Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A

Electronic Supplemental Information

New Alkylthienyl Substituted Benzo[1,2-*b*:4,5-*b*']dithiophene-based Polymers for High Performance Solar Cells

Bo Liu,[a,b] Xuewen Chen,[b] Yuehui He,[a] Yongfang Li[c], Xinjun Xu,[d] Lu Xiao,[b] Lidong Li,[d] Yingping Zou*[b,e]

a. State Key Laboratory for Powder Metallurgy, Central South University, Changsha 410083, China

b. College of Chemistry and Chemical Engineering, Central South University, Changsha 410083, China E-mail: yingpingzou@csu.edu.cn(Y.Zou)

c. Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

d. School of Materials Science and Engineering, University of Science and Technology Beijing, Beijing 100083, China

e. State Key Laboratory of Optoelectronic Materials and Technologies, SunYat-sen Unversity, Guangzhou, 510275, China

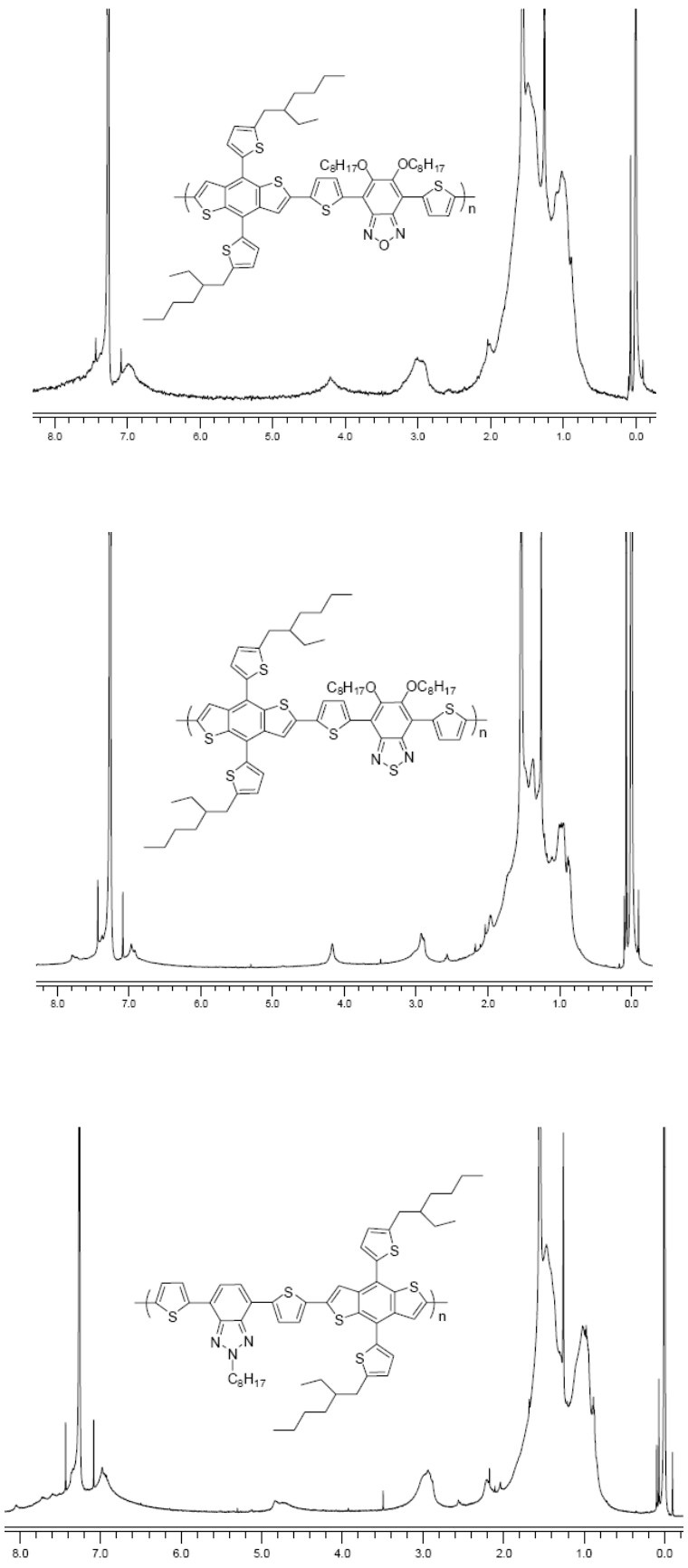


Fig. S1 ^{1}H NMR spectra of the copolymers in $CDCl_3$.

