

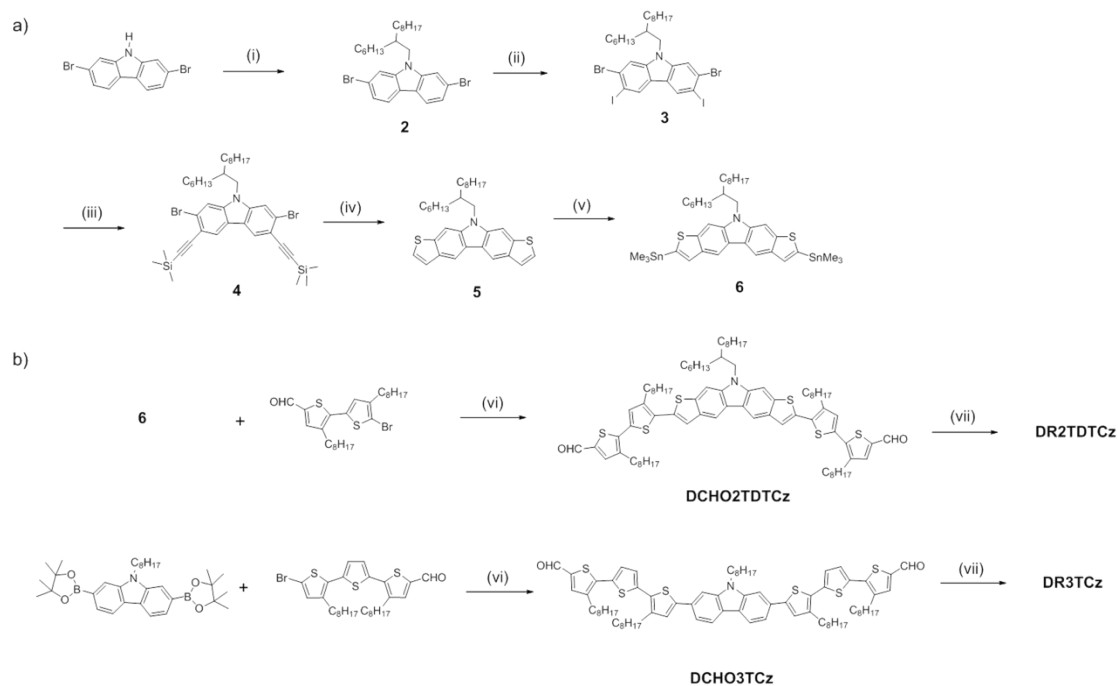
## Supporting Information

### Investigation of the effect of large aromatic fusion in the small molecule backbone on the solar cell device fill factor

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**Scheme S1.** Synthetic routes for DR2TDTcZ and DR3TCz. (i)  $K_2CO_3$ ,  $C_{16}H_{33}Br$ , DMF, 80 °C; (ii) KI,  $KIO_3$ , AcOH, 80 °C; (iii) trimethylsilylacetylene,  $Pd(PPh_3)_2Cl_2$ , CuI,  $Et_3N$ , THF, room temperature; (iv)  $Na_2S_3 \cdot 9H_2O$ , NMP, 185 °C; (v) n-BuLi,  $Bu_3SnCl$ , THF, -78°C to room temperature; (vi)  $Pd(PPh_3)_4$ , 100 °C ; (vii) piperidine, 3-octylrhodanine,  $CHCl_3$ , 65°C.

### **Synthesis of N-(2-hexyldecyl)-2,7-dibromocarbazole (2)**

To a solution of 2,7-dibromocarbazole (4.0g, 12.3mmol) in 100ml of DMF, anhydrous  $K_2CO_3$  was added. The solution was stirred at 80 °C for 8h under argon followed by the addition of 2-hexyldecylbromide. The reaction mixture was stirred at 80 °C for 20h and then quenched with 50 ml of water. The aqueous layer was extracted with petroleum ether, and the organic layer was washed with water then dried over anhydrous  $Na_2SO_4$ . After removal of solvent, the crude product was purified by column chromatography on silica gel using petroleum ether as eluant to afford compound **2** (6.30 g, 93%) as liquid.  $^1H$  NMR (400 MHz,  $CHCl_3$ ):  $\delta$ (ppm) 7.87 (d, 2H), 7.48 (s, 2H), 7.34 (d, 2H), 4.02 (d, 2H), 2.06 (s, 1H), 1.28-1.22 (m, 24H), 0.90-0.85 (m, 6H).  $^{13}C$  NMR (100 MHz,  $CHCl_3$ ):  $\delta$  (ppm) 141.86, 122.52, 121.43, 121.25, 119.56, 112.33, 47.90, 37.59, 31.87, 31.66, 29.72, 29.59, 29.50, 29.27, 26.39, 22.64, 14.10.

### **Synthesis of N-(2-hexyldecyl)-2,7-dibromo-3,6-diiodocarbazole(3).**

A mixture of the N-(2-hexyldecyl)-2,7-dibromocarbazole (6.2 g, 11.2 mmol) and AcOH (150 mL) was degassed twice with argon then heated to 80°C, and followed by the addition of KI (4.9 g, 29.3 mmol) and  $KIO_3$  (3.2 g, 14.6 mmol). After being stirred at 80°C for 12h under argon, the reaction mixture was poured into water and extracted with  $CH_2Cl_2$ . The organic layer was thoroughly washed with water, aqueous sodium bicarbonate, brine and again with water, and then dried over anhydrous  $Na_2SO_4$ . After removal of solvent, the crude product was purified by column chromatography on silica gel using petroleum ether as eluant to afford compound **3** (8.30 g, 92%) as a

white solid. <sup>1</sup>H NMR (400 MHz, CHCl<sub>3</sub>): δ (ppm) 8.31 (s, 2H), 7.57 (s, 2H), 3.89(d, 2H), 1.96 (m, 1H), 1.20-1.28(m, 24H), 0.84-0.89(q, 6H). <sup>13</sup>C NMR (100 MHz, CHCl<sub>3</sub>): δ (ppm) 141.44, 131.30, 126.67, 122.16, 113.24, 88.88, 47.92, 31.88, 31.78, 31.61, 31.58, 29.86, 29.56, 29.50, 29.28, 26.34, 22.69, 22.65, 18.48, 14.18, 14.13. MS(MALDI-TOF): calcd for C<sub>28</sub>H<sub>37</sub>Br<sub>2</sub>I<sub>2</sub>N[M]<sup>+</sup>, 801.22; found, 801.01.

