Supporting Information

Effects of Oxygen Atoms Introduced at Different Positions of Non-Fullerene Acceptors in the Performance of Organic Solar Cells with Poly(3-hexylthiophene)

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Materials. Chemicals were purchased from Alfa, Aldrich, TCI or Wako and used without further purification. Solvents were bought from the Beijing Chemical Plant.

Synthesis of compound 3

Under a nitrogen atmosphere, compound **2** (388 mg, 0.4 mmol), compound **1** (284 mg, 0.84 mmol), K_2CO_3 (170 mg, 1.2 mmol), $Pd_2(dba)_3$ (18 mg, 20 μmol), (*o*-MeOPh)$_3$P (14 mg, 40 μmol), PivOH (20 mg, 0.2 mmol), and 1,2-dimethylbenzene (2 ml) were added in a reaction vial with a magnetic stirring bar. The vial was sealed with a rubber cap and then heated in a 100 °C oil bath for 24 hours. After being cooled to room temperature, the reaction mixture was diluted with chloroform and purified by column chromatography to obtain the target product as a red solid (512 mg, 86%). ^{1}HNMR (400 M, $CDCl_3$): δ (ppm) 10.41 (s, 1H), 8.17 (s, 1H), 7.96 (d, J = 8 Hz, 1H), 7.78 (d, J = 8 Hz, 1H), 7.55 (s, 1H), 7.31 (d, J = 8 Hz, 4H), 6.86 (d, J = 8 Hz, 4H), 4.87 (t, J = 8 Hz, 2H), 3.94 (m, 4H), 2.23 (m, 2H), 1.79 (m, 4H), 1.75 (m, 22H), 0.90 (m, 9H).

Synthesis of BTA43

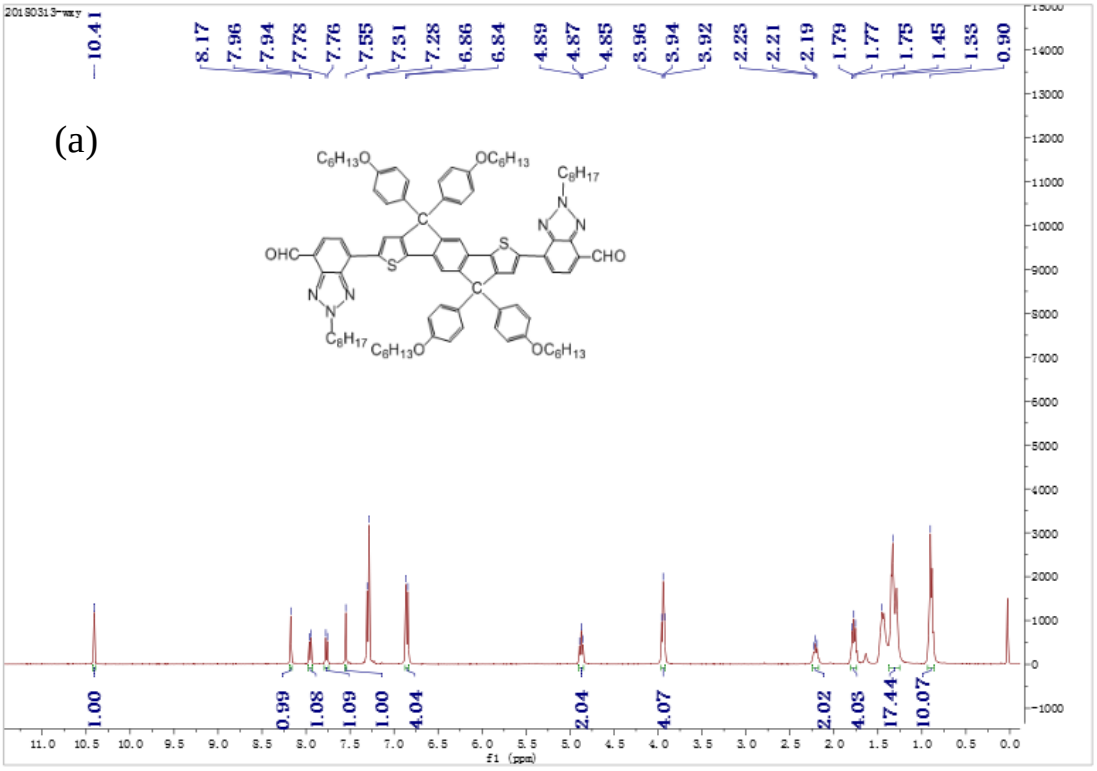
Compound **3** (400 mg, 0.27 mmol), 2-(3-ethyl-4-oxothiazolidin-2-ylidene)malononitrile (518 mg, 2.69 mmol), chloroform (100 mL) and triethylamine (4 mL) were added to a two-necked round-bottom flask. The mixture was deoxygenated with nitrogen for 10 minutes, and then refluxed for 1 hours. After cooling to room temperature, the mixture was poured into methanol (300 mL) and stirred for 10 minutes, then filtered. The residue was purified by column chromatography on silica gel with CH_2Cl_2 as an eluent yielding a blue solid (370 mg, 75%). ^{1}HNMR (400 M, $CDCl_3$): δ (ppm) 8.26 (s, 1H), 8.04 (s, 1H), 7.64 (d, J = 8 Hz, 1H), 7.49 (m, 2H), 7.20 (m, 4H), 6.77 (d, J = 8 Hz, 4H), 4.76 (t, J = 8 Hz, 2H), 4.28 (t, J = 8 Hz, 2H), 3.86 (t, J = 8 Hz, 4H), 2.15 (m, 2H), 1.68 (m, 4H), 1.35 (m, 11H), 1.24 (m, 14H), 0.82 (t, J = 8 Hz, 9H). MS(MALDI-TOF): m/z: calcd. for $C_{110}H_{122}N_{12}O_6S_4$, 1834.85; Found: 1836.1.