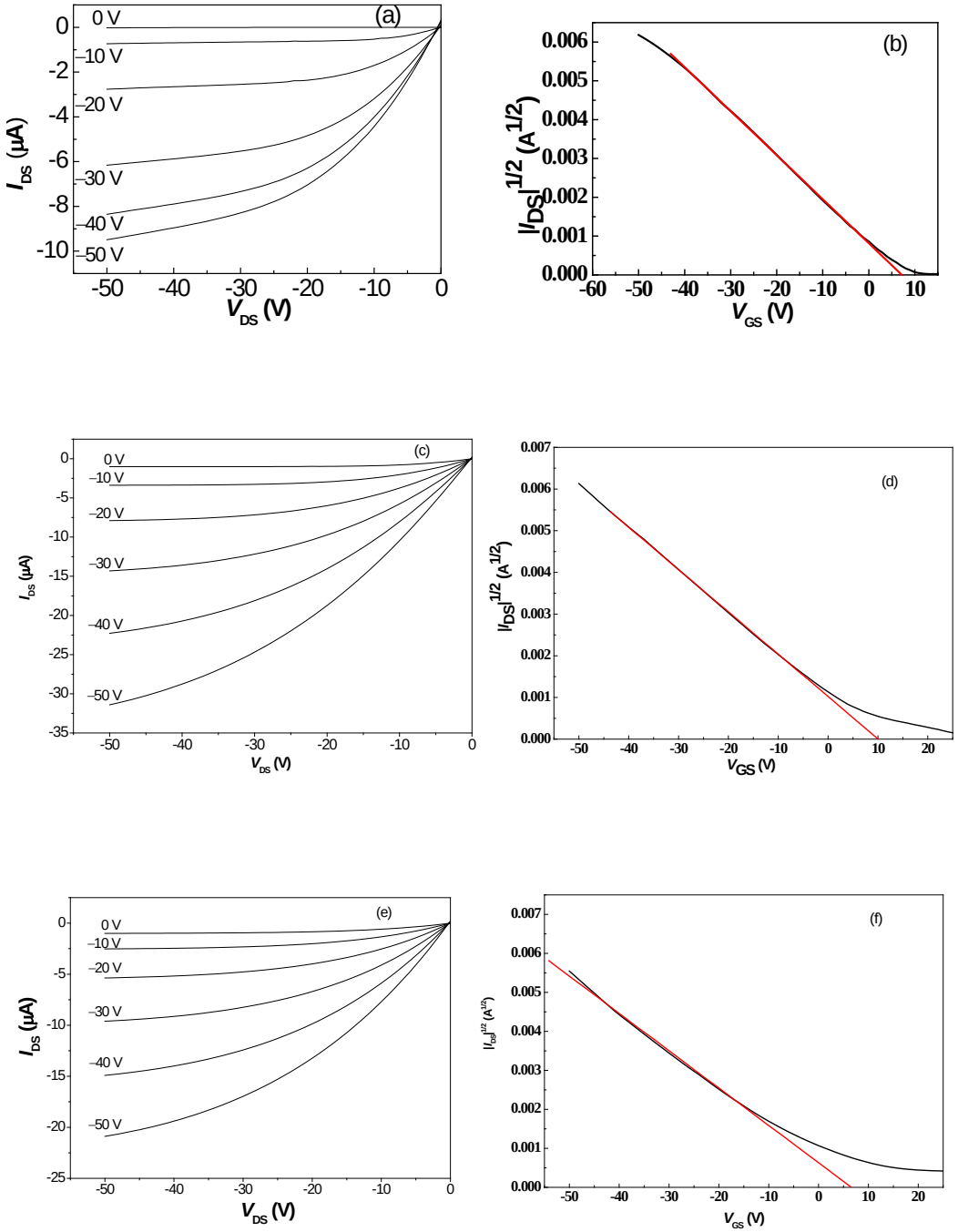
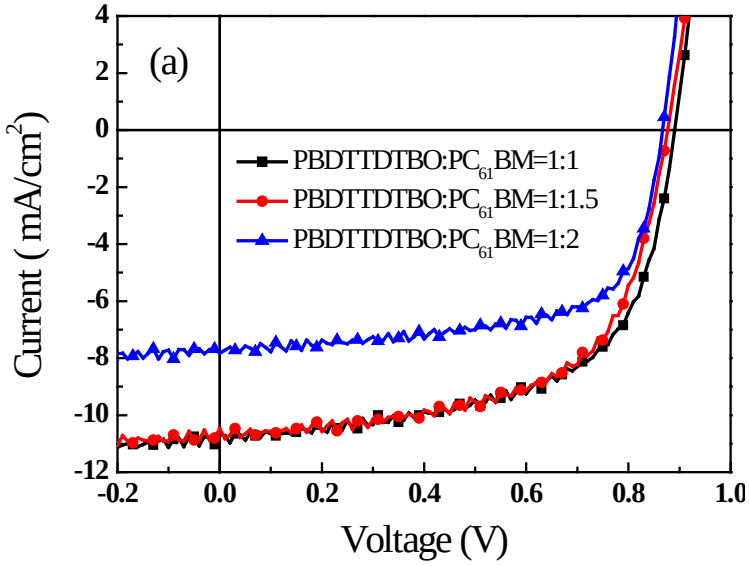