**Synthesis of N-(2-hexyldecyl)-2,7-dibromo-3,6-di(trimethylsilylethynyl)carbazole(4).**

Compound **3** (7.28g, 9.0mmol) was dissolved in the mixed solvent of Et<sub>3</sub>N and THF (150ml, 1:1, v:v) and Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (120 mg, 0.16 mmol) and CuI (68 mg, 0.35 mmol) were added. Then trimethylsilylacetylene (1.86g, 18.9 mmol) were added in small portions. After being stirred for 12h at room temperature under argon, the reaction mixture was poured into water and extracted with ethyl acetate. The organic layer was washed with saturated aqueous ammonium chloride and brine, and then dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After removal of solvent, the crude product was purified by column chromatography on silica gel using a mixture of dichloromethane and petroleum ether (1:12) as eluant to afford compound **4** (5.8 g, 86%). <sup>1</sup>H NMR (400 MHz, CHCl<sub>3</sub>): δ (ppm) 8.08 (s, 2H), 7.51 (s, 2H), 3.99(d, 2H), 1.99 (m, 1H), 1.20-1.25(m, 24H), 0.84-0.89(q, 6H), 0.32(s, 18H). <sup>13</sup>C NMR (100 MHz, CHCl<sub>3</sub>): δ (ppm) 141.39, 125.42, 123.42, 121.01, 116.27, 113.11, 103.92, 97.36, 53.42, 47.93, 31.83, 31.73, 29.53, 29.43, 29.23, 26.29, 22.65, 22.60, 14.13, 14.07. MS(MALDI-TOF): calcd for C<sub>38</sub>H<sub>55</sub>Br<sub>2</sub>NSi<sub>2</sub>[M]<sup>+</sup>, 741.83; found, 742.22.

**Synthesis of N-(2-hexyldecyl)-dithieno[2,3-b;7,6-b]carbazole (5).**

To a solution of **4** (5.80g, 7.8mmol) in NMP (150ml), sodium sulfide nonahydrate (7.49 g, 31.2mmol) was added. After being stirred at 185°C for 10h, the reaction mixture was poured into water and extracted with Et<sub>2</sub>O. The organic layer was washed with saturated aqueous ammonium, and then dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After removal of solvent, the crude product was purified by column chromatography on silica gel using a mixture of dichloromethane and petroleum ether (1:15) as eluant to afford compound **5** (2.3 g, 58%). <sup>1</sup>H NMR (400 MHz, CHCl<sub>3</sub>): δ (ppm) 8.49 (s, 2H), 7.73 (s, 2H), 7.47(d, 2H), 7.34(d, 2H), 4.09(d, 2H), 2.19-2.22 (m, 1H), 1.22-1.38(m, 24H), 0.85-0.90(q, 6H). <sup>13</sup>C NMR (100 MHz, CHCl<sub>3</sub>): δ (ppm) 141.25, 138.91, 132.75, 123.87, 122.90, 122.46, 114.44, 100.94, 48.10, 31.90, 31.87, 29.58, 29.32, 26.60, 22.70, 22.68, 14.18, 14.14. MS(MALDI-TOF): calcd for C<sub>32</sub>H<sub>41</sub>NS<sub>2</sub>[M]<sup>+</sup>, 503.27; found, 503.25.

**Synthesis of N-(2-hexyldecyl)-3,8-bis(tributylstannyl)dithieno[2,3-b;7,6-b]-carbazole(6)**

Under the protection of argon, n-butyllithium (2.0M, 2.5 ml, 5.0mmol) was dropwise added to THF (40 mL) solution of **5** (1.00 g, 1.98 mmol) at -78°C for 0.5h. After stirring for 1h, the reaction mixture was warmed to room temperature. And then the reaction mixture was cooled to -78°C to added in a solution of Bu<sub>3</sub>SnCl (1.2 g, 3.6mmol). After being stirred overnight at room temperature under argon, the reaction mixture was poured into water and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic phase was wash by water, dried over anhydrous NaSO<sub>4</sub> and concentrated to afford the yellow crude product **6** as dark yellow oil.

### Synthesis of DCHO2TDTCz

A solution of **6** (1.64 g, 2.88 mmol) and Br2TCHO (2.00 g, 4.0 mmol) in toluene (50 mL) was degassed twice with argon followed by the addition of Pd(PPh<sub>3</sub>)<sub>4</sub> (60 mg, 0.02 mmol). After being stirred at 100°C for 20 h under argon, the reaction mixture was poured into water (100 mL) and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was washed with water and then dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After removal of solvent, the crude product was purified by column chromatography on silica gel using a mixture of dichloromethane and petroleum ether (3:1) as eluant to afford compound **DCHO2TDTCz** (1.60 g, 78%) as a red solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 9.80(s, 2H), 8.32(s, 2H), 7.57(s, 2H), 7.54(s, 2H), 7.40(s, 2H), 7.13(s, 2H), 3.99(d, 2H), 2.79-2.87(m, 8H), 2.15(s, 1H), 1.68-1.74(m, 8H), 1.21-1.46(m, 64H), 0.80-0.91(m, 18H). <sup>13</sup>C NMR (100 MHz, CHCl<sub>3</sub>): δ (ppm) 182.47, 141.21, 141.07, 140.57, 140.18, 139.92, 139.14, 133.54, 133.13, 133.01, 131.94, 130.42, 122.60, 122.34, 114.48, 100.50, 31.98, 31.90, 30.67, 30.28, 30.04, 29.74, 29.63, 29.57, 29.51, 29.40, 29.38, 29.34, 26.62, 22.77, 22.71, 14.22, 14.18, 14.14. MS(MALDI-TOF): calcd for C<sub>82</sub>H<sub>113</sub>NO<sub>2</sub>S<sub>6</sub>[M]<sup>+</sup>, 1335.71; found, 1335.72.