Synthesis of compound 5

Compound 5 was synthesized by the same method as compound 3. It is a red solid (270 mg, 93%). δ (ppm) ^{1}HNMR (400 M, $CDCl_3$): δ (ppm) 10.37 (s, 1H), 8.10 (s, 1H), 7.87 (d, J = 8 Hz, 1H), 7.59 (d, J = 8 Hz, 1H), 7.22 (m, 8H), 6.68 (s, 1H), 4.82 (t, J = 8 Hz, 2H), 2.61 (t, J = 8 Hz, 4H), 2.17 (m, 2H), 1.61 (m, 4H), 1.29 (m, 22H), 0.85 (m, 9H).

Synthesis of BTA53

Compound **5** (61 mg, 0.042 mmol), 3-ethylrhodanine (39 mg, 0.20 mmol), chloroform (12 mL) and pyridine (0.1 mL) were added to a two-necked round-bottom flask. The mixture was deoxygenated with nitrogen for 10 minutes, and then refluxed. Use the thin layer chromatography to track the reaction until the reaction complete. After cooling to room temperature, the mixture was poured into methanol (30 mL) and stirred for 10 minutes, then filtered. The residue was purified by column chromatography on silica gel with CH_2Cl_2 as an eluent yielding a blue solid (68 mg, 90%). ^{1}HNMR (400 M, $CDCl_3$): δ (ppm) 8.30 (s, 2H), 8.04 (s, 2H), 7.53 (d, J = 16 Hz, 4H), 7.26 (m, 8H), 7.16 (m, 8H), 6.67 (s, 2H), 4.79 (s, 4H), 4.35 (d, J = 8 Hz, 4H), 2.61 (m, 7H), 2.21 (m, 4H), 1.56 (m, 16H), 1.42 (m, 56H), 0.85 (m, 18H). MS(MALDI-TOF): m/z: calcd. for $C_{110}H_{122}N_{12}O_4S_4$, 1802.86; Found: 1803.0.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10.41
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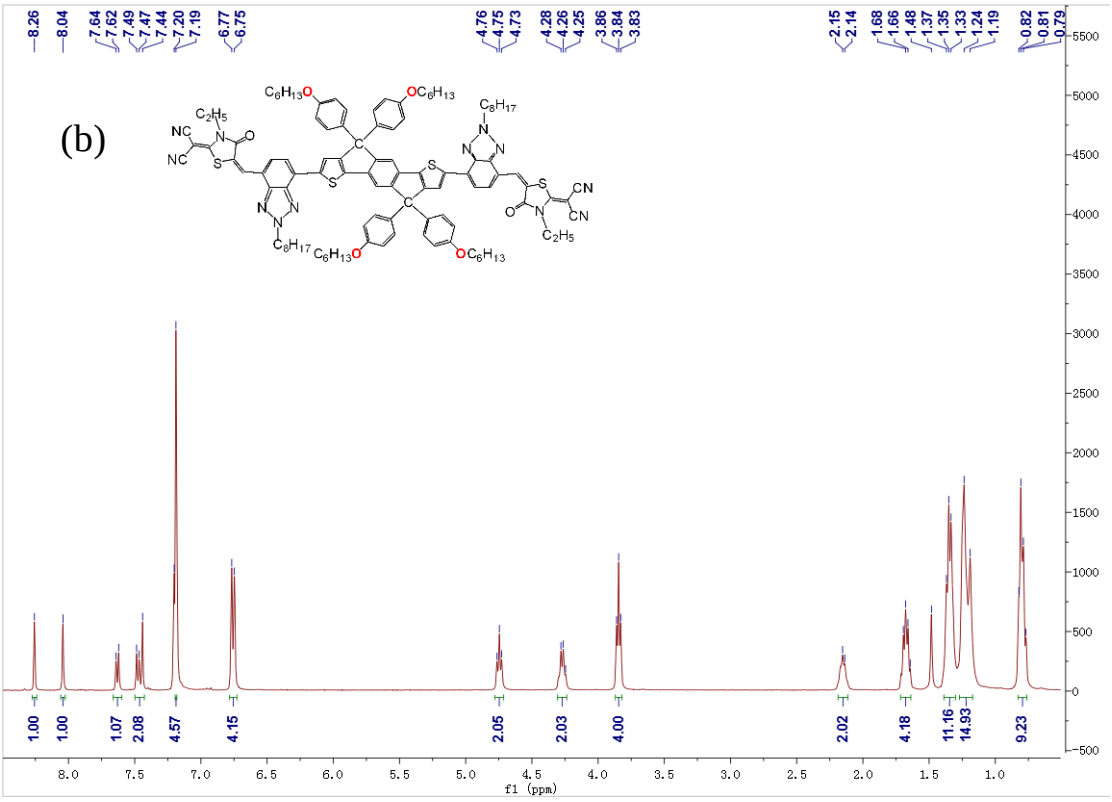
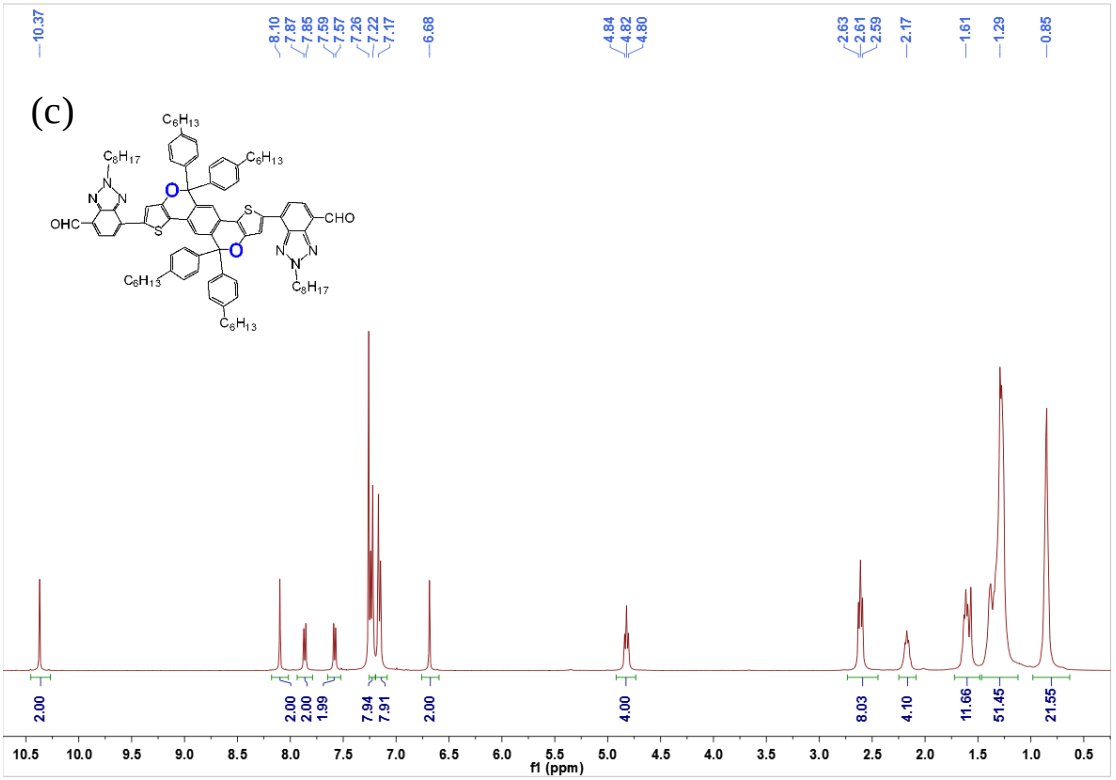
7.96
7.94
7.78
7.76
7.55
7.31
7.28
6.86
6.84
4.89
4.87
4.85
3.96
3.94
3.92
2.23
2.21
2.19
1.79
1.77
1.75
1.45
1.33
0.90
1.00
0.99
1.08
1.09
1.00
4.04
2.04
4.07
2.02
4.03
17.44
10.07
f1 (ppm)


