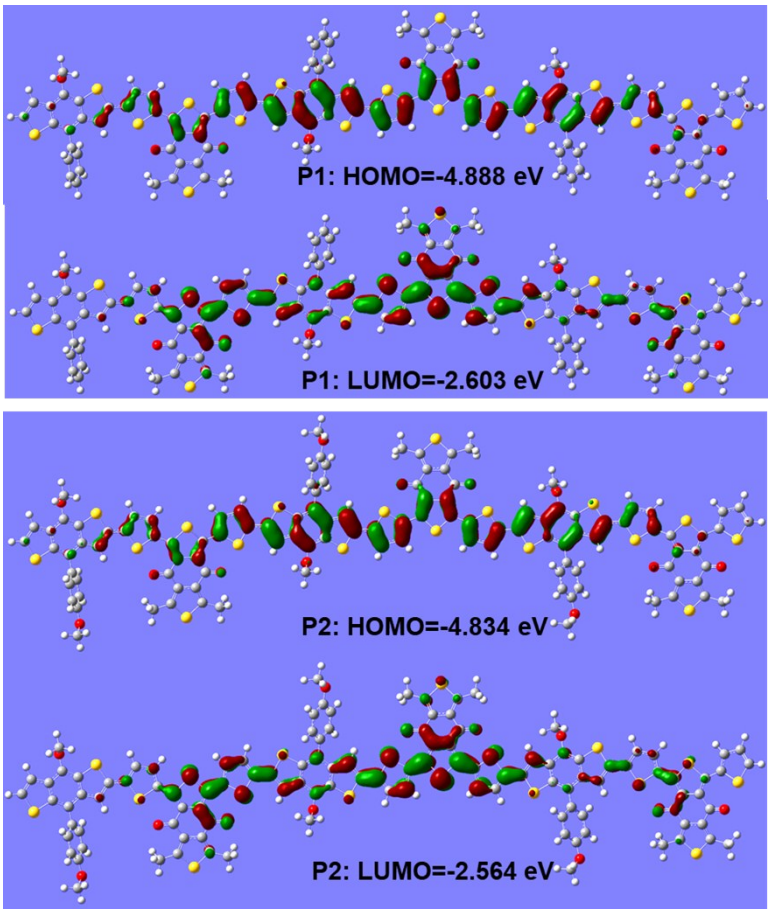

Fig. S3 The distributions of electron clouds and energy levels values of HOMO/LUMO energy orbitals.

6. Photovoltaic properties

Table S1. Photovoltaic data of PSCs with different weight ratios and pre-treatment method under the illumination of AM 1.5G at 100 mW cm^{-2}

Blend		Additive [a]	V_{OC} (V)	J_{SC} mA cm^{-2}	FF (%)	PCE[b] (%)
P1:$PC_{71}BM$	1.5:1	-	0.86	11.83	58.1	5.91 (5.73)
	1:1	-	0.86	12.98	63.1	7.04 (6.85)
	1:1.5	-	0.85	11.55	64.5	6.36 (6.21)
P2:$PC_{71}BM$	1.5:1	-	0.86	14.51	57.1	7.16 (7.03)
	1:1	-	0.85	15.30	66.0	8.58 (8.32)
	1:1.5	-	0.84	15.03	62.2	7.87 (7.69)
P1:ITIC	1.5:1	-	0.88	12.72	51.4	5.82 (5.70)
	1:1	-	0.88	14.01	52.7	6.50 (6.33)
	1:1.5	-	0.88	13.27	51.9	6.06 (5.88)
P2:ITIC	1.5:1	-	0.89	14.46	51.6	6.73 (6.52)
	1:1	-	0.89	15.58	55.1	7.64 (7.41)
	1:1.5	-	0.9	14.17	56.7	7.23 (7.02)
P1:ITIC	1:1	1% T	0.89	13.35	53.4	6.34 (6.18)
	1:1	3% T	0.90	13.81	59.9	7.46 (7.30)
	1:1	5% T	0.89	12.89	56.3	6.46 (6.33)
	1:1	3%DIO	0.86	10.54	43.0	3.90 (3.69)
	1:1	3%CN	0.87	10.65	45.3	4.20 (3.98)
	1:1	120 °C(10 min)	0.87	13.85	48.8	5.88 (5.62)
P2:ITIC	1:1	1%DIO	0.89	14.24	50.1	6.35 (6.07)
	1:1	1%CN	0.90	13.93	51.2	6.42 (6.11)
	1:1	1% T	0.89	16.03	58.8	8.38 (8.19)
	1:1	3% T	0.90	16.70	60.3	9.06 (8.91)

	1:1	5% T	0.90	16.59	58.3	8.71 (8.56)

[a] The additive T represents toluene; [b] PCEs were provided in optimal (average) results based on no less than 10 devices for each case; the thickness of all blend films are 110±15 nm.