### Synthesis of DR2TDTCz

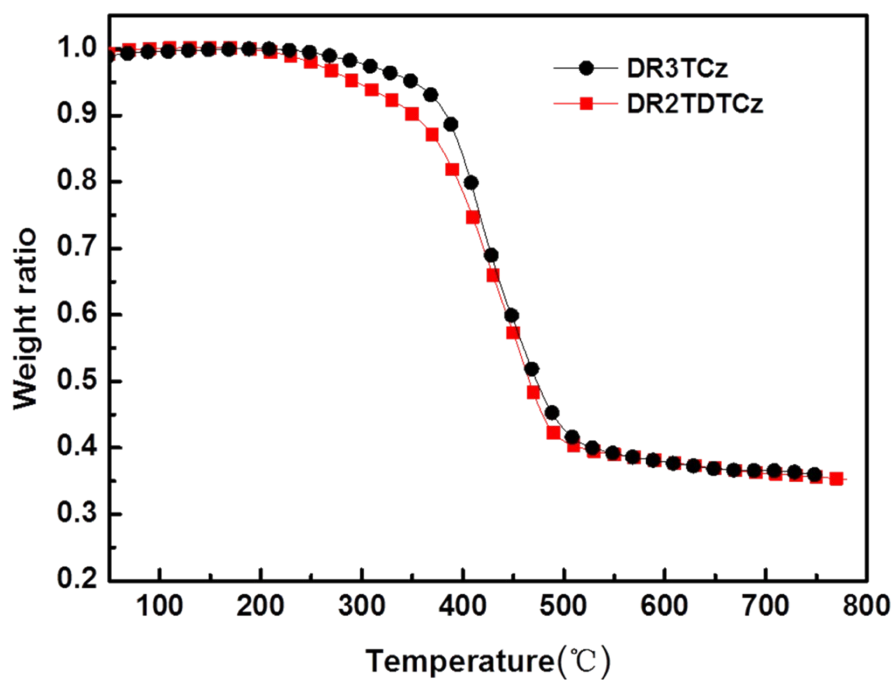
**DCHO2TDTCz** (0.31 g, 0.22 mmol) was dissolved in a solution of dry chloroform (50 mL); three drops of piperidine and 3-octylrhodanine (0.80 g, 3.2 mmol) were added, and the resulting solution was refluxed and stirred for 12 h under argon. The solvent was then removed by a rotating evaporator and the crude product was dissolved in 10 mL of chloroform, then precipitated from methanol and the precipitate was filtered off.

The residue was purified by silica gel chromatography using a mixture of petroleum ether and chloroform (2:1) as eluent and the crude solid was recrystallized from a hexane and chloroform mixture two times to afford **DR2TDTCz** as a black solid (0.20 g, 46%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 8.41(d, 2H), 7.72(d, 2H), 7.64(d, 2H), 7.46(d, 2H), 7.19(d, 2H), 7.12(d, 2H), 4.11-4.14(m, 2H), 4.03-4.08(m, 4H), 2.90(t, 4H), 2.83(t, 4H), 2.21(s, 1H), 1.68-1.75(m, 12H), 1.21-1.38(m, 84H), 0.83-0.89(m, 24H). <sup>13</sup>C NMR (100 MHz, CHCl<sub>3</sub>): δ (ppm) 192.23, 167.47, 141.15, 140.91, 140.68, 139.78, 139.19, 137.38, 134.94, 133.25, 133.19, 133.08, 132.09, 129.88, 124.86, 122.66, 122.77, 120.28, 114.51, 100.57, 48.22, 44.81, 37.45, 31.94, 31.79, 29.61, 29.52, 29.46, 29.36, 29.34, 29.16, 22.72, 22.65, 14.17, 14.13, 14.11. MS(MALDI-TOF): calcd for C<sub>104</sub>H<sub>147</sub>N<sub>3</sub>O<sub>2</sub>S<sub>10</sub>[M]<sup>+</sup>, 1789.87; found, 1789.85.

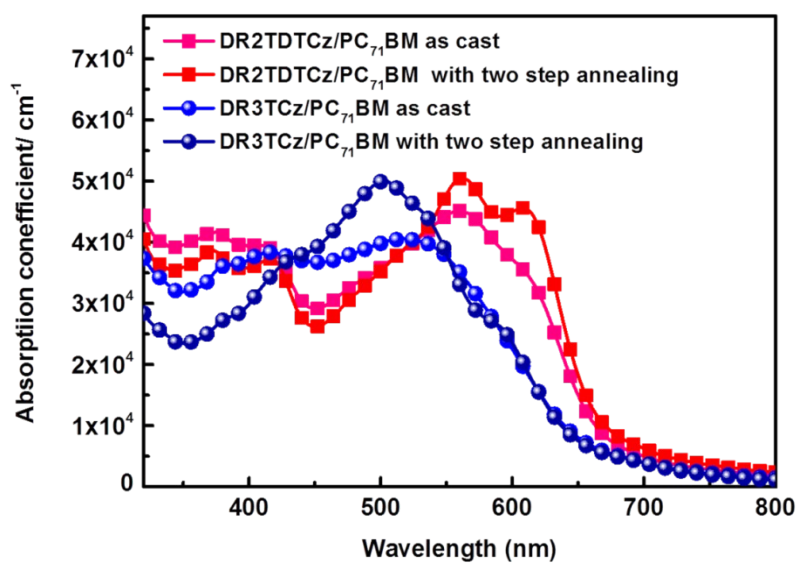
### Synthesis of **DR3TCz**

**DCHO3TCz** (0.30 g, 0.24 mmol) was dissolved in a solution of dry chloroform (50 mL); three drops of piperidine and 3-octylrhodanine (0.80 g, 3.2 mmol) were added, and the resulting solution was refluxed and stirred for 12 h under argon. The solvent was then removed by a rotating evaporator and the crude product was dissolved in 10 mL of chloroform, then precipitated from methanol and the precipitate was filtered off. The residue was purified by silica gel chromatography using a mixture of petroleum ether and chloroform (3:2) as eluent and the crude solid was recrystallized from a hexane and chloroform mixture three times to produce **DR3TCz** (0.21 g, 51%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 8.01 (d, 2H), 7.75 (s, 2H), 7.51 (s, 2H), 7.48 (d, 2H), 7.14-7.25 (m, 8H), 4.33 (s, 2H), 4.09 (t, 4H), 2.83 (s, 8H), 1.93 (t, 2H), 1.66-1.77 (m,