(b)
8.26
8.04
7.64
7.62
7.49
7.47
7.44
7.20
7.19
6.77
6.75
4.76
4.75
4.73
4.28
4.26
4.25
3.86
3.84
3.83
2.15
2.14
1.68
1.66
1.48
1.37
1.35
1.33
1.24
1.19
0.82
0.81
0.79
1.00
1.00
1.07
2.08
4.57
4.15
2.05
2.03
4.00
2.02
4.18
11.16
14.93
9.23
f1 (ppm)


(c)
10.37
8.10
7.87
7.85
7.59
7.57
7.26
7.22
7.17
6.68
4.84
4.82
4.80
2.63
2.61
2.59
2.17
1.61
1.29
0.85
2.00
2.00
2.00
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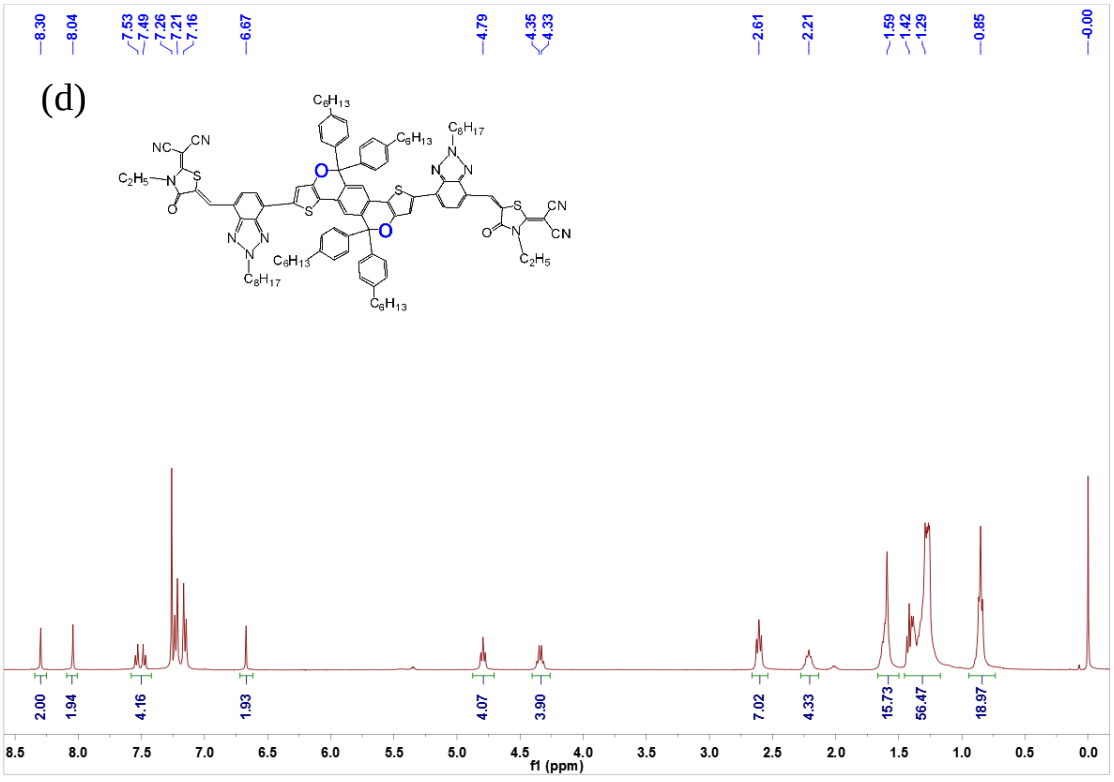
51.45
21.55
f1 (ppm)