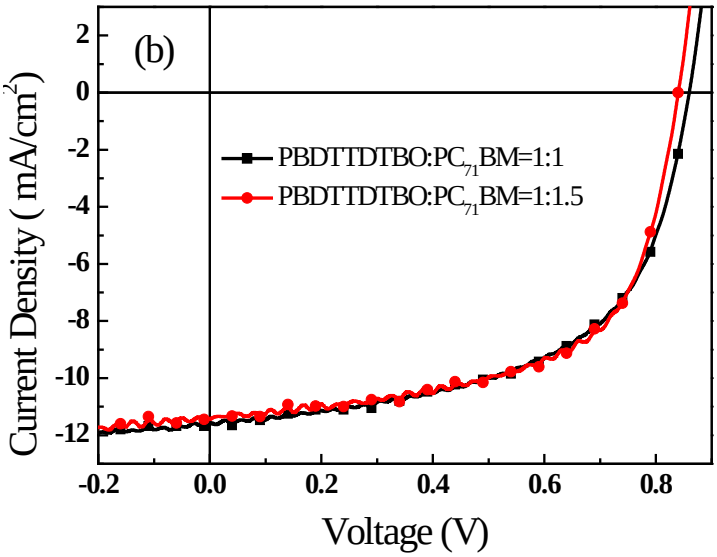