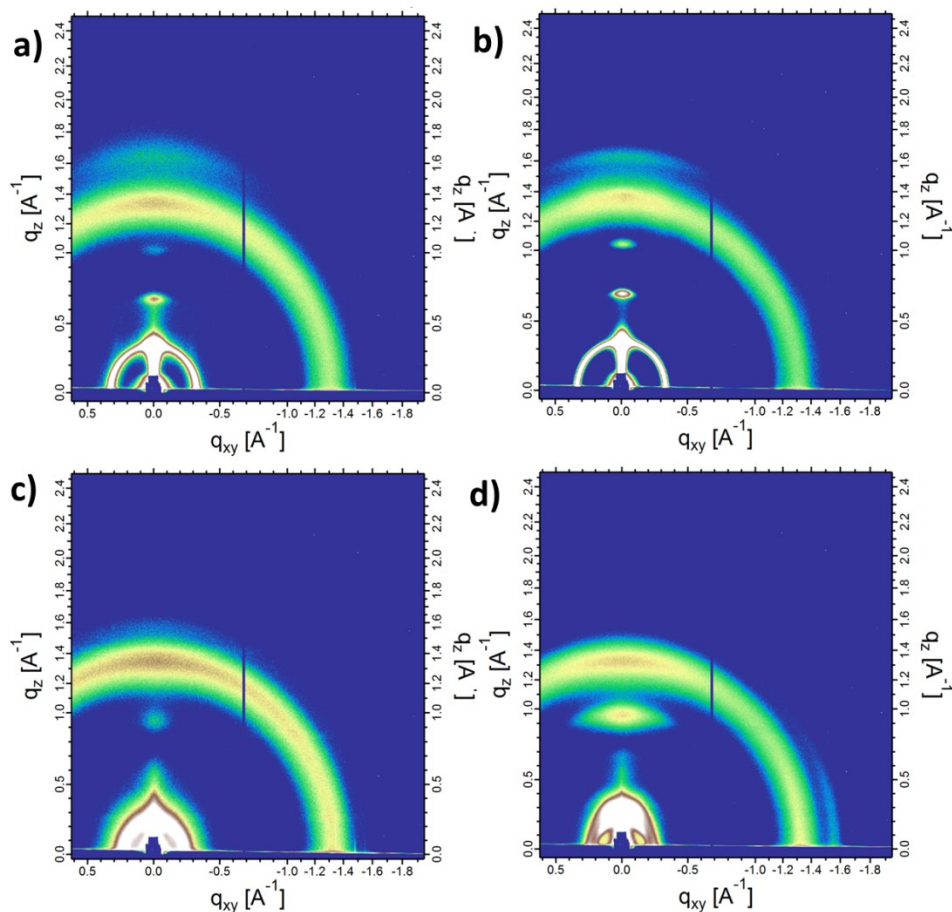
14H), 1.29-1.46 (m, 68H), 0.84-0.90 (m, 21H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$ (ppm), 192.25, 167.47, 143.75, 141.48, 141.22, 139.58, 138.19, 137.29, 135.15, 134.41, 131.62, 129.44, 127.16, 126.30, 125.99, 124.79, 122.38, 120.66, 117.43, 105.49, 44.84, 43.02, 31.96, 31.91, 31.80, 30.66, 30.31, 29.89, 29.77, 29.62, 29.56, 29.48, 29.38, 29.33, 29.25, 29.17, 29.16, 28.97, 27.27, 26.99, 26.82, 22.73, 22.71, 22.66, 14.15, 14.12. MS (MALDI-TOF): calcd for  $\text{C}_{100}\text{H}_{135}\text{N}_3\text{O}_2\text{S}_{10}$   $[\text{M}]^+$ , 1729.78; found, 1729.73.



**Fig.S1.** TGA curves of DR3TCz and DR2TDTCz with a heating rate of 10 °C/min under  $\text{N}_2$  atmosphere.



**Fig.S2.** Uv-vis absorption spectra of DR3TCz:PC<sub>71</sub>BM and DR2TDTcZ:PC<sub>71</sub>BM blend films without and with two step annealing treatment.



**Fig.S3.** GIWAXS patterns for blend films of (a, b) DR2TDTcZ:PC<sub>71</sub>BM without/with thermal and solvent annealing treatment. (c, d) DR3TCz:PC<sub>71</sub>BM blend films without/with thermal and solvent annealing treatment.



**Table S1.** Morphology data of out-of-plane GIWAXS.

Donor	Without post treatment		With two step annealing	
	DR2TDCz	DR3TCz	DR2TDCz	DR3TCz
Q(100)	0.336 Å <sup>-1</sup>	0.251 Å <sup>-1</sup>	0.360 Å <sup>-1</sup>	0.288 Å <sup>-1</sup>
d(100)	18.7 Å <sup>-1</sup>	24.3 Å <sup>-1</sup>	17.4 Å <sup>-1</sup>	21.8 Å <sup>-1</sup>
Q (010)	1.68 Å <sup>-1</sup>	-	1.68 Å <sup>-1</sup>	-
d(010)	3.7 Å <sup>-1</sup>	-	3.7 Å <sup>-1</sup>	-

