

## Supporting Information

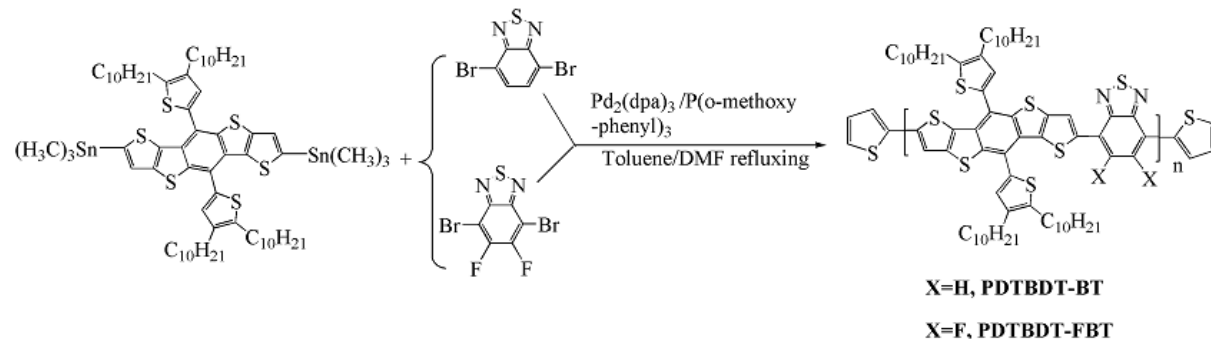
# Boosting up Performance of Inverted Photovoltaic Cells from Bis(alkylthien-2-yl)dithieno[2,3-*d*:2',3'-*d'*]benzo[1,2-*b*:4,5-*b'*]di- thiophene-based Copolymers by Advantageous Vertical Phase Separation

*Pengzhi Guo, Guoping Luo, Qiang Su, Jianfeng Li, Peng Zhang, Junfeng Tong, Chunyan Yang,  
Yangjun Xia, and Hongbin Wu*

### Table of Contents

1. Synthesis of copolymers of PDTBDT-BT and PDTBDT-FBT .....	2
1.1. Synthesis of PDTBDT-BT .....	2
1.2. Synthesis of PDTBDT-FBT .....	3
2. Photovoltaic properties of the PDTBDT-BT and PDTBDT-FBT .....	3
3. AFM topography images of the PDTBDT-BT/PC <sub>71</sub> BM and PDTBDT-FBT/PC <sub>71</sub> BM (W: W, 1:2) .....	4
4. Dark current density-voltage characteristics of the optimal photovoltaic cells from the copolymers and PC <sub>71</sub> BM. ....	7
5. Optical refractive and extinction characteristics of the copolymer and PC <sub>71</sub> BM blend films with weight ratio of 1:2 .....	8
6. Charge transporting properties of the copolymer/PC <sub>71</sub> BM (W: W, 1:2) blend films .....	9
7. Distribution of the copolymers and PC <sub>71</sub> BM on the top and bottom surface by XPS .....	11

## 1. Synthesis of copolymers of PDTBDT-BT and PDTBDT-FBT



Scheme S1. Synthesis routes of the PDTBDT-BT and PDTBDT-FBT

### 1.1. Synthesis of PDTBDT-BT

2,7-Di(trimethylstannyl)-5,10-bis(4,5-didecylthien-2-yl)dithieno[2,3-*d'*:2',3'-*d'*]benzo[1,2-*b'*:4,5-*b'*]dithiophene (0.20 mmol, 270.9 mg) and 4,7-dibromobenzothiadiazole (0.20 mmol, 58.4 mg) were dissolved into the mixture solution 6 mL of toluene and 0.7 mL of DMF in a mono-microwave reaction tube. After being purged with argon for 20 min, tris(dibenzylideneacetone)dipalladium (0) ( $\text{Pd}_2(\text{dba})_3$ ) (2.0 mg) and tris(3-methoxyphenyl)phosphine (4.0 mg) was added. Then the tube was transferred into a glove box with moisture and oxygen under 1 ppm, and the mixture was purged with argon for another 10 min. The screwed-up tube was subjected to the following reaction conditions in a microwave reactor: 120 °C for 5 min, 140 °C for 5 min and 160 °C for 20 min. At the end of polymerization, the polymers were end-capped with 2-(tributylstannyl)thiophene and 2-bromothiophene to remove bromo and trimethylstannyl end groups. The mixture was then poured into methanol. The precipitated material was collected and extracted with ethanol, acetone, hexane and toluene in a Soxhlet extractor. The solution of the copolymer in toluene was condensed to 20 mL and then