Fig. S2 Output and transfer characteristics of **PBDTTDTBO** (a) output; (b) transfer; **PBDTTDTBT** (c) output; (d) transfer; **PBDTTDTBTz**(e) output; (f) transfer;





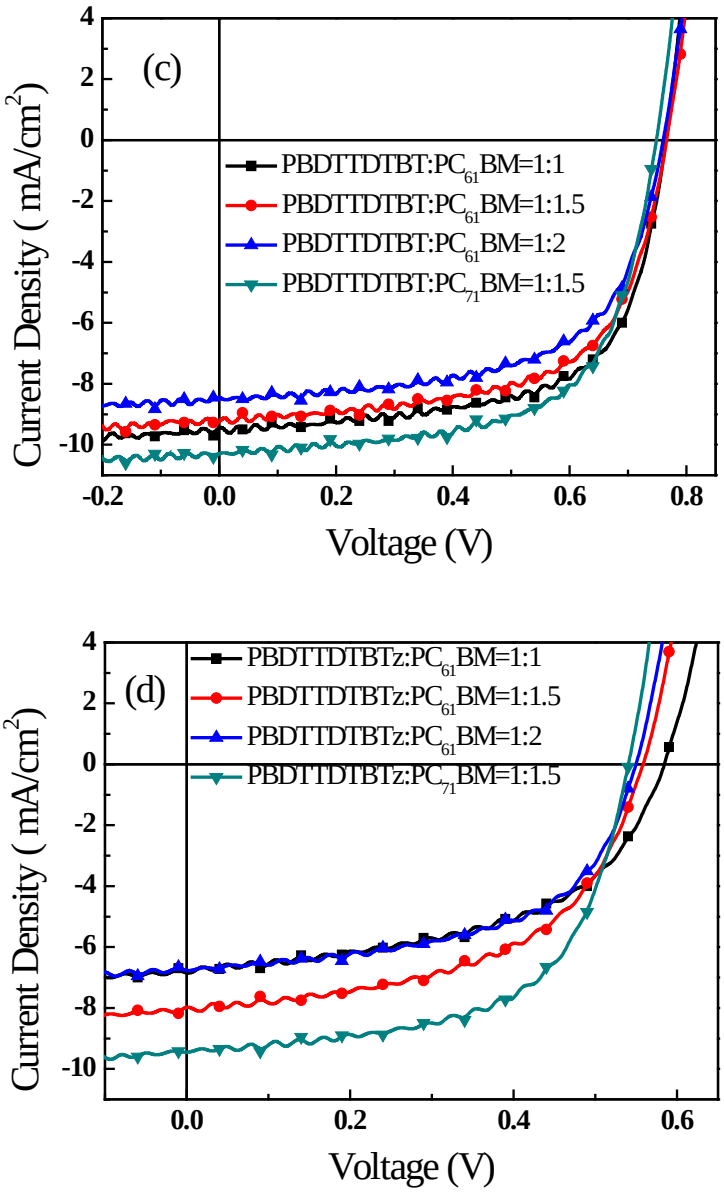
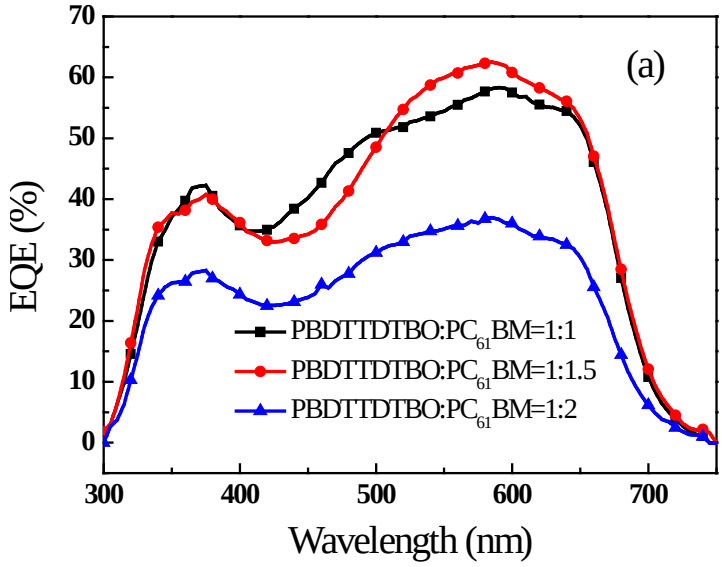
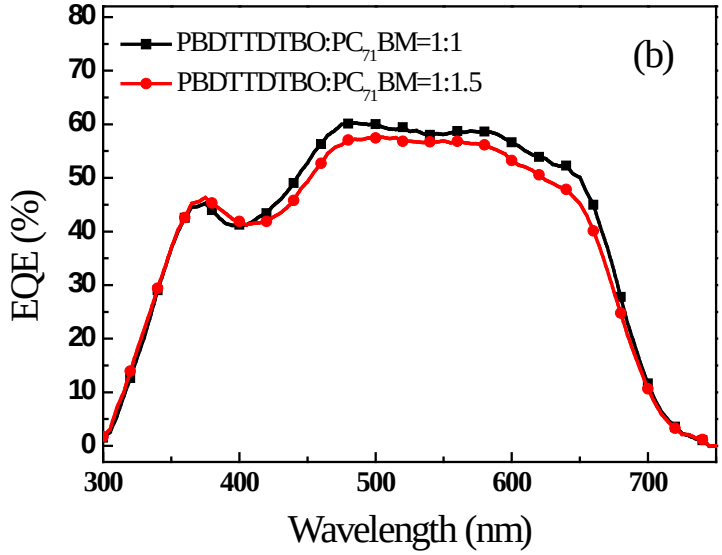


Fig. S3 *J-V* curves of the PSCs based on polymers/PCBM with different ratios (1:1, 1.1.5 and 1:2) under illumination of AM1.5G, 100 mW/cm^2.