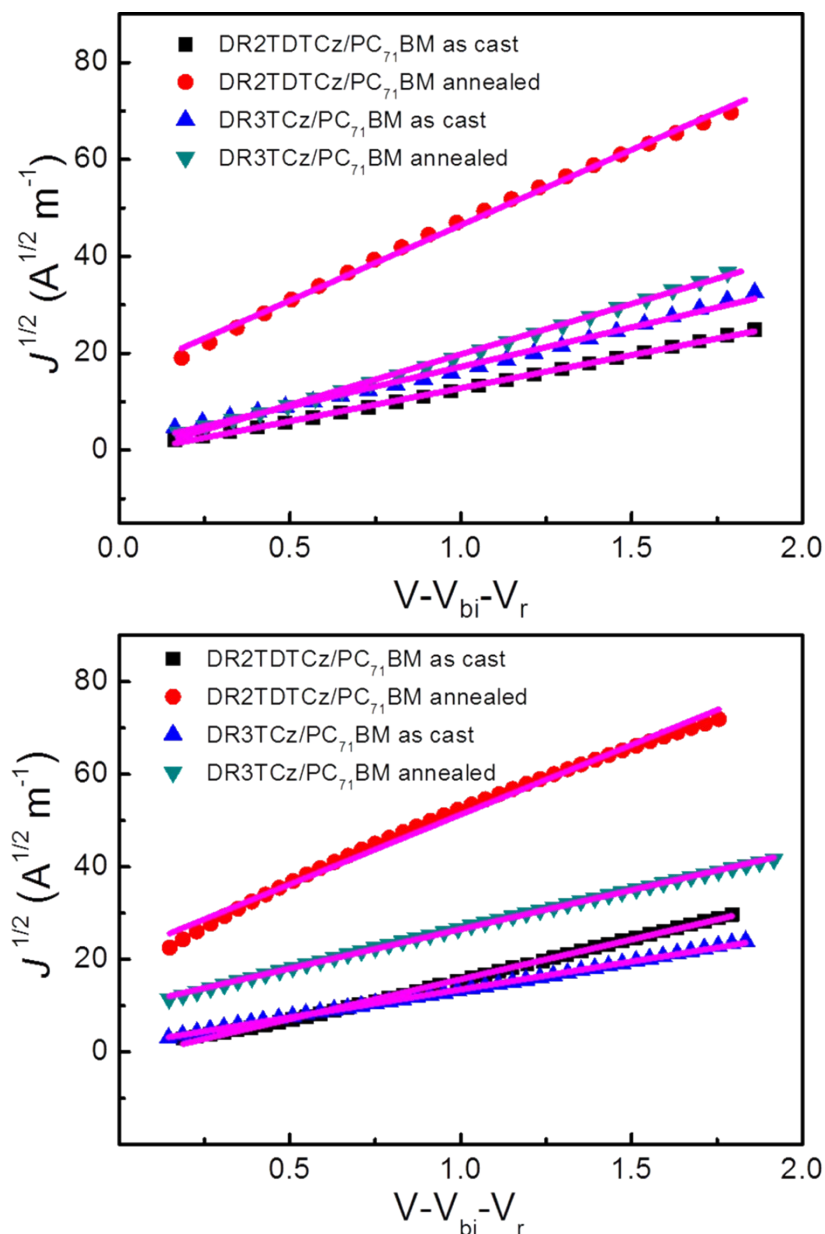
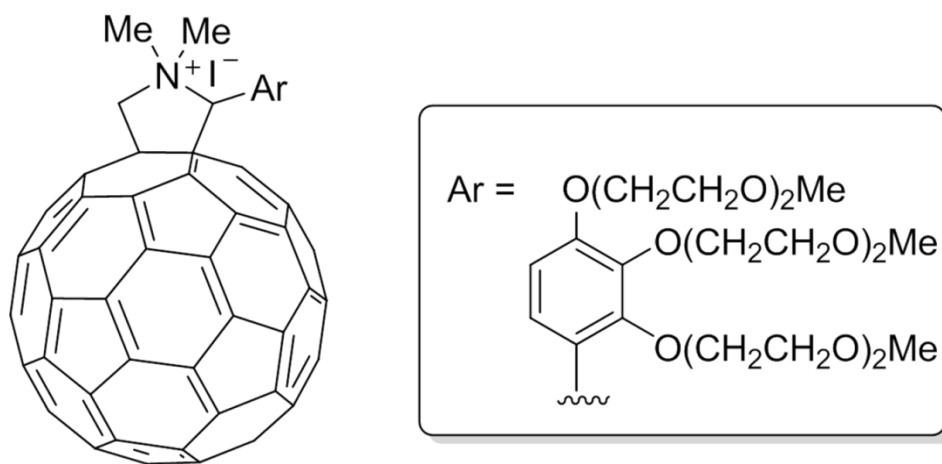
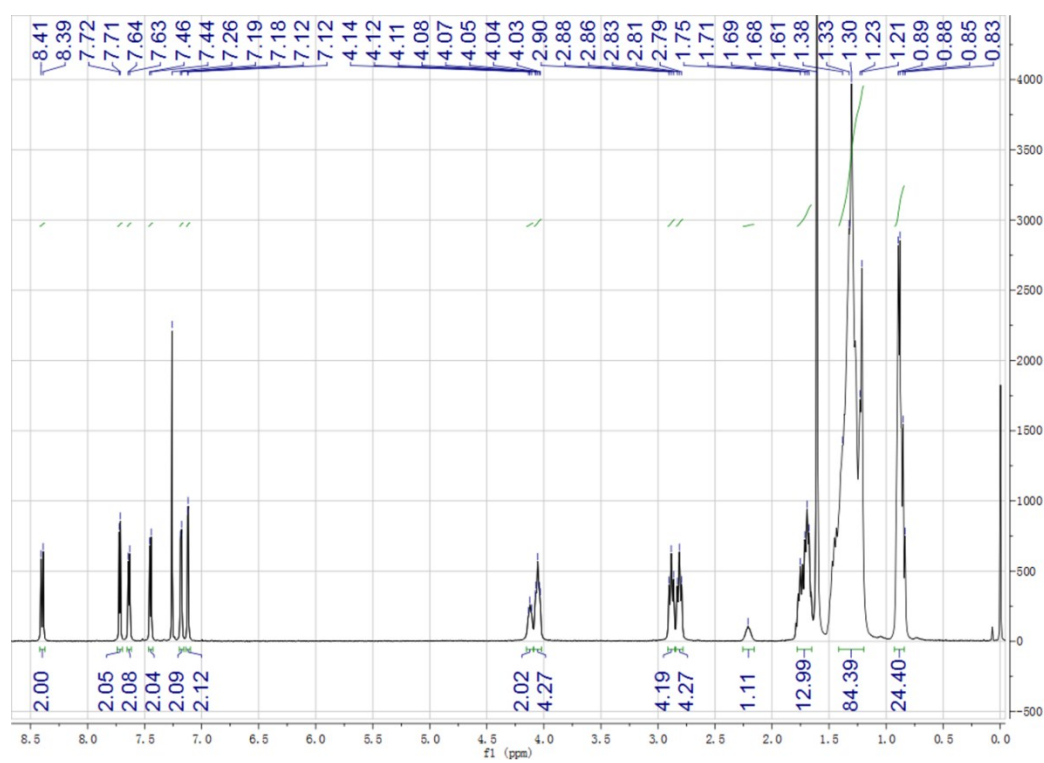