poured into methanol (500 mL). The precipitation was collected and dried under vacuum overnight (yield: 71%).  $M_n = 46,830$  g/mol with a polydispersity index (PDI) of 2.36.

### 1.2. Synthesis of PDTBDT-FBT

The PDTBDT-FBT was synthesized as the procedure of PDTBDT-BT, except that the polymerization was carried out with 2,7-di(trimethylstannyl)-5,10-bis(4,5-didecylthien-2-yl)dithieno[2,3-*d*:2',3'-*d'*]benzo[1,2-*b*:4,5-*b'*]dithiophene (0.20 mmol, 270.9 mg) and 4,7-dibromo-5,6-difluorobenzothiadiazole (0.2 mmol, 65.6 mg). Yield: 68%.  $M_n = 53,320$  g/mol with PDI of 2.13.

## 2. Photovoltaic properties of the PDTBDT-BT and PDTBDT-FBT

Table S1 Parameters of the regular photovoltaic cells from PDTBDT-BT and PDTBDT-FBT with devices configuration as ITO/PEDOT: PSS/active layer/Ca/Al.

Active layer	Weight ratio of copolymer to PC <sub>71</sub> BM	Additive	V <sub>oc</sub> (V)	J <sub>sc</sub> (mA/cm <sup>2</sup> )	FF (%)	PCE (%)
PDTBDT-BT/PC <sub>71</sub> BM	1:1	0% DIO	0.80	6.48	53.51	2.77
	1:1.5	0% DIO	0.80	7.15	54.76	3.13
	1:2	0% DIO	0.81	9.43	56.53	4.31
	1:3	0% DIO	0.80	8.52	56.38	3.84
	1:2	3% DIO	0.80	10.32	60.20	4.97
PDTBDT-FBT/PC <sub>71</sub> BM	1:1	0% DIO	0.88	9.77	57.62	4.93
	1:1.5	0% DIO	0.88	10.08	57.28	5.31
	1:2	0% DIO	0.88	10.43	62.70	5.74
	1:3	0% DIO	0.89	9.33	60.30	5.01
	1:2	3% DIO	0.88	10.98	61.25	5.92