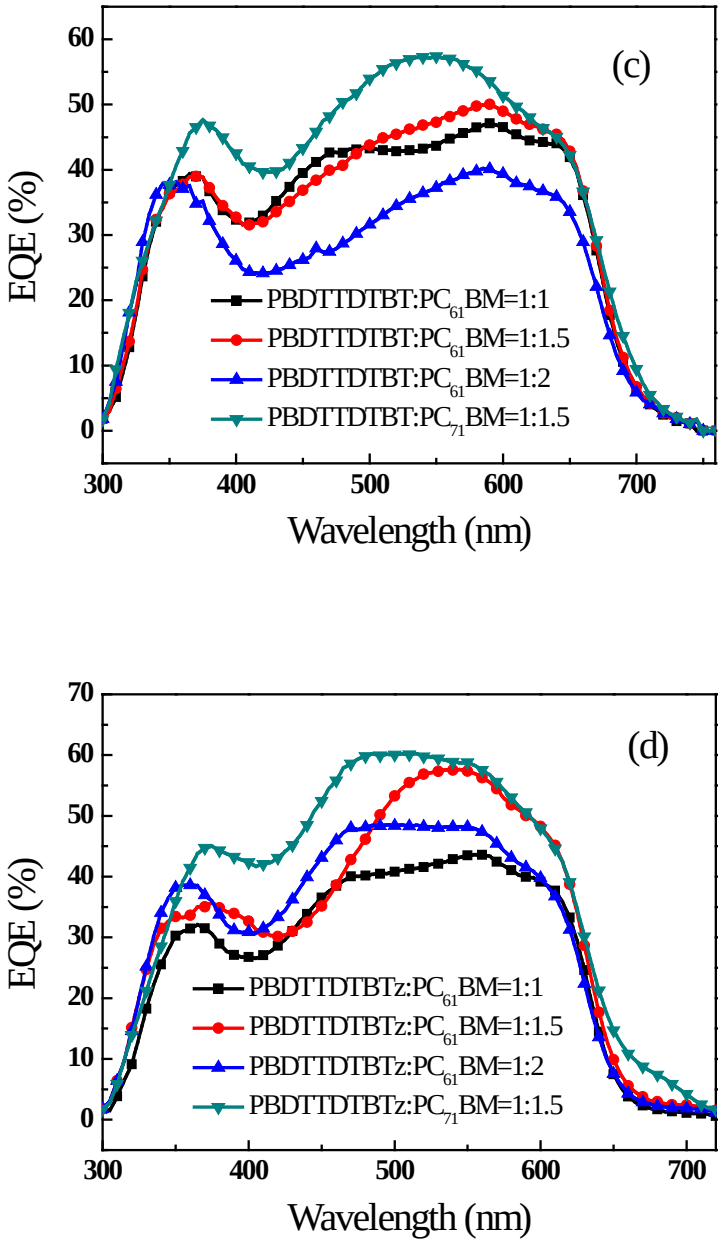


Fig. S4. The *EQE* curves of the PSCs based on polymers:PCBM with different ratios (1:1, 1.1.5 and 1:2) in ODCB.

Table S1. Optical and electrochemical properties of **PBDTTDTBO**, **PBDTTDTBT** and **PBDTTDTBTz ,** the related data of their corresponding BDT or BDF based polymers for comparison.

Polymers	Absorption spectra				Cyclic voltammetry		
	Sol[a]		Film[b]		*p*-doping	*n*-doping	
	λ_{max} (nm)	λ_{max} (nm)	λ_{onset} (nm)	E_g^{opt} (eV)	E_{on}^{ox} /HOMO[d] (V)/(eV)	E_{on}^{red} /LUMO[d] (V)/(eV)	E_g^{EC} (eV)
PBDTTDTBO	590	592	732	1.69	0.54 /-5.25	-1.43 /-3.28	1.87
PBDT-DTBX[ref1]	570	590	755	1.64	0.49/-5.20	-1.11/-3.60	1.60
PBDFDTBO[ref2]	578	580	717	1.70	0.48/-5.19	--/-3.49	-
PBDTTDTBT	583	640	748	1.66	0.44/-5.15	-1.41/-3.30	1.85
PBDTDODTBT[ref3]	548	600	758	1.64	--/-5.17	--/-3.61	1.56
PBDFDODTBT[ref2]	569	583	709	1.73	0.40/-5.11	--/-3.38	--
PBDTTDTBTz	540	556	697	1.78	0.21/-4.92	-1.70/-3.01	1.91
PBDTDTBTz[ref4]	524	527	635	1.95	0.35/-5.06	--/-3.11	--
PBDFDTBTz[ref2]	527	536	642	1.93	0.28/-4.99	--/-3.06	--

[a]Measured in chloroform solution. [b]Cast from chloroform solution. [c]Bandgap estimated from the onset wavelength of the optical absorption. [d]HOMO= -e(E_{on}^{ox} +4.71) (eV); LUMO= -e(E_{on}^{red} +4.71) (eV) using Ag/Ag^+ as the reference electrode.