Fig. S4.  $J$ - $V$  characteristics for the electron-only (a) and hole-only (b) devices fabricated from donor:PC<sub>71</sub>BM ( $w$ :  $w = 1:0.8$ ). The solid lines represent the fit using a model of single carrier SCLC with field-independent mobility. The  $J_D$ - $V$  characteristics are corrected for the built-in voltage  $V_{bi}$  that arises from the work function difference between the contacts.



**Fig. S5.** The chemical structure of ETL-1.



**Fig. S6.** <sup>1</sup>H NMR spectra of compound DR2TDTCz at 300K in CDCl<sub>3</sub>.

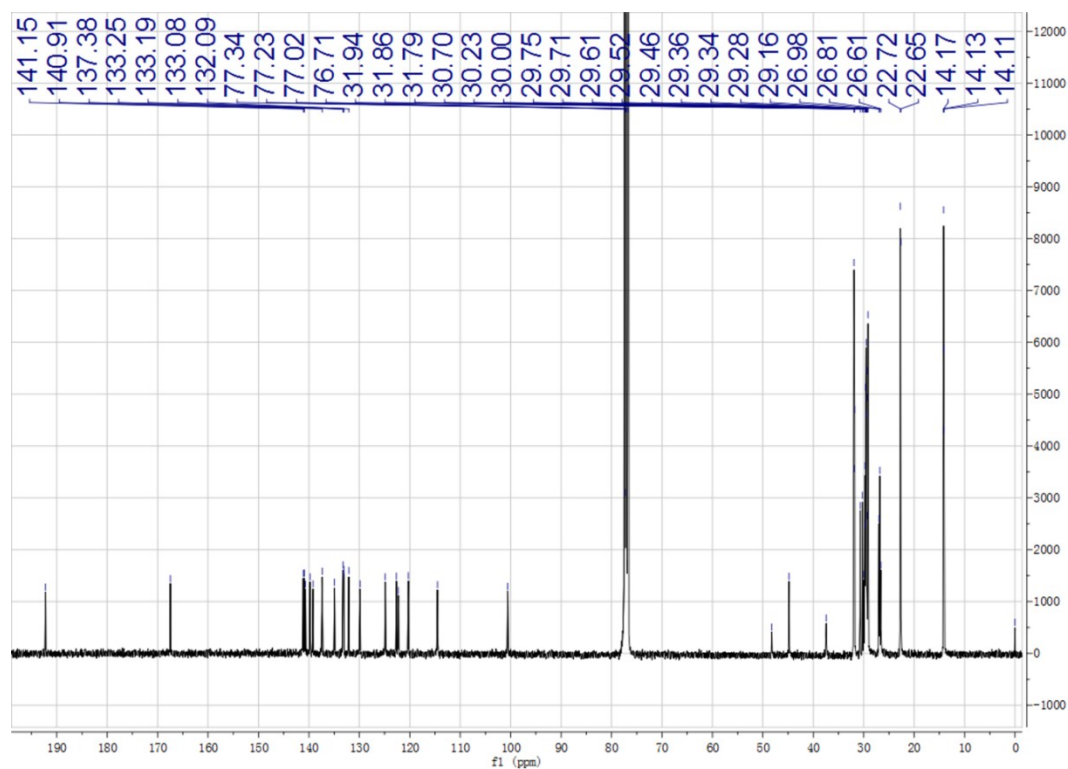


Fig. S7.  $^{13}\text{C}$  NMR spectra of compound DR2TDTCz at 300K in  $\text{CDCl}_3$ .