3. AFM topography images of the PDTBDT-BT/PC<sub>71</sub>BM and PDTBDT-FBT/PC<sub>71</sub>BM (W:W, 1:2)

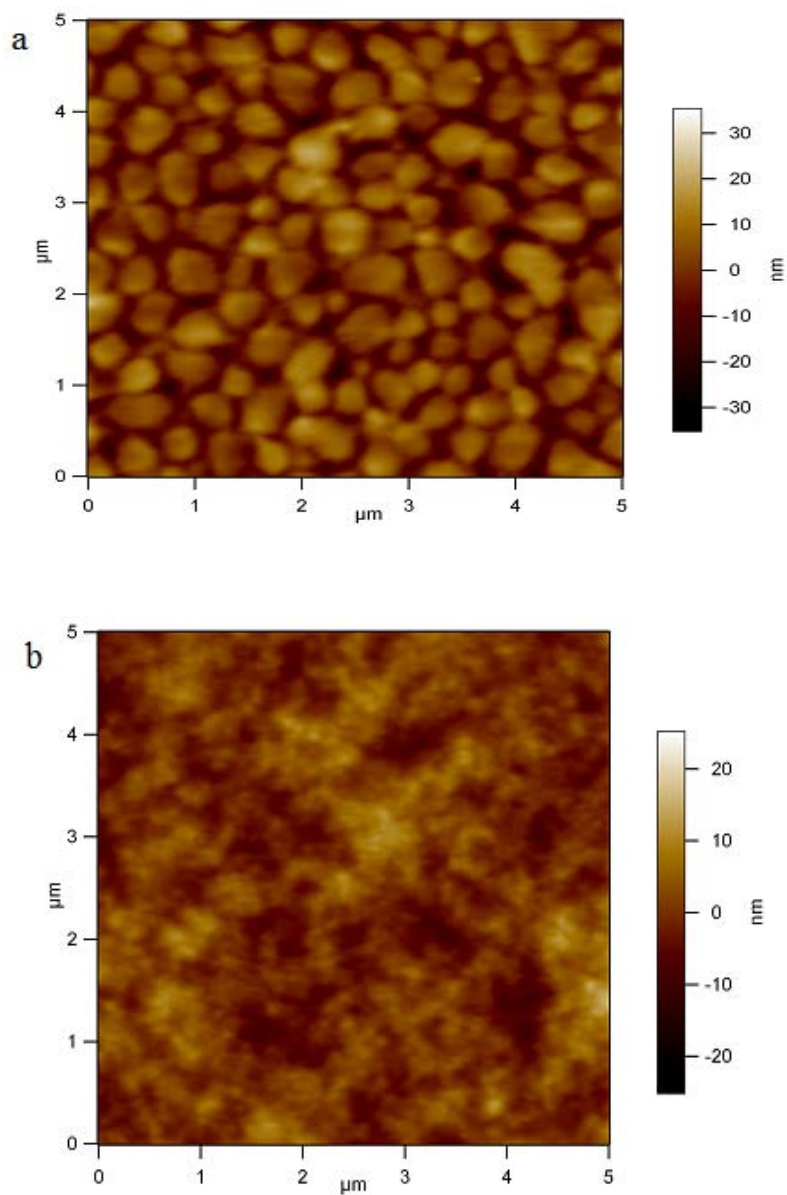


Figure S1. AFM topography images