

## Electronic Supplementary Information

### Ladder-type Tetra-*p*-phenylene-based Copolymers for Efficient Polymer

### Solar Cells with Open-circuit Voltages Approaching 1.1 V

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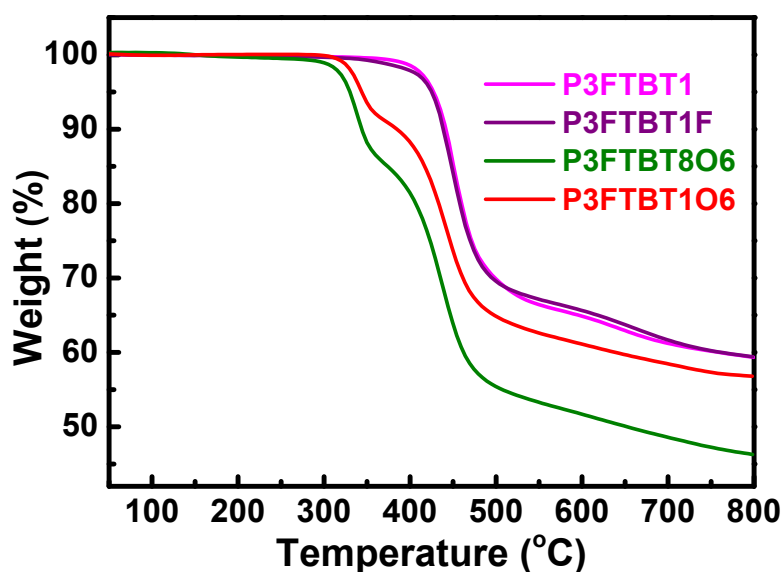


Fig. S1 TGA plots of the polymers with a heating rate of 10 °C/min under an inert atmosphere.

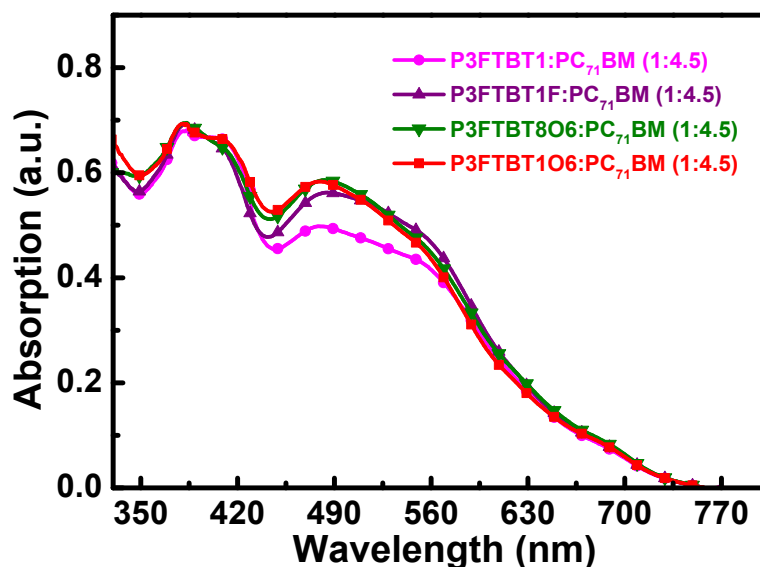


Fig. S2 UV-vis absorption spectra of the copolymers blended with PC<sub>71</sub>BM.