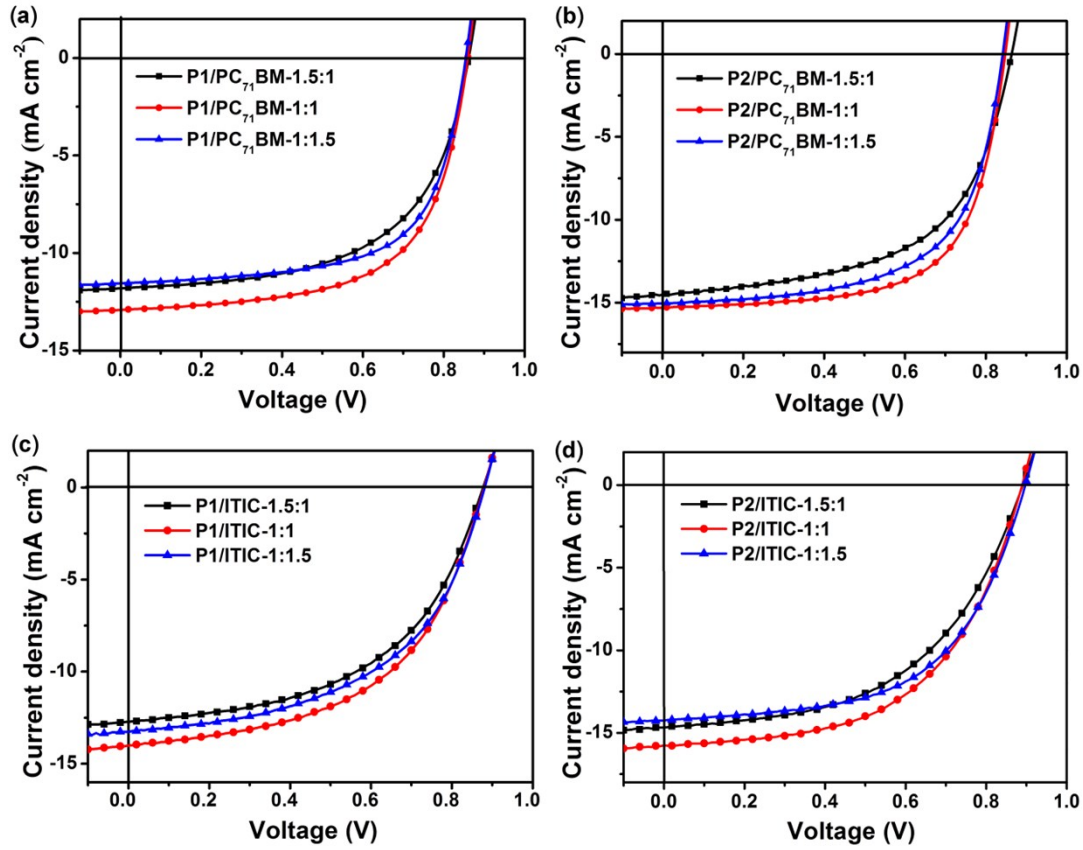

Fig. S4 The *J-V* curves of P1 and P2 based fullerene (a, b) and fullerene-free polymers solar cells (c, d) with different polymer/acceptor weight ratios.

7. Mobilities measurements

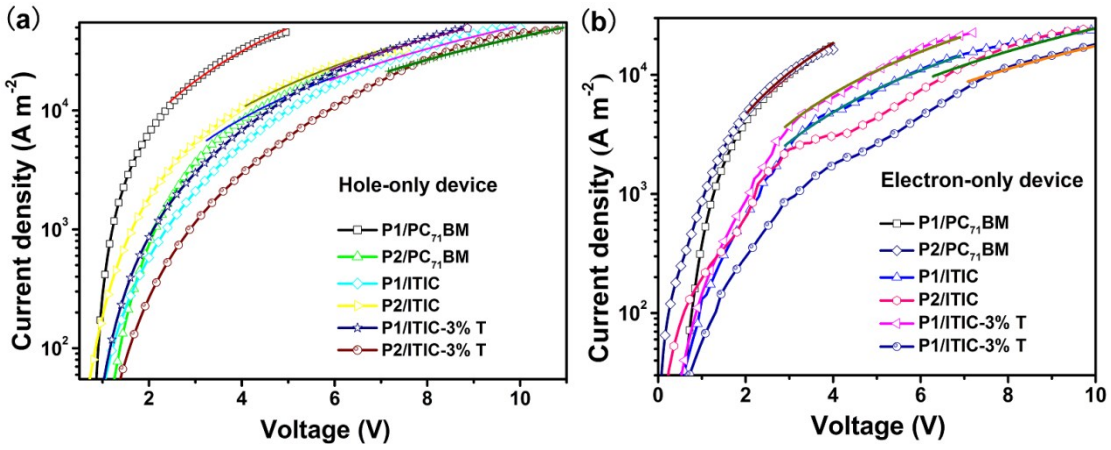

Fig. S5 SCLC curves for polymer/acceptor based hole-only (a) and electron-only (b) devices

under optimal weight ratios.