of the PDTBDT-BT/PC<sub>71</sub>BM (W:W, 1:2) with (a) and without DIO as solvent additives (b).

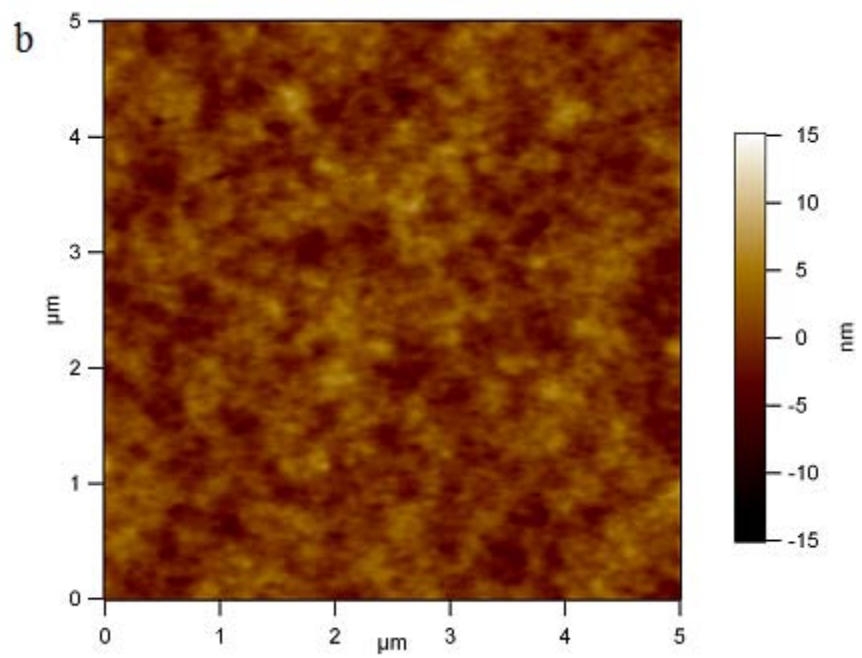
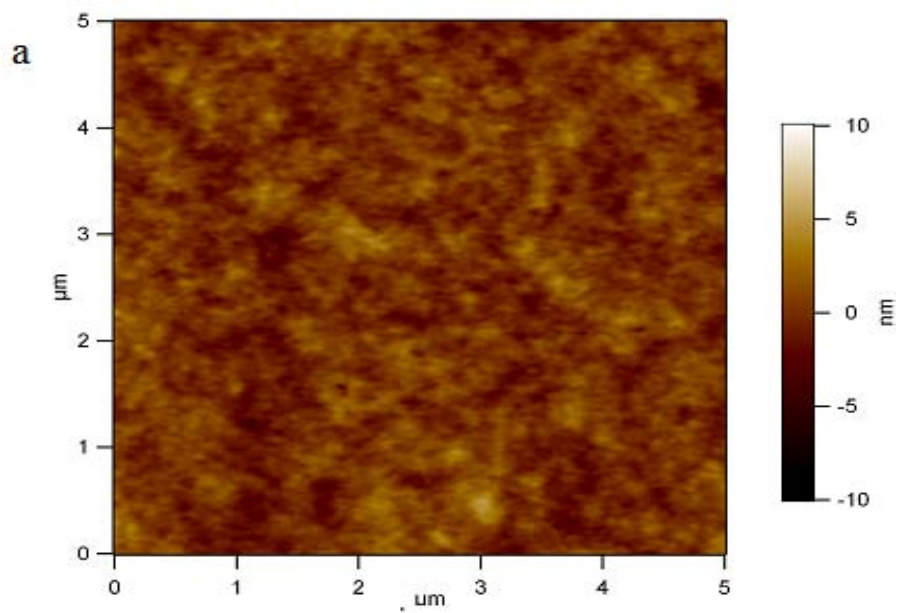