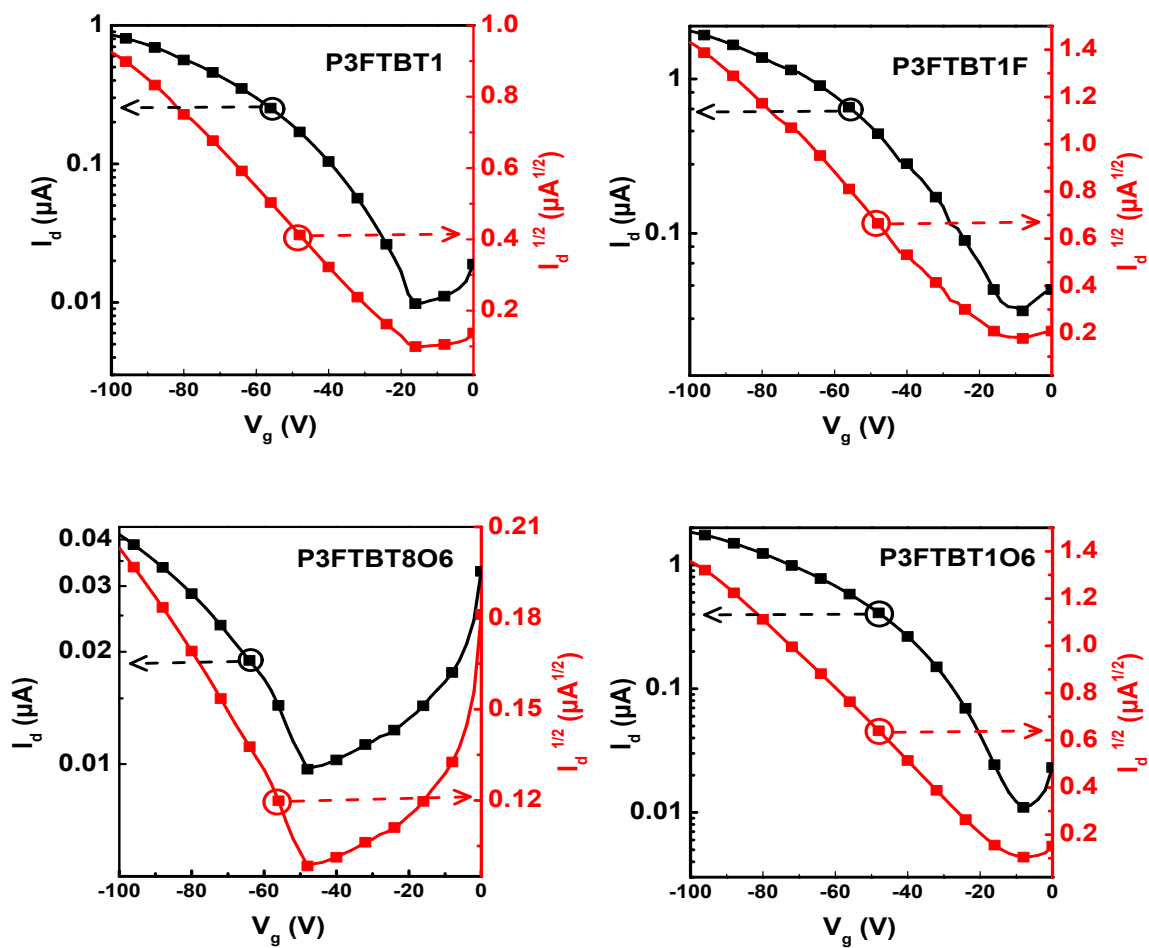


Fig. S3 Transfer curves in air of OFETs based on the polymers.

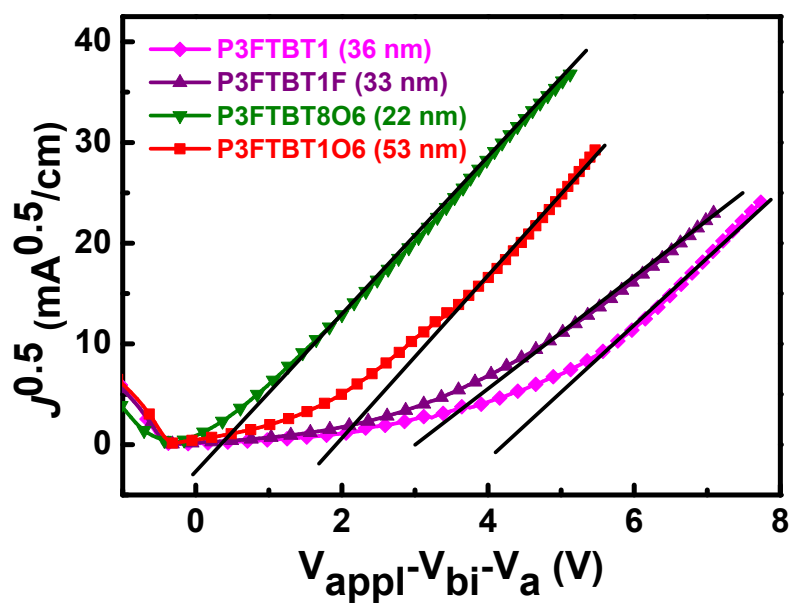


Fig. S4  $J^{0.5} \sim V$  characteristics of hole-only devices based on the polymers.

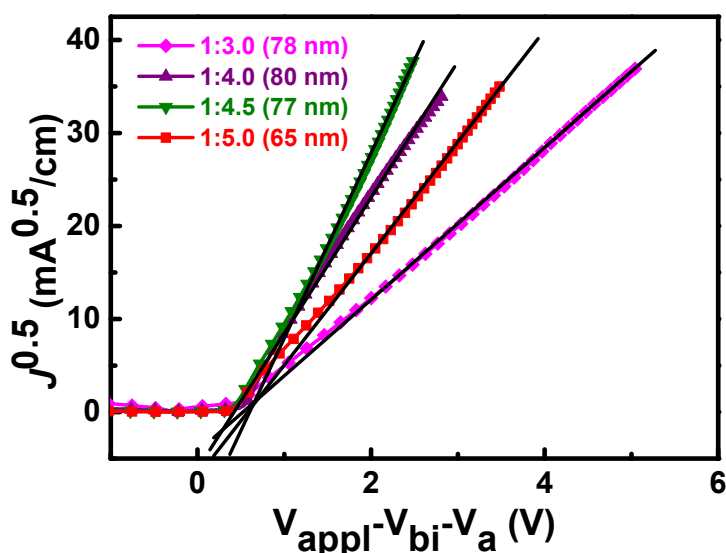


Fig. S5  $J^{0.5}\sim V$  characteristics of hole-only devices based on P3FTBT1O6:PC<sub>71</sub>BM with different blend ratios.