8. Absorption spectra

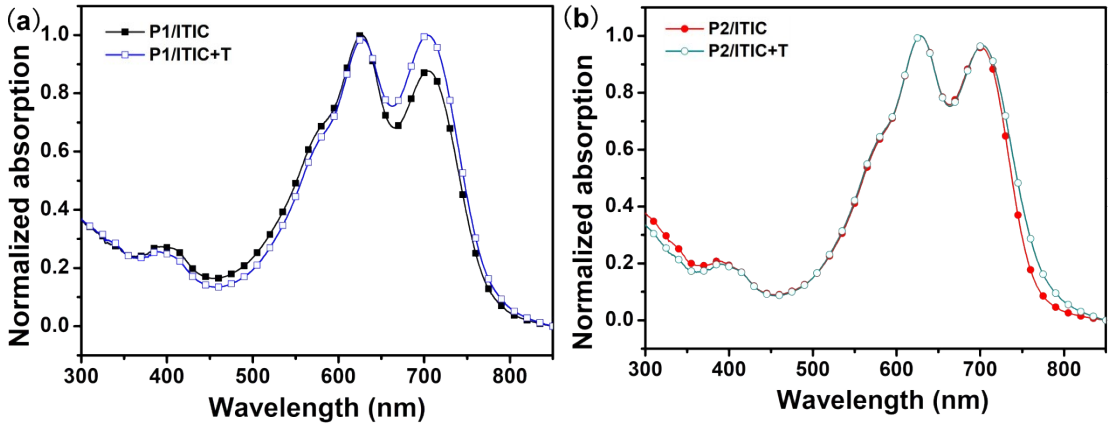

Fig. S6 (a) Normalized absorption spectra of P1/ITIC blends (*w*/*w*=1:1) with and without additive optimization; (b) normalized absorption spectra of P2/ITIC blends (*w*/*w*=1:1) with and without additive optimization.

9. Morphology studies

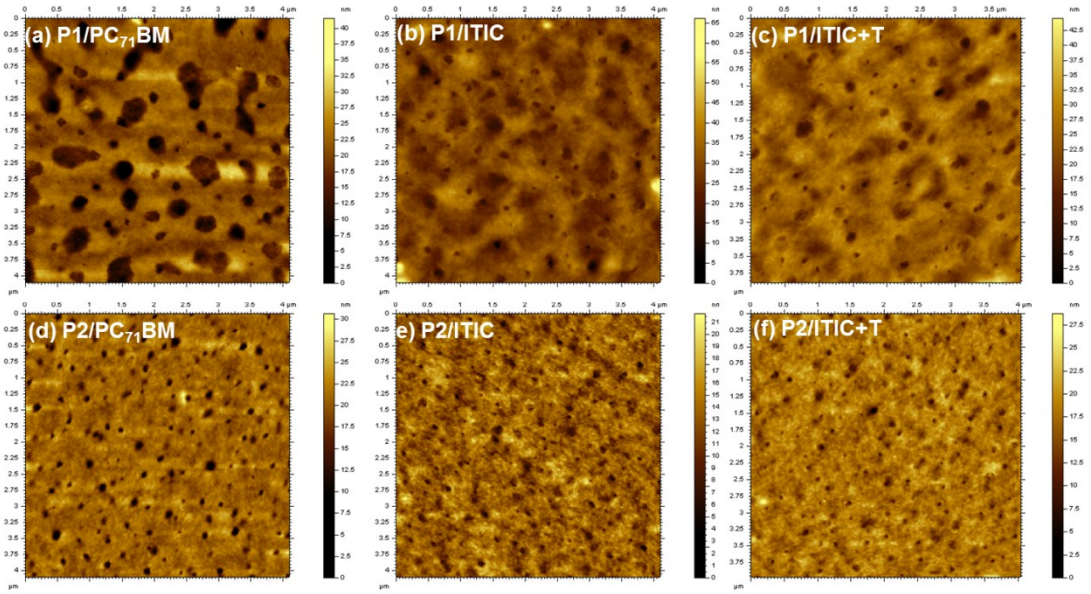

Fig. S7 AFM topography images of different polymer/acceptor blend films under optimal weight ratios.