Figure S2. AFM topography images of the PDTBDT-FBT/ $\text{PC}_{71}\text{BM}$  (W:W, 1:2) with (a) and without DIO as solvent additives (b).

Table S2. The Root-mean-squares (RMS) of the blend films from the copolymers/PC<sub>71</sub>BM (W:W; 1:2) with and without DIO as solvent additives.

Blend films	Solvent additives	RMS (nm)
PDTBDT-BT/PC <sub>71</sub> BM (W:W; 1:2)	DIO 0%	7.04
	DIO 3%	3.78
PDTBDT-BT/PC <sub>71</sub> BM (W:W; 1:2)	DIO 0%	1.91
	DIO 3%	1.15

4. Dark current density-voltage characteristics of the optimal photovoltaic cells from the copolymers and PC<sub>71</sub>BM.

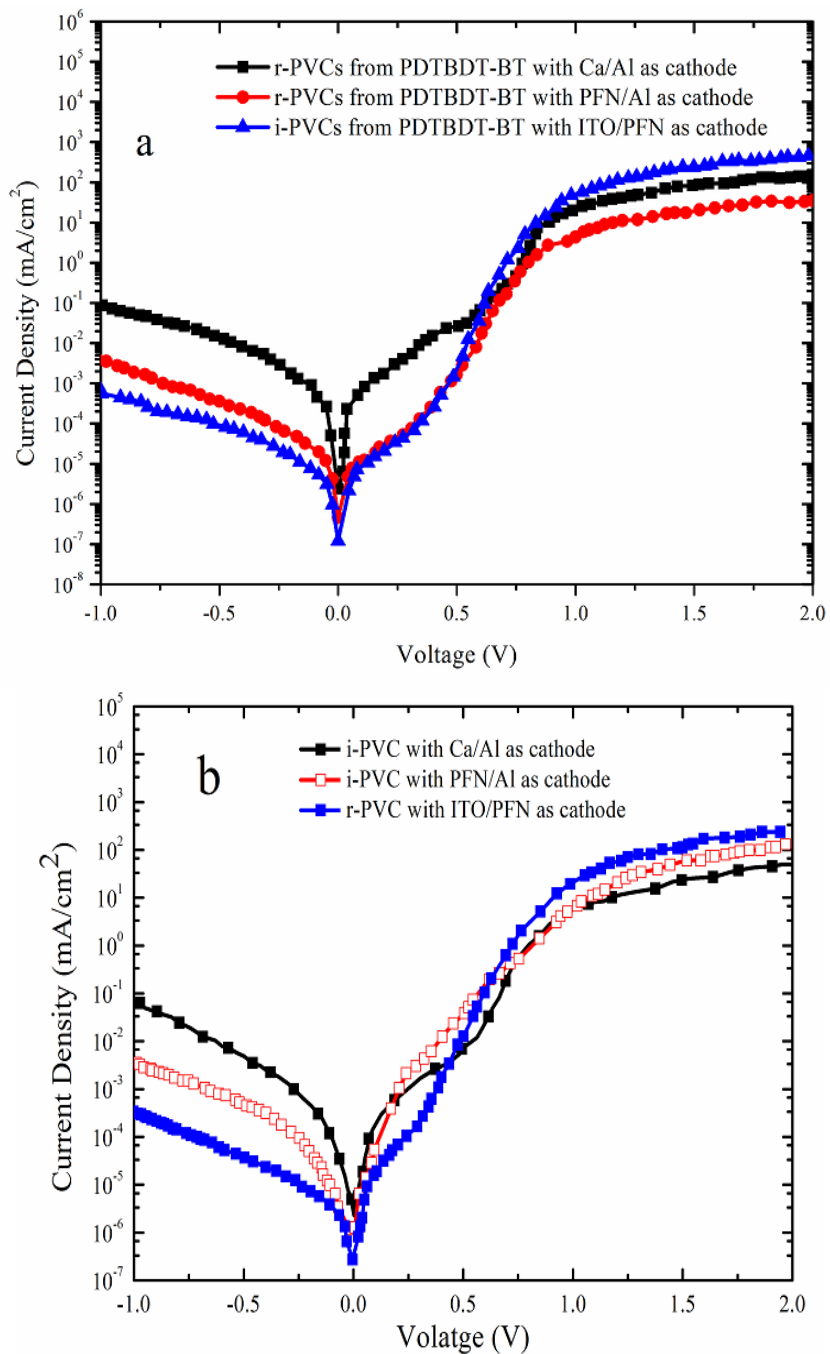


Figure S3. Dark current density curves of the PVCs from PDTBDT-BT/PC<sub>71</sub>BM and PDTBDT-FBT/PC<sub>71</sub>BM with weight ratio of 1:2

5. Optical refractive and extinction characteristics of the copolymer and PC<sub>71</sub>BM blend films with weight ratio of 1:2.