Table S1 Device parameters of PSCs based on P3FTBT1F

Polymers	D:A <sup>a</sup>	$V_{oc}$ (V)	$J_{sc}$ (mA/cm <sup>2</sup> )	FF (%)	PCE <sub>ave</sub> <sup>b</sup> (%)	PCE <sub>max</sub> (%)
P3FTBT1F	1:3.0	1.08 ± 0.01	8.54 ± 0.20	43.78 ± 1.10	4.04 ± 0.08	4.12
P3FTBT1F	1:4.0	1.08 ± 0.01	8.59 ± 0.23	45.93 ± 2.07	4.25 ± 0.15	4.40
P3FTBT1F	1:4.5	1.08 ± 0.01	8.81 ± 0.49	47.06 ± 1.52	4.47 ± 0.18	4.60
P3FTBT1F	1:5.0	1.08 ± 0.01	8.62 ± 0.16	44.00 ± 0.32	4.08 ± 0.09	4.16

<sup>a</sup>Blend ratios of polymer:PC<sub>71</sub>BM (w/w). <sup>b</sup>The average PCE is obtained from eight devices.

Table S2 Device parameters of PSCs based on P3FTBT1

Polymers	D:A <sup>a</sup>	$V_{oc}$ (V)	$J_{sc}$ (mA/cm <sup>2</sup> )	FF (%)	PCE <sub>ave</sub> <sup>b</sup> (%)	PCE <sub>max</sub> (%)
P3FTBT1	1:3.0	1.03 ± 0.01	9.64 ± 0.14	46.40 ± 0.78	4.62 ± 0.14	4.70
P3FTBT1	1:4.0	1.02 ± 0.01	9.70 ± 0.30	50.70 ± 1.46	5.04 ± 0.22	5.26
P3FTBT1	1:4.5	1.02 ± 0.01	9.77 ± 0.47	51.02 ± 0.87	5.10 ± 0.29	5.39
P3FTBT1	1:5.0	1.02 ± 0.01	9.71 ± 0.31	50.34 ± 1.03	5.00 ± 0.10	5.10

<sup>a</sup>Blend ratios of polymer:PC<sub>71</sub>BM (w/w). <sup>b</sup>The average PCE is obtained from eight devices.

Table S3 Device parameters of PSCs based on P3FTBT8O6

Polymers	D:A <sup>a</sup>	$V_{oc}$ (V)	$J_{sc}$ (mA/cm <sup>2</sup> )	FF (%)	PCE <sub>ave</sub> <sup>b</sup> (%)	PCE <sub>max</sub> (%)
P3FTBT8O6	1:3.0	1.04 ± 0.01	5.62 ± 0.15	32.75 ± 0.69	1.92 ± 0.15	1.99
P3FTBT8O6	1:4.0	1.02 ± 0.02	6.57 ± 0.18	32.83 ± 0.66	2.20 ± 0.14	2.30
P3FTBT8O6	1:4.5	1.03 ± 0.02	7.24 ± 1.19	34.99 ± 4.30	2.60 ± 0.26	2.86
P3FTBT8O6	1:5.0	1.03 ± 0.01	5.74 ± 0.10	37.66 ± 0.52	2.24 ± 0.06	2.30