(d)
8.30
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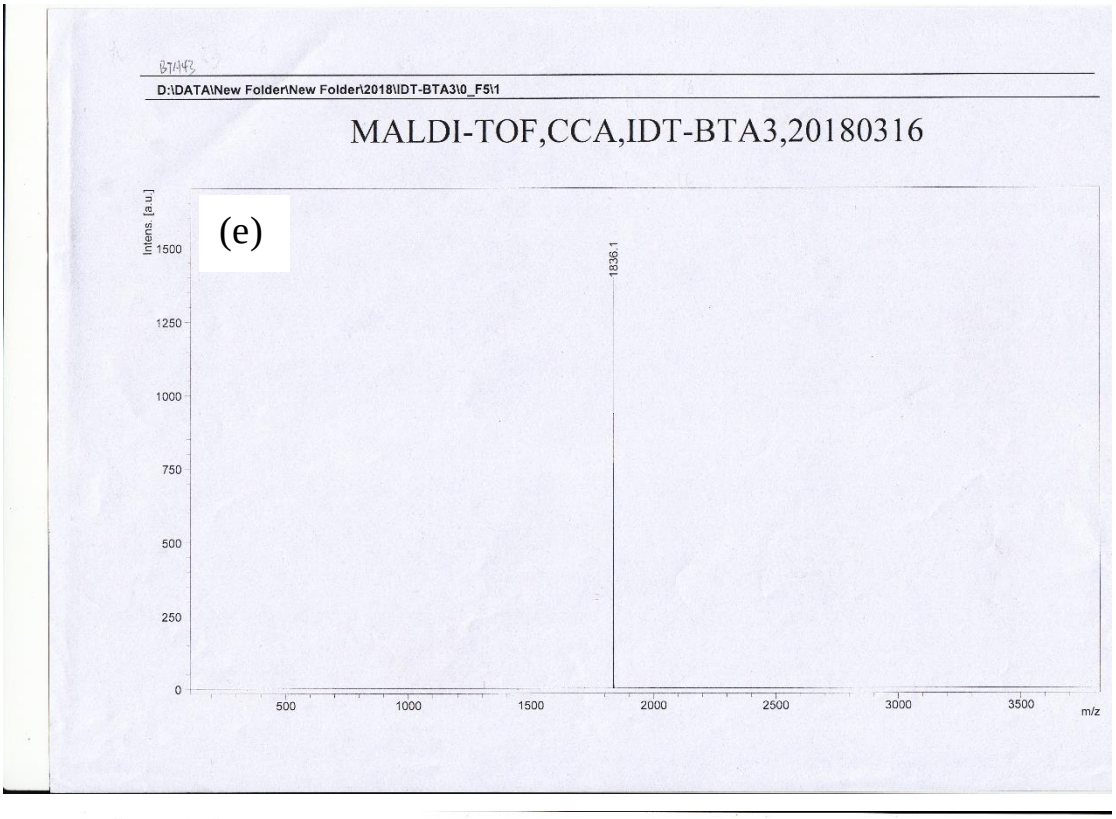
7.53
7.49
7.26
7.21
7.16
6.67
4.79
4.35
4.33
2.61
2.21
1.59
1.42
1.29
0.85
0.00
2.00
1.94
4.16
1.93
4.07
3.90
7.02
4.33
15.73
56.47
18.97
f1 (ppm)