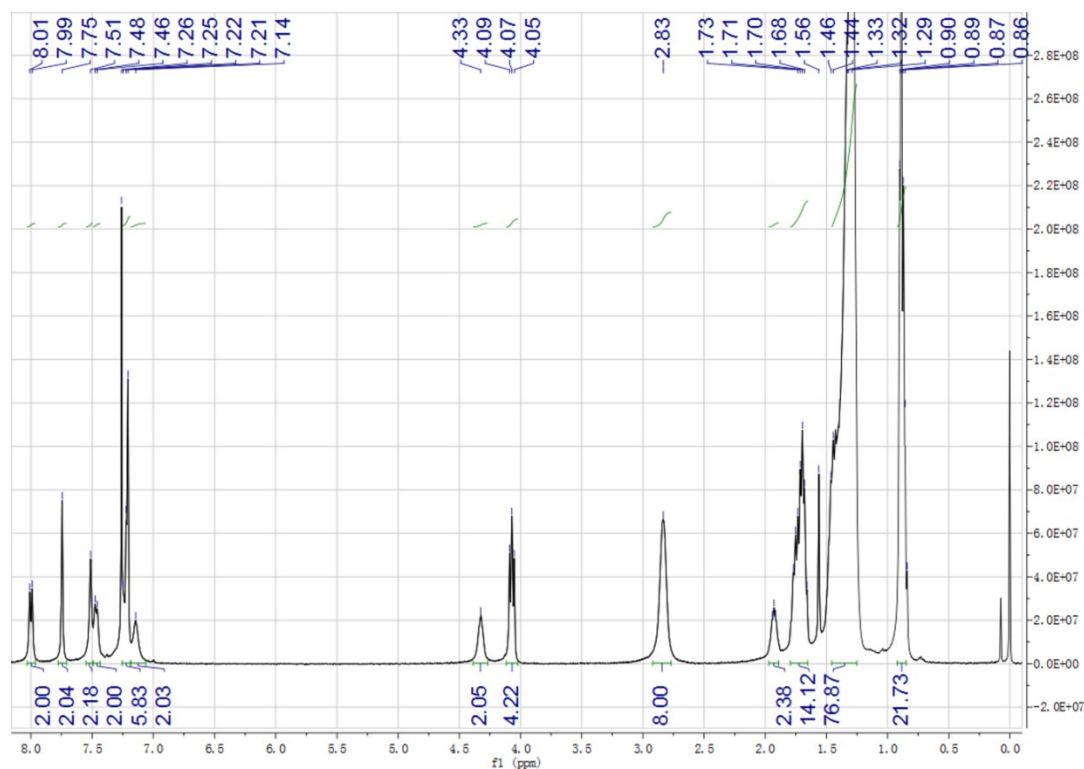
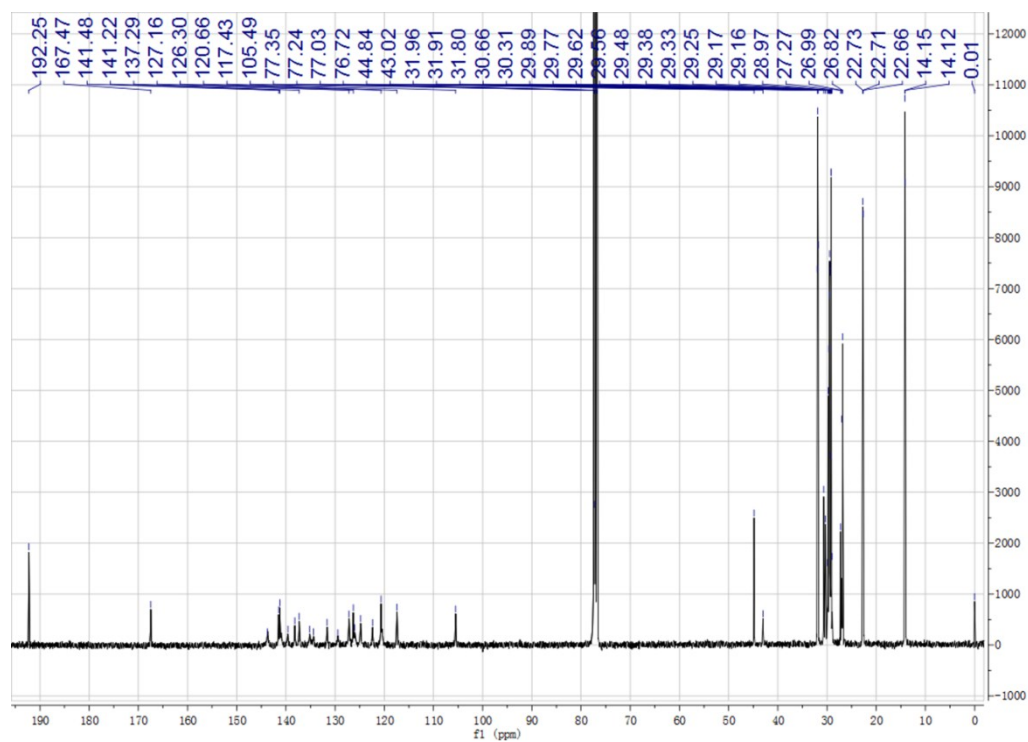
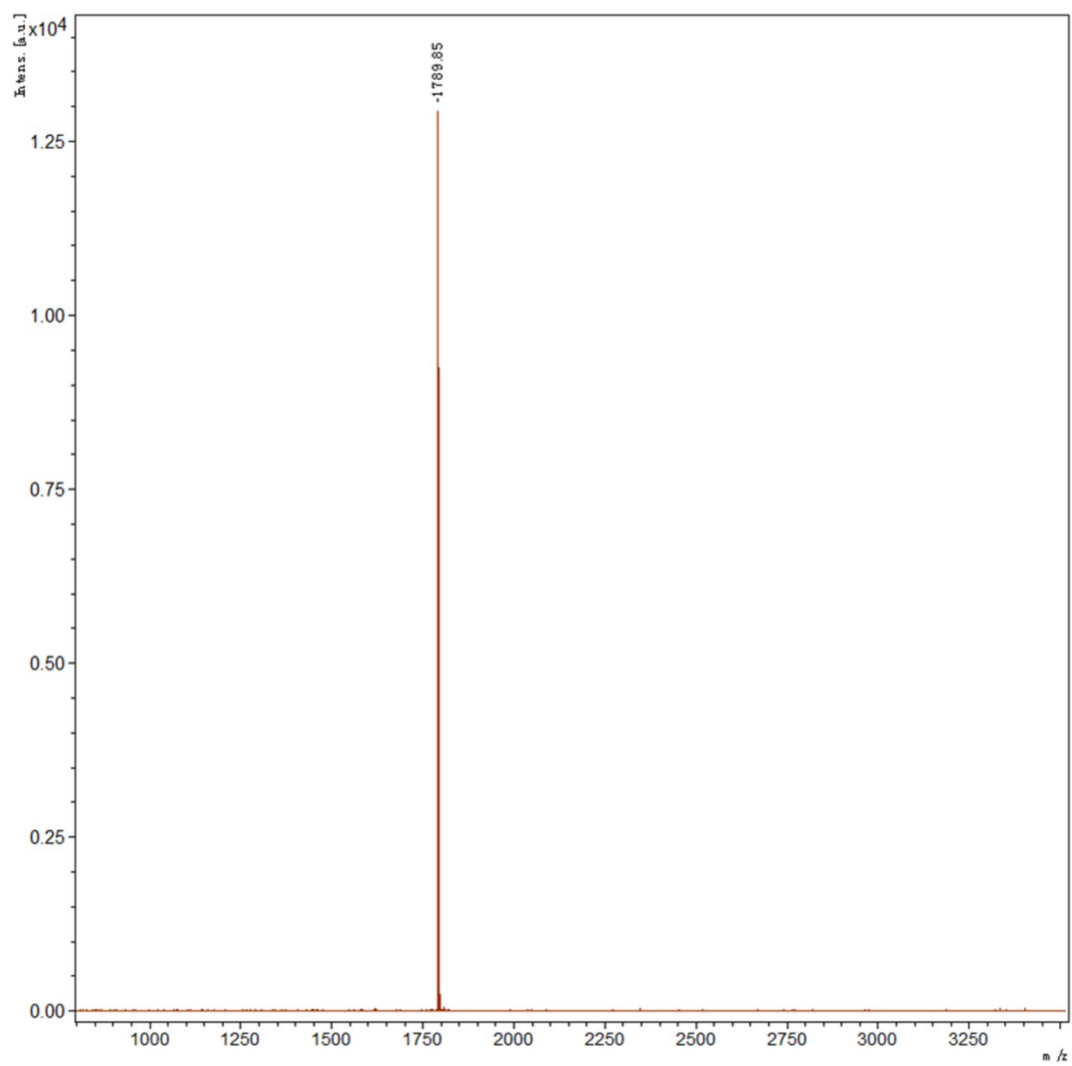