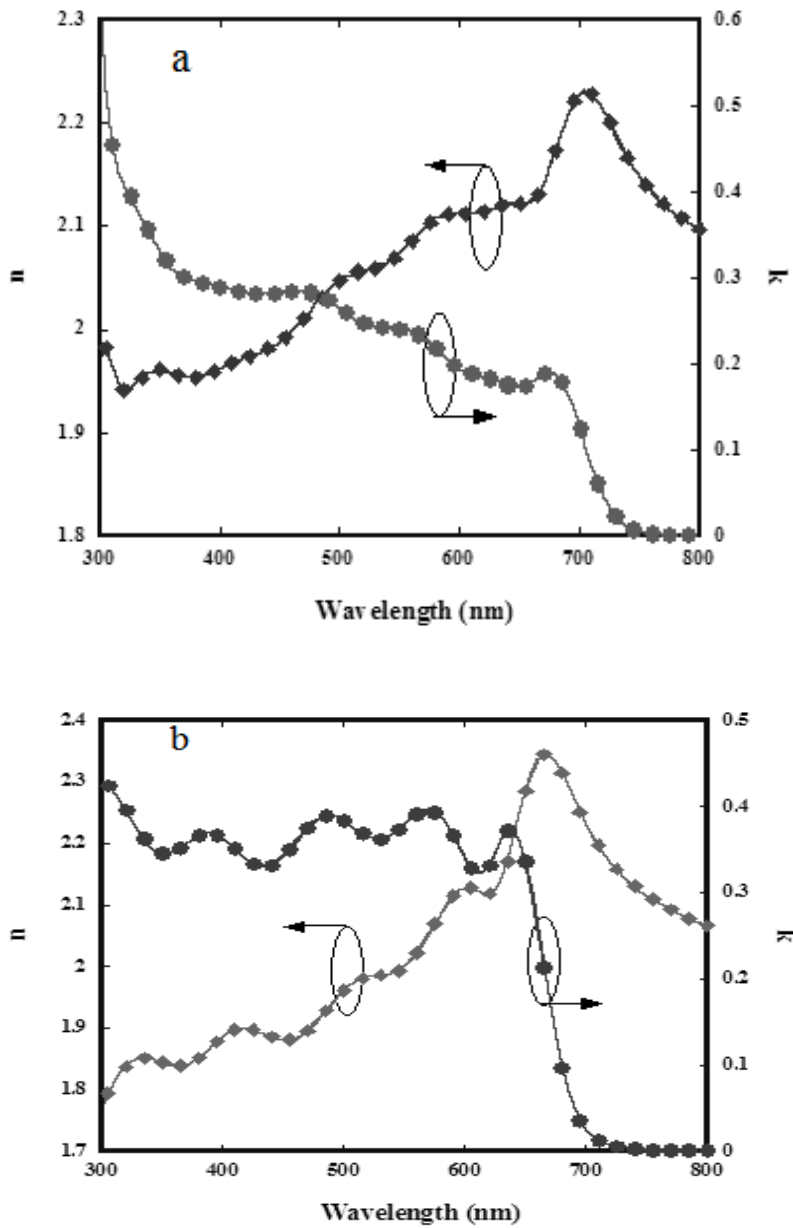


Figure S4. The refractive index (n) and extinction coefficient (k) of PDTBDT-FBT/PC<sub>71</sub>BM (a) and PDTBDT-FBT/PC<sub>71</sub>BM (b) with weight ratios of 1:2 casting from o-dichlorobenzene+3% DIO solution.



6. Charge transporting properties of the copolymer/PC<sub>71</sub>BM (W:W, 1:2) blend films.

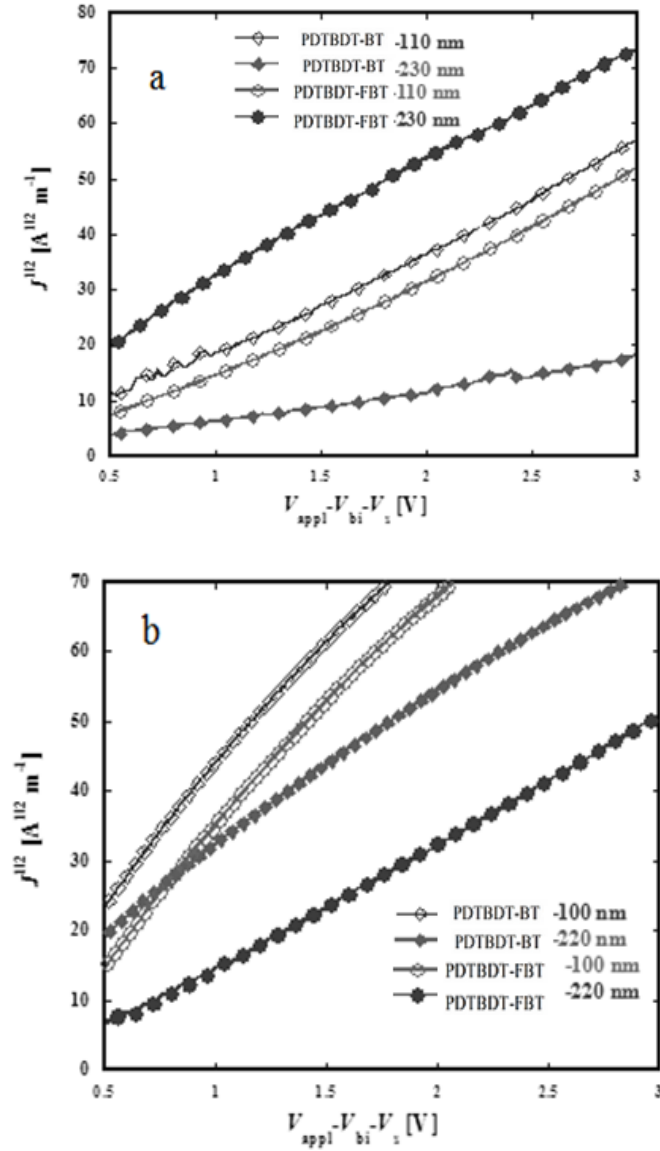


Figure S5.  $J$ - $V$  curves of the electron-only (a) and hole-only (b) devices of PDTBDT-BT/PC<sub>71</sub>BM (W:W, 1:2) and PDTBDT-FBT/PC<sub>71</sub>BM (W:W, 1:2).