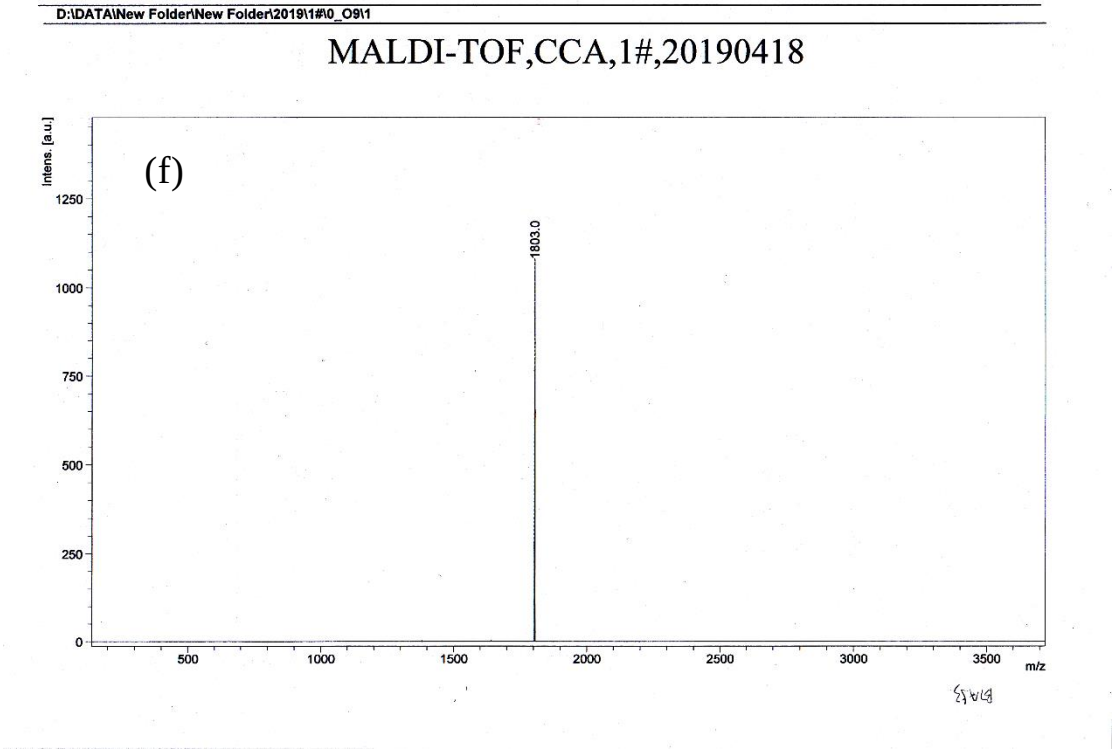


Figure S1. (a-d**)** ^{1}H NMR of intermediate compounds and final non-fullerene small molecule BTA43 and BTA53 and (e, f) MALDI-TOF of BTA43 and BTA53.

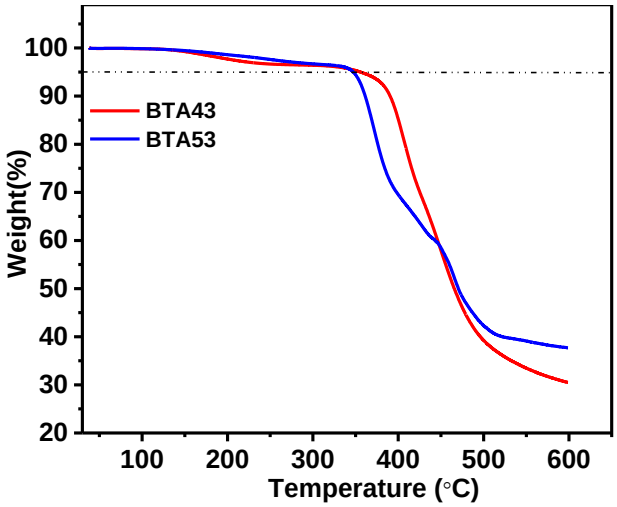


Figure S2. Thermogravimetric analysis (10 °C·min^{-1} at N_2 atmosphere) of BTA43 and BTA53.