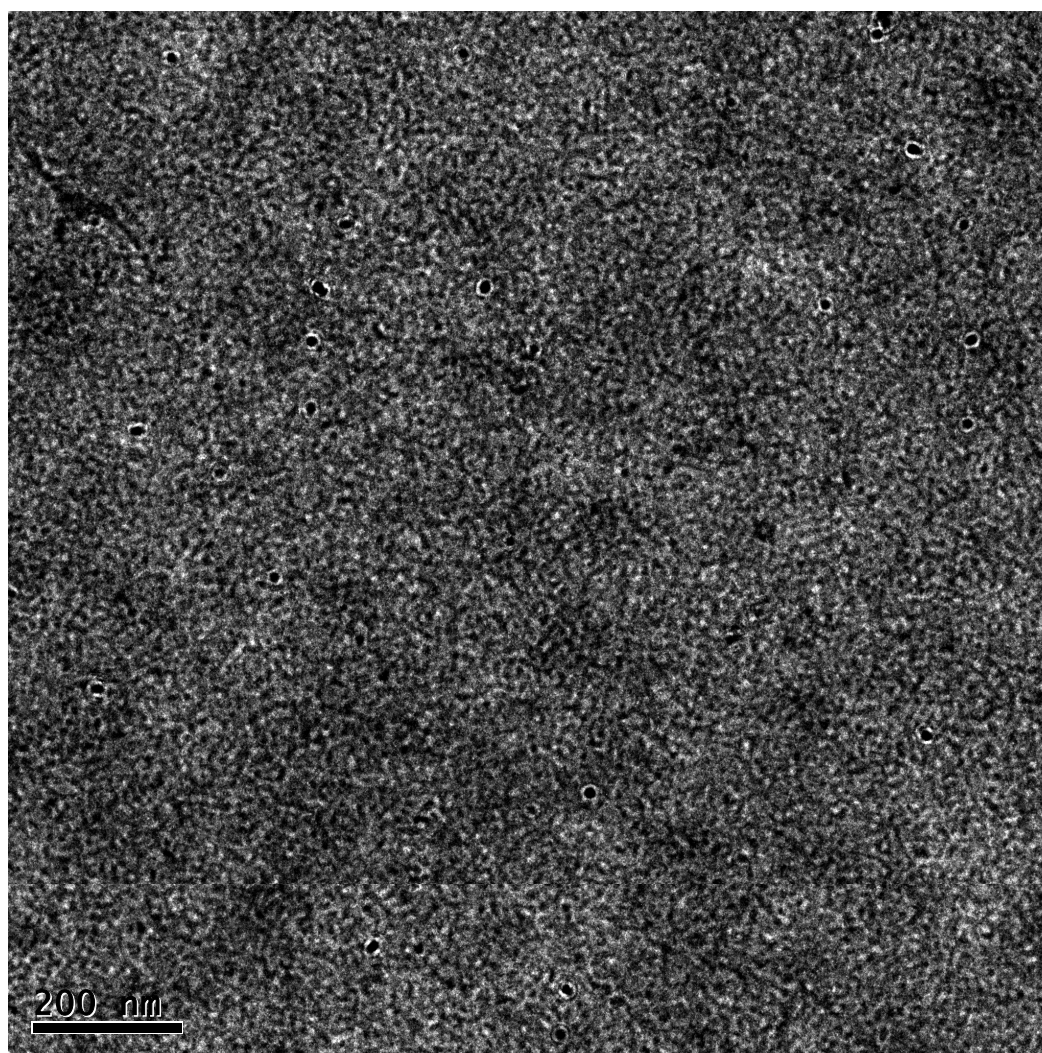
<sup>a</sup>Blend ratios of polymer:PC<sub>71</sub>BM (w/w). <sup>b</sup>The average PCE is obtained from eight devices.

**Table S4** Device parameters of PSCs based on **P3FTBT1F**:PC<sub>71</sub>BM (1:4.5)

Measurement	$V_{oc}$ (V)	$J_{sc}$ (mA/cm <sup>2</sup> )	FF (%)	PCE (%)
1	1.08	9.16	46.65	4.60
2	1.08	9.00	47.14	4.58
3	1.07	8.91	47.66	4.55
4	1.09	8.88	46.51	4.50
5	1.08	8.88	46.42	4.47
6	1.08	8.38	48.52	4.39
7	1.07	8.32	48.01	4.29
8	1.07	8.96	45.54	4.35

## Transmission Electron Microscopy (TEM)

The active layer (~ 70 nm) was spun cast on the PEDOT:PSS coated ITO. After putting the substrate in deionized water, the film was floated off the PEDOT:PSS and collected on copper TEM grids. TEM image of the thin-film morphology was obtained by a FEI Tecnai G<sup>2</sup> F-20 S-TWIN with an accelerating voltage of 200 kV, using a gantan 832 CCD camera.



**Fig. S6** TEM images of the thin-film morphology in optimized photovoltaic devices based on **P3FTBT1O6**:PC<sub>71</sub>BM (1:4.5).

## Synthesis

**Compound 2.** Compound 1 (4.6 g, 10 mmol) was dissolved in 100 ml of anhydrous THF in a 250 ml two neck flask under nitrogen protection. The solution was cooled to -78 °C by a liquid nitrogen-ethanol bath and n-hexyllithium (2.0 M in hexane, 50 ml, 100 mmol) was added dropwise under vigorous stirring. The reaction mixture was then slowly warmed to room temperature and stirred overnight. After quenched by adding saturated NH<sub>4</sub>Cl solution, the mixture was extracted with petroleum ether three times. The organic phase was separated, washed with water twice, brine solution, then dried over anhydrous MgSO<sub>4</sub>. After removing the solvent, the product was redissolved in anhydrous dichloromethane (100 ml) with the protection of nitrogen. Then 6 ml of BF<sub>3</sub>·Et<sub>2</sub>O was added dropwise. After the resulting mixture was stirred at room temperature for 30 min, methanol (200 ml) was added, where upon compound 2 started to precipitate. The solid was filtered and further purified by silica chromatography using hexane as eluent to give a white crystalline solid (2.74 g, 39% based on compound 1). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm): 7.75-7.73 (m, 4H), 7.69 (s, 2H), 7.34 (t, *J* = 7.6 Hz, 4H), 7.29 (d, *J* = 7.6 Hz, 2H), 2.04 (t, *J* = 8.4 Hz, 8H), 1.62 (s, 6H), 1.15-1.01 (m, 24H), 0.81-0.64 (m, 20H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, ppm): 153.5, 151.2, 150.3, 141.5, 140.5, 139.1, 126.8, 126.7, 123.0, 119.4, 114.0, 113.9, 54.8, 46.3, 40.7, 31.6, 29.9, 27.9, 23.9, 22.7, 14.1. HRMS (MALDI) *m/z*: calcd. for C<sub>53</sub>H<sub>70</sub>: 706.5472; found: 706.5465.