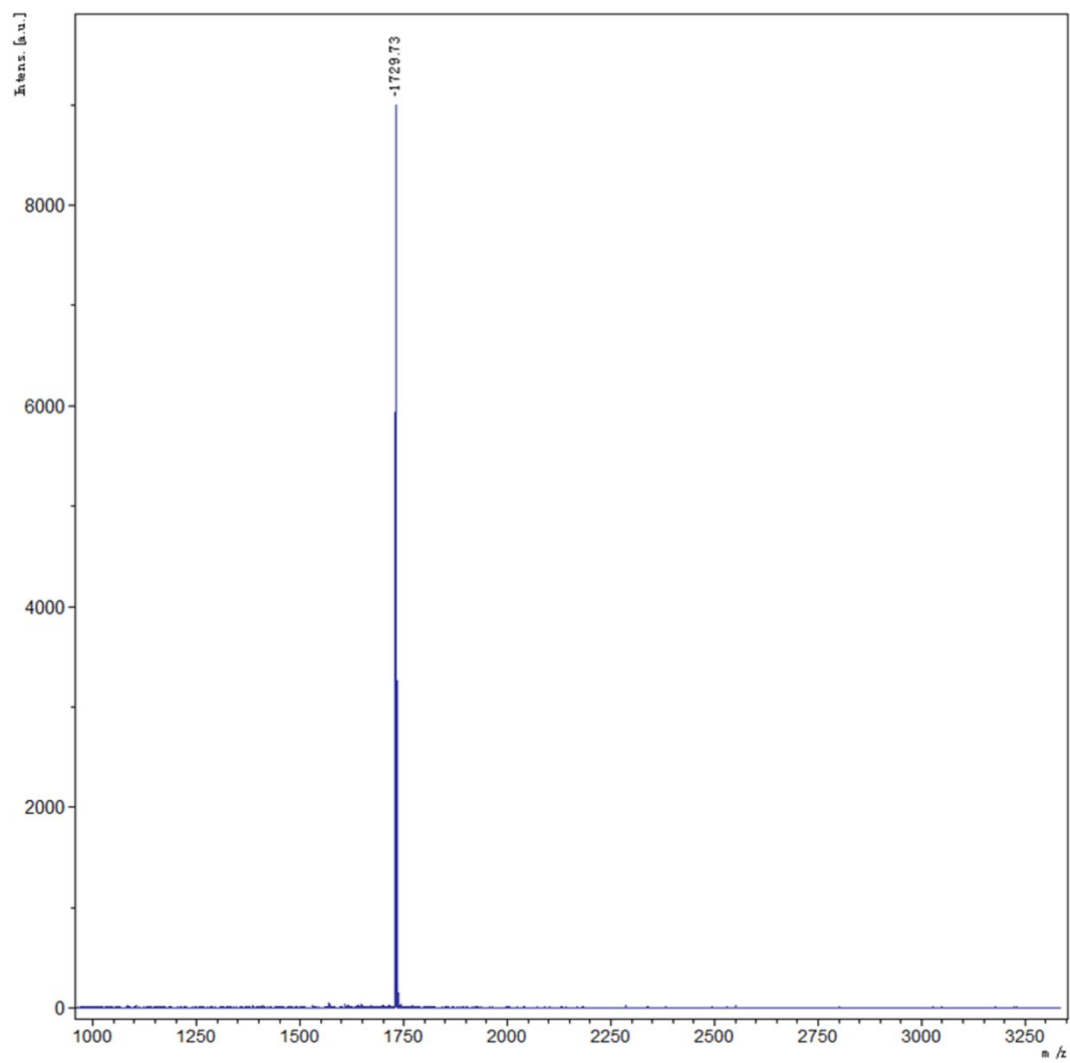
Fig. S8.  $^1\text{H}$  NMR spectra of compound DR3TCz at 300K in  $\text{CDCl}_3$ .



**Fig. S9.**  $^{13}\text{C}$  NMR spectra of compound DR3TCz at 300K in  $\text{CDCl}_3$ .



**Fig.S10.** TheMALDI-TOF plot of compound **DR2TDTCz**.



**Fig. S11.** TheMALDI-TOF plot of compound **DR3TCz**.