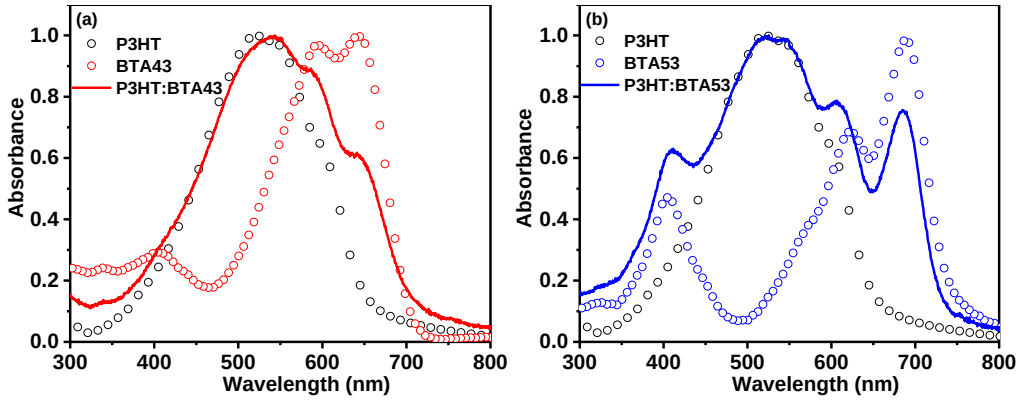


Figure S3. UV-vis absorption spectra for the pure films and blend films of (a) P3HT:BTA43 and (b) P3HT:BTA53.

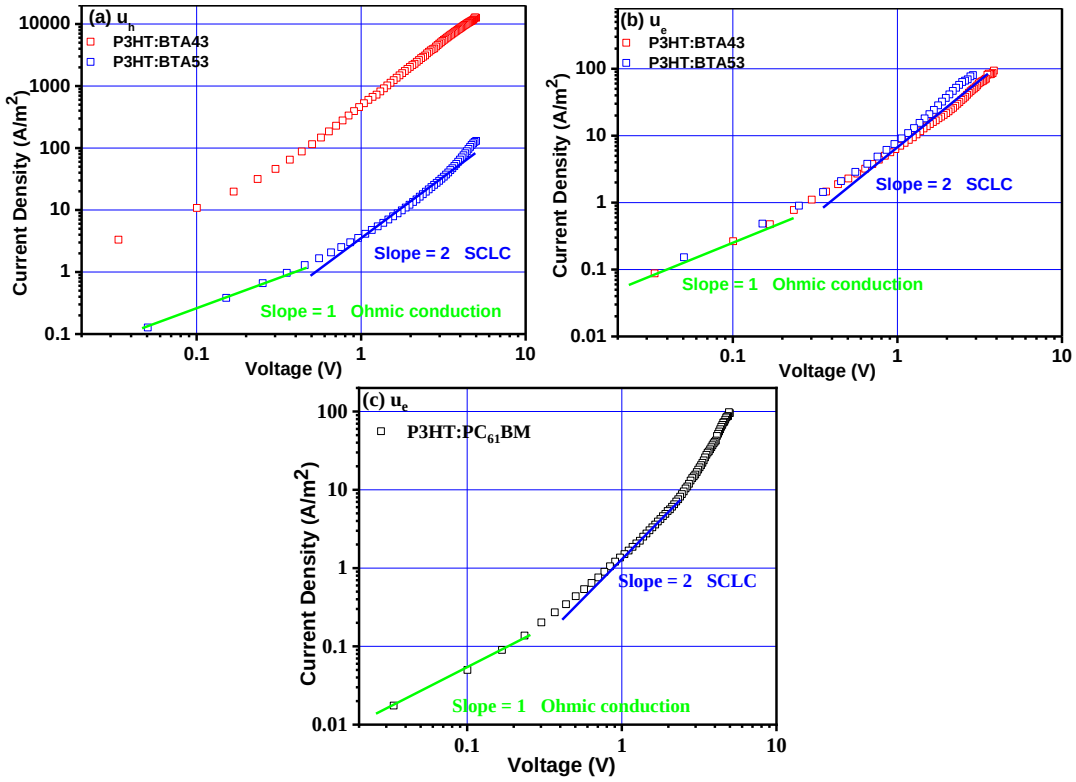


Figure S4 Space-charge limited current (SCLC): (a) ITO/ PEDOT:PSS/ active layer/ Au for holes; (b) device structure: ITO/ TIPD/ active layer/ Al for electrons; (c) device structure of P3HT:PC_{61}BM: ITO/ TIPD/ active layer/ Al for electron.