**Compound 3.** Copper(II) bromide (3.8 g, 17 mmol) on aluminum oxide (7.6 g, 74.5 mmol) was added to compound 2 (2.4 g, 3.4 mmol) in dry CCl<sub>4</sub>. And the mixture was allowed to reflux for 24 h, and then it was cooled to room temperature and filtered. After removal of the solvent, a crude product was obtained. A further purification by silica chromatography using hexane as eluent gave a pale yellow crystalline solid (4.1 g, 88%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm): 7.69 (s, 2H), 7.66 (s, 2H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.47-7.46 (m, 4H), 2.10-1.92 (m, 8H), 1.60 (s, 6H), 1.16-1.02 (m, 24H), 0.77-0.60 (m, 20H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, ppm): 153.7, 153.4, 150.0, 140.4, 139.5, 139.3, 129.9, 126.2, 120.7, 120.6, 114.1, 114.0, 55.2, 46.3, 40.6, 31.5, 29.8, 27.8, 23.8, 22.7, 14.0. HRMS (MALDI) *m/z*: calcd. for C<sub>53</sub>H<sub>68</sub>Br<sub>2</sub>: 862.3682; found: 862.3692.

**Compound 5.** Compound 5 was synthesized using the same procedures as described above for compound 2, Yield: 2.18 g (31%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm): 7.74-7.73 (m, 2H), 7.65-7.64 (m, 4H), 7.35-7.33 (m, 4H), 7.29-7.27 (m, 2H), 2.09-2.03 (m, 12H), 1.08-1.05 (m, 24H), 0.89-0.45 (m, 50H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, ppm): 151.0, 150.4, 149.9, 141.9, 141.3, 139.9, 126.7, 126.5, 122.8, 119.2, 115.1, 113.5, 54.8, 54.0, 45.3, 40.9, 40.7, 34.8, 33.6, 31.5, 29.8, 29.7, 28.3, 27.3, 23.7, 23.6, 22.6, 22.5, 14.0, 10.6. HRMS (MALDI) *m/z*: calcd. for C<sub>67</sub>H<sub>98</sub>: 902.7663; found: 902.7654.

**Compound 6.** Compound 6 was synthesized using the same procedures as described above for compound 3, Yield: 2.32 g (81%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm): 7.62-7.56 (m, 6H), 7.47-7.45 (m, 4H), 2.07-2.01 (m, 12H), 1.06-1.03 (m, 24H), 0.79-0.44 (m, 50H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, ppm): 153.3, 150.6, 149.7, 141.5, 140.8, 139.0, 129.9, 126.1,

120.6, 120.5, 115.2, 113.6, 55.2, 54.1, 45.1, 40.7, 40.6, 34.8, 33.6, 31.5, 29.7, 29.6, 28.3, 27.3, 23.6, 23.6, 22.5, 22.5, 14.0, 10.6. HRMS (MALDI) m/z: calcd. for C<sub>67</sub>H<sub>96</sub>Br<sub>2</sub>: 1058.5873; found: 1058.5871.

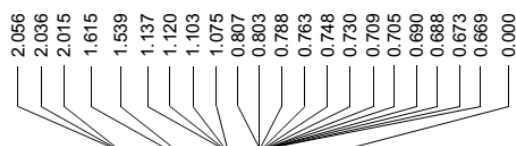
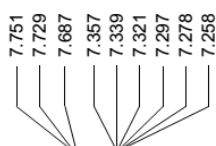
**P3FTBT1.** The Compound **3** (0.26 g, 0.30 mmol), 4,7-bis(5-(trimethylstannyl)thiophen-2-yl)benzo[c][1,2,5]thiadiazole (**10**) (0.19 g, 0.30 mmol), 20 ml of dry toluene were added into a 50 ml two neck flask. The mixture was degassed by bubbling with nitrogen for 0.5 h, then 8 mg of Pd<sub>2</sub>(dba)<sub>3</sub> and 16 mg P(o-tol)<sub>3</sub> were added. After heated at 90 °C for 24 h, 0.15 ml 2-tributylstannylthiophene was added to the mixture solution and reacted for 6 h. Then, 0.3 ml of 2-bromothiophene was added to the mixture and reacted another 6 h to complete the end-capping reaction. After the mixture was cooled to room temperature, it was precipitated into methanol. The solid was collected by filtration and further purified in a Soxhlet setup with methanol, acetone and hexane for 24 h each. Then the residue solid was redissolved in chloroform and precipitated into methanol. Finally, a dark purple solid (0.25 g, 83%) was obtained by filtration and dried in vacuum overnight. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm): 8.22 (br, 2H), 8.00 (br, 2H), 7.83-7.72 (m, 10H), 7.56 (br, 2H), 2.16 (br, 8H), 1.69 (br, 6H), 1.23-1.08 (m, 24H), 0.87-0.77 (m, 20H). M<sub>n</sub> = 22.0 KDa, polydispersity = 2.10.