Table S3. Electron mobility of PDTBDT-BT/PC<sub>71</sub>BM and PDTBDT-FBT/PC<sub>71</sub>BM with weight ratios of 1: 2 in different thickness.

Active layer	Thickness (nm)	SCLC Electron mobility (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )
PDTBDT-BT: PC <sub>71</sub> BM (W:W; 1:2)	110	1.02×10 <sup>-4</sup>
	230	3.04×10 <sup>-4</sup>
PDTBDT-FBT: PC <sub>71</sub> BM (W:W; 1:2)	110	1.40×10 <sup>-4</sup>
	230	1.49×10 <sup>-3</sup>

Table S4 Hole mobilities of PDTBDT-BT/PC<sub>71</sub>BM and PDTBDT-FBT/PC<sub>71</sub>BM with weight ratios of 1:2 in different thickness.

Active layer	Thickness (nm)	SCLC Hole mobility (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )
PDTBDT-BT: PC <sub>71</sub> BM (W:W; 1:2)	110	8.87×10 <sup>-4</sup>
	220	1.63×10 <sup>-4</sup>
PDTBDT-FBT: PC <sub>71</sub> BM (W:W; 1:2)	110	5.62×10 <sup>-4</sup>
	220	1.19×10 <sup>-3</sup>

## 7. Distribution of the copolymers and PC<sub>71</sub>BM on the top and bottom surface

Table S5. Integrated area of the C 1s, N 1s, O 1s, S 2p and F 1s peaks of the XPS measurements from the copolymers and PC<sub>71</sub>BM (W: W, 1:2) blend films on the substrates like of ITO/PEDOT: PSS and ITO/PFN.

Blend	Substrate	Surface	Area of C 1s Peaks	Area of N 1s Peaks	Area of O 1s Peaks	Area of F 1s Peaks	Area of S 2p Peaks	
PDTBDT-FBT/PC <sub>71</sub> BM (W:W, 1:2)	ITO/PEDOT:PSS	Top	7276.18	320.56	1879.80	0	1143.75	
		Bottom	78562.51	1937.11	54970.93	0	10369.95	
	ITO/PFN/	Top	154133.49	7214.90	44743.24	0	27674.02	
		Bottom	4494.02	141.62	3048.82	0	614.70	
		ITO/PEDOT: PSS	Top	213729.39	9007.14	21390.98	14949.23	37505.08
			Bottom	137268.23	5838.49	24173.27	8076.38	19893.59
ITO/PFN	Top	9480.63	437.70	994.38	685.40	1744.28		
	Bottom	198372.25	5714.32	22441.79	7476.64	18738.71		

Table S6. PDTBDT-FBT to PC<sub>71</sub>BM weight ratios at the top surfaces of the blend films on the substrates of ITO/PEDOT: PSS and ITO/PFN calculated from XPS investigation

Top Surface	Content of C atom (%)	Content of N atom (%)	Content of O atom (%)	Content of S atom (%)	Content of F atom (%)	Ratio of S/F determined by XPS results	Copolymer to PC <sub>71</sub> BM weight ratio by C/S	Copolymer to PC <sub>71</sub> BM weight ratio by C/F
ITO/PEDOT:PSS/ PDTBDT-FBT/PC <sub>71</sub> BM (W:W, 1:2)	85.60	2.27	3.68	1.87	6.58	2/6.96	4.13:1	4.03:1
ITO/PFN/PDTBDT-FBT/PC <sub>71</sub> BM (W:W, 1:2)	86.13	2.11	3.17	1.90	6.69	2/7.04	4.23:1	4.19:1