Table S1. P3HT:BTA43 devices fabricated with CF as solvent

w/w	Annealing	additive	V_{OC} (V)	J_{SC} (mA·cm^{-2})	FF	PCE (%)
0.8:1	130	w/o	0.87	8.56	0.40	2.98
1:1	130	w/o	0.87	9.05	0.39	3.07
1:0.8	130	w/o	0.88	10.42	0.48	4.40
1:0.6	130	w/o	0.88	11.19	0.58	5.71
1:0.5	120	w/o	0.90	9.88	0.66	5.87
1:0.5	**130**	**w/o**	**0.89**	**10.84**	**0.68**	**6.56**
1:0.5	130	0.8%DIO	0.85	5.48	0.61	2.84
1:0.5	130	0.8%DPE	0.89	9.44	0.72	6.05
1:0.5	130	0.8%CN	0.89	10.03	0.69	6.16
1:0.5	140	w/o	0.88	9.99	0.66	5.80
1:0.5	150	w/o	0.89	9.54	0.69	5.86
1:0.4	130	w/o	0.89	9.47	0.61	5.14
1:0.3	130	w/o	0.89	7.67	0.53	3.62

Table S2. P3HT:BTA53 devices fabricated with CF as solvent

w/w	Annealing	additive	V_{OC} (V)	J_{SC} (mA·cm^{-2})	FF	PCE (%)
0.8:1	150	w/o	0.87	8.83	0.50	3.84
1:1	150	w/o	0.88	10.63	0.56	5.24
1:0.8	150	w/o	0.88	10.64	0.61	5.71
1:0.6	150	w/o	0.88	8.98	0.64	5.06
1:0.5	150	w/o	0.88	7.94	0.62	4.33
1:0.4	150	w/o	0.89	6.60	0.57	3.35
1:0.8	140	w/o	0.86	11.48	0.55	5.43
1:0.8	**160**	**w/o**	**0.88**	**11.57**	**0.62**	**6.31**
1:0.8	170	w/o	0.88	9.20	0.65	5.26
1:0.8	180	w/o	0.88	9.14	0.64	5.15
1:0.8	160	1%DPE	0.88	6.44	0.66	3.74
1:0.8	160	1%DIO	0.86	2.97	0.58	1.48
1:0.8	160	1%CN	0.88	1.18	0.49	0.51

Table S3. The scattering peaks of lamellar stacking and π-π stacking and calculated distances in the parenthesis of as cast pristine and blend film under optimized device condition.

Film	In-plane				Out-of-plane			
	(100)	(200)	(300)	(010)	(100)	(200)	(300)	(010)
P3HT	0.37 (1.70)	0.74 (0.85)	1.17 (0.54)	1.66 (0.38)	0.35 (1.80)	0.72 (0.87)		1.64 (0.38)
BTA43	0.33 (1.90)	0.60 (1.05)	1.22 (0.52)		0.33 (1.90)		1.30 (0.48)	1.75 (0.36)
BTA53	0.35 (1.79)	0.71 (0.88)	1.23 (0.51)	1.72 (0.37)	0.36 (1.75)	0.73 (0.86)	1.24 (0.51)	1.79 (0.35)
P3HT:BTA43	0.36 (1.74)	0.72 (0.87)	1.26 (0.50)	1.64 (0.38)	0.36 (1.75)	0.72 (0.87)		1.68 (0.37)
P3HT:BTA53	0.36 (1.74)	0.72 (0.87)	1.21 (0.52)	1.62 (0.39)	0.37 (1.70)	0.80 (0.79)		1.73 (0.36)