**P3FTBT1F.** Polymer **P3FTBT1F** was prepared according to the same procedure as that for **P3FTBT1**, using compound **3** (0.26 g, 0.30 mmol) and compound **8** (0.20 g, 0.30 mmol). Yield: 0.27 g (86%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm): 8.34 (br, 2H), 7.78-7.74 (m, 10H), 7.57 (br, 2H), 2.14 (br, 8H), 1.67 (br, 6H), 1.25-1.07 (m, 24H), 0.81-0.69 (m, 20H). M<sub>n</sub> = 14.6 KDa, polydispersity = 1.75.

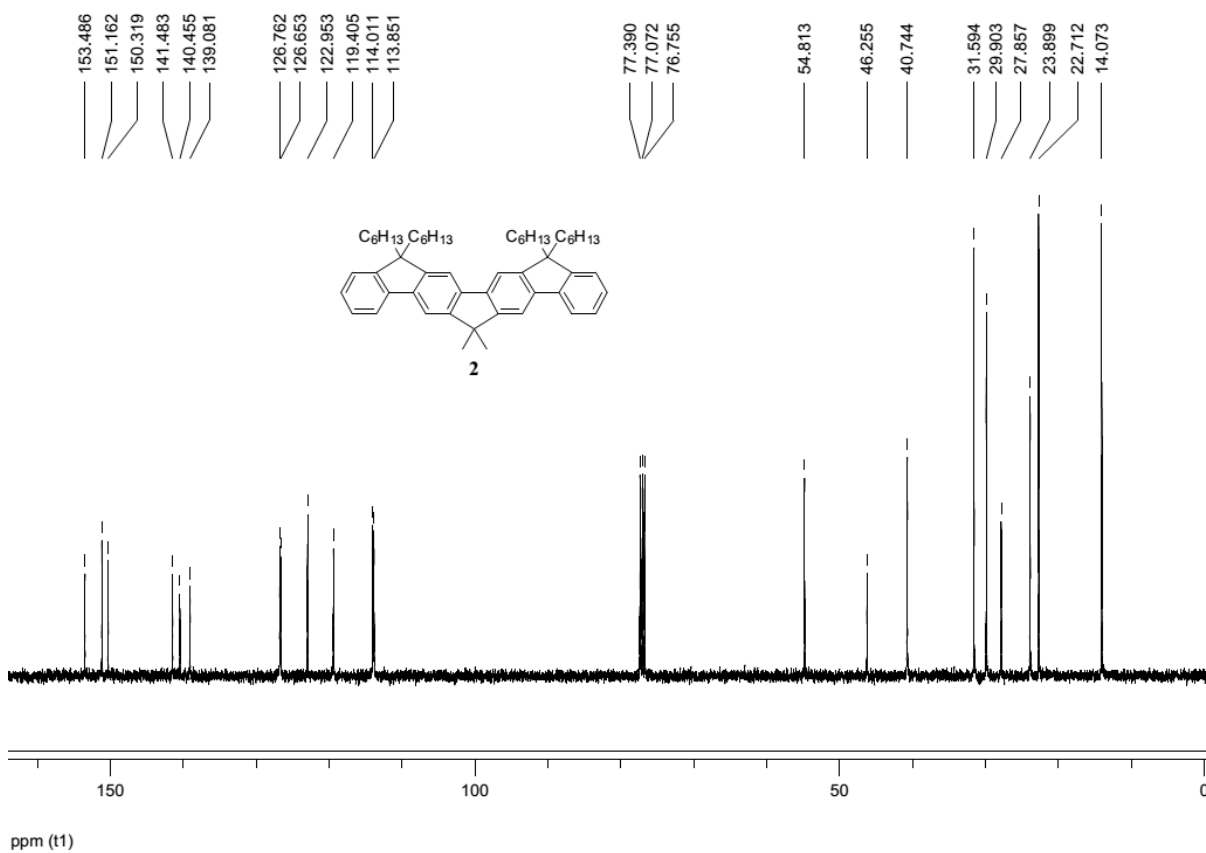
**P3FTBT8O6.** Polymer **P3FTBT8O6** was prepared according to the same procedure as that for **P3FTBT1**, using compound **6** (0.30 g, 0.28 mmol) and compound **9** (0.25 g, 0.30 mmol). Yield: 0.15 g (38%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm): 8.59-8.55 (m, 2H), 7.79-7.67 (m, 10H), 7.57 (br, 2H), 4.26 (br, 4H), 2.15-2.07 (m, 16H), 1.44-1.42 (m, 8H), 1.12-1.11 (m, 24H), 0.97-0.52 (m, 60H). M<sub>n</sub> = 11.6 KDa, polydispersity = 1.76.