Table S2. Photovoltaic properties of PSCs based on BDTT, BDT and BDF based copolymers with the best blend ratios, the hole mobilities of the polymers:PCBM blend and FET hole mobilities of the polymers.

Active layer	V_{oc} (V)	J_{sc} (mAcm^{-2})	*FF* (%)	*PCE* (%)	Mobility(cm^2/Vs)	
					SCLC[a]	OFET[b]
PBDTTDTBO:$PC_{71}BM$=1:1.5	0.84	11.45	61.3	5.9	4.9*10^{-1}	0.02
PBDT-DTBX:$PC_{61}BM$=1:2 [ref1]	0.75	5.25	58.8	2.90	2.0*10^{-5}	--
PBDFDTBO:$PC_{71}BM$=1:2 [ref2]	0.82	5.04	70.0	2.88	2.2*10^{-4}	--
PBDTTDTBT:$PC_{71}BM$=1:1.5	0.75	10.29	64.0	4.94	2.4*10^{-1}	0.017
PBDTDODTBT:$PC_{71}BM$=1:2 [ref3]	0.76	8.96	59.0	4.02	7.15*10^{-3}	--
PBDFDODTBT:$PC_{71}BM$=1:2 [ref2]	0.69	9.87	65.3	4.45	6.72*10^{-2}	0.002
PBDTTDTBTz:$PC_{71}BM$=1:1.5	0.54	9.47	60.6	3.1	5.4*10^{-1}	0.015
PBDTDTBTz:$PC_{71}BM$=1:4 [ref4]	0.61	4.5	62.0	1.7	--	--
PBDFDTBTz:$PC_{71}BM$=1:2 [ref2]	0.44	4.92	57.5	1.24	3.69*10^{-3}	--

[a]Measured by using the space-charge-limited current (SCLC) method. [b]Measured by using the organic field-effect transistor (OFET) method.

Table S3. Photovoltaic properties of PSCs based on BDTT based polymers:PCBM.

Active layer	V_{oc} (V)	J_{sc} (mA/cm^2)	*FF* (%)	PCE (%)
PBDTTDTBO:$PC_{61}BM$=1:1	0.89	10.68	61.4	5.83
PBDTTDTBO:$PC_{61}BM$=1:1.5	0.88	10.48	62.3	5.75
PBDTTDTBO:$PC_{61}BM$=1:2	0.87	7.82	65.3	4.44
PBDTTDTBO:$PC_{71}BM$=1:1	0.86	11.50	58.0	5.73
PBDTTDTBO:$PC_{71}BM$=1:1.5	0.84	11.45	61.3	5.90
PBDTTDTBT:$PC_{61}BM$=1:1	0.76	9.56	66.9	4.76
PBDTTDTBT:$PC_{61}BM$=1:1.5	0.77	9.27	61.8	4.41
PBDTTDTBT:$PC_{61}BM$=1:2	0.76	8.45	62.5	4.02
PBDTTDTBT:$PC_{71}BM$=1:1.5	0.75	10.29	64.0	4.94
PBDTTDTBTz:$PC_{61}BM$=1:1	0.58	6.89	53.2	2.12
PBDTTDTBTz:$PC_{61}BM$=1:1.5	0.56	7.91	55.3	2.45
PBDTTDTBTz:$PC_{61}BM$=1:2	0.55	6.80	56.8	2.12
PBDTTDTBTz:$PC_{71}BM$=1:1.5	0.54	9.47	60.6	3.10

References:

1. P. Ding, C. Zhong, Y. Zou, C. Pan, H. Wu, Y. Cao. *J. Phys. Chem. C*, 2011, **115**, 16211.

2. B. Liu, X. Chen, Y. Zou, L. Xiao, X. Xu, Y. He, L. Li, Y. Li. *Macromolecules*, 2012, **45** , 6898.

3. P. Ding, C. Chu, B. Liu, B. Peng, Y. Zou, Y. He, K.Zhou, C.Hsu. *Macromol. Chem. Phys*. 2010, **211**, 2555.

4. Z.Zhang, B. Peng, B. Liu, C. Pan, Y. Li, Y. He, K. Zhou, Y. Zou. *Polym. Chem*. 2010, **1**, 1441.