**P3FTBT1O6.** Polymer **P3FTBT1O6** was prepared according to the same procedure as that for **P3FTBT1**, using compound **3** (0.26 g, 0.30 mmol) and compound **9** (0.25 g, 0.30 mmol). Yield: 0.21 g (58%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm): 8.60 (br, 2H), 7.84-7.74 (m, 10H), 7.58 (br, 2H), 4.28 (br, 4H), 2.18-2.03 (m, 12H), 1.69-1.61 (m, 10H), 1.15-1.07 (m, 32H), 0.90-0.77 (m, 26H). M<sub>n</sub> = 16.6 KDa, polydispersity = 2.06.

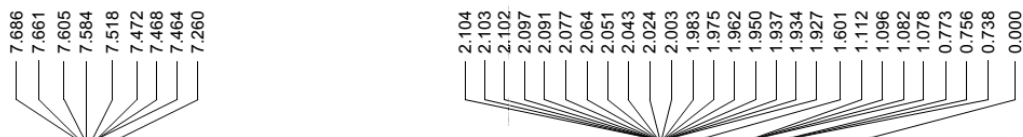
#### NMR data



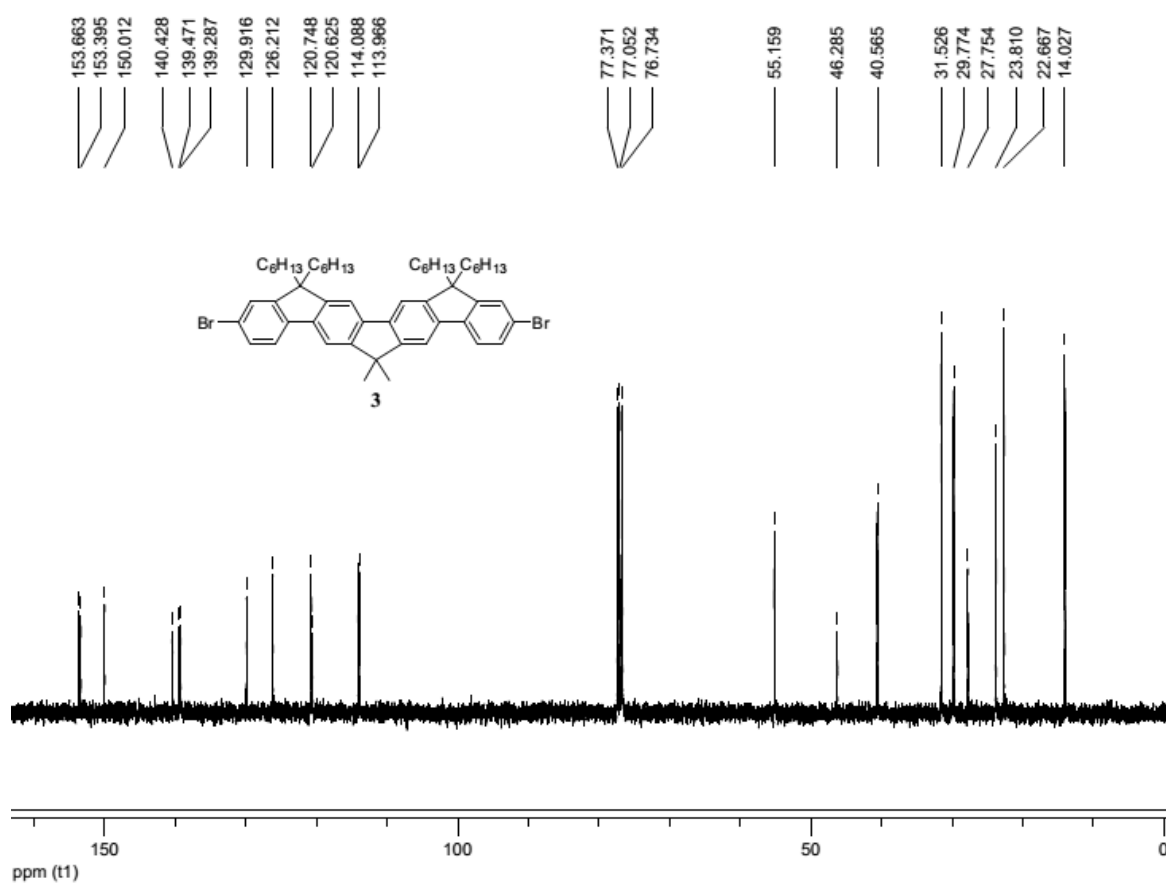
$^1\text{H}$  NMR of compound **2** in  $\text{CDCl}_3$



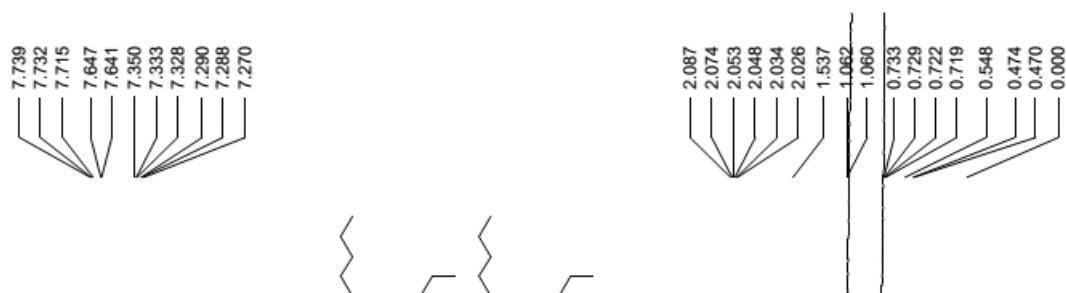
$^{13}\text{C}$  NMR of compound **2** in  $\text{CDCl}_3$



<sup>1</sup>H NMR of compound **3** in CDCl<sub>3</sub>

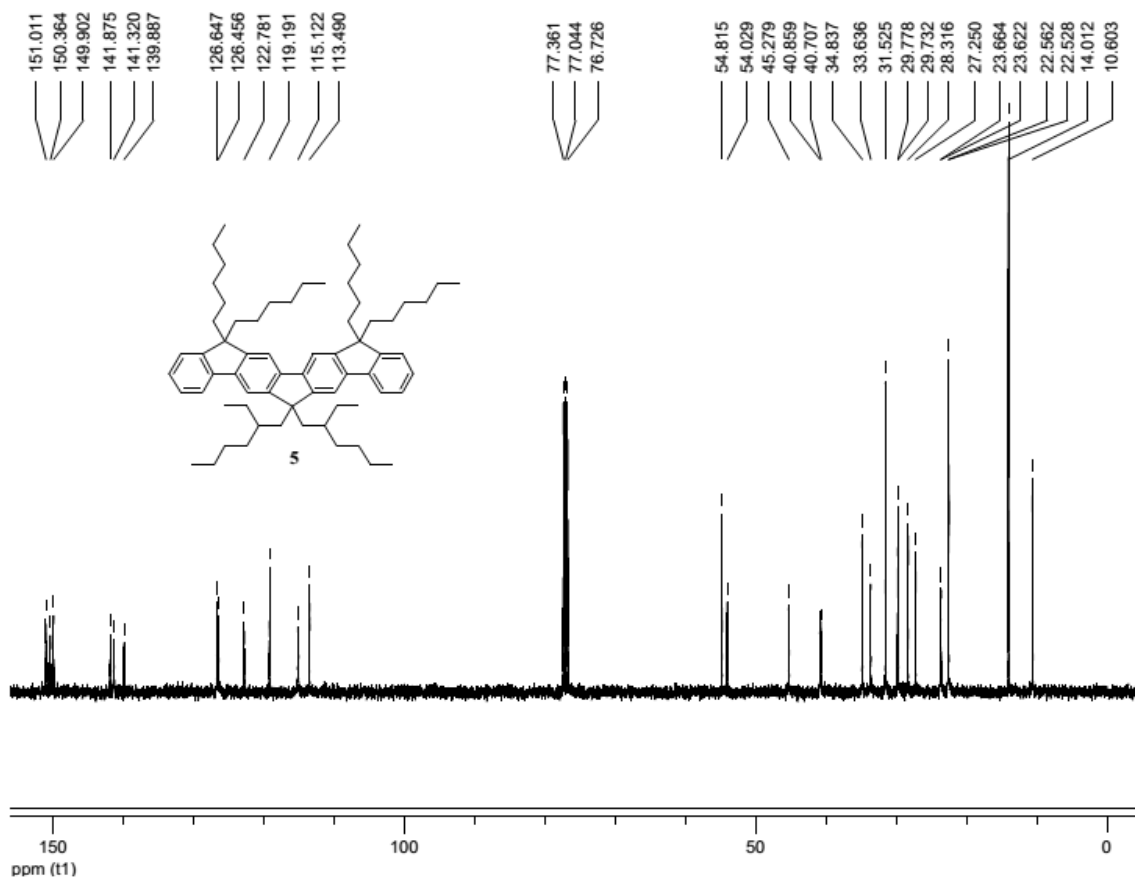


<sup>13</sup>C NMR of compound **3** in CDCl<sub>3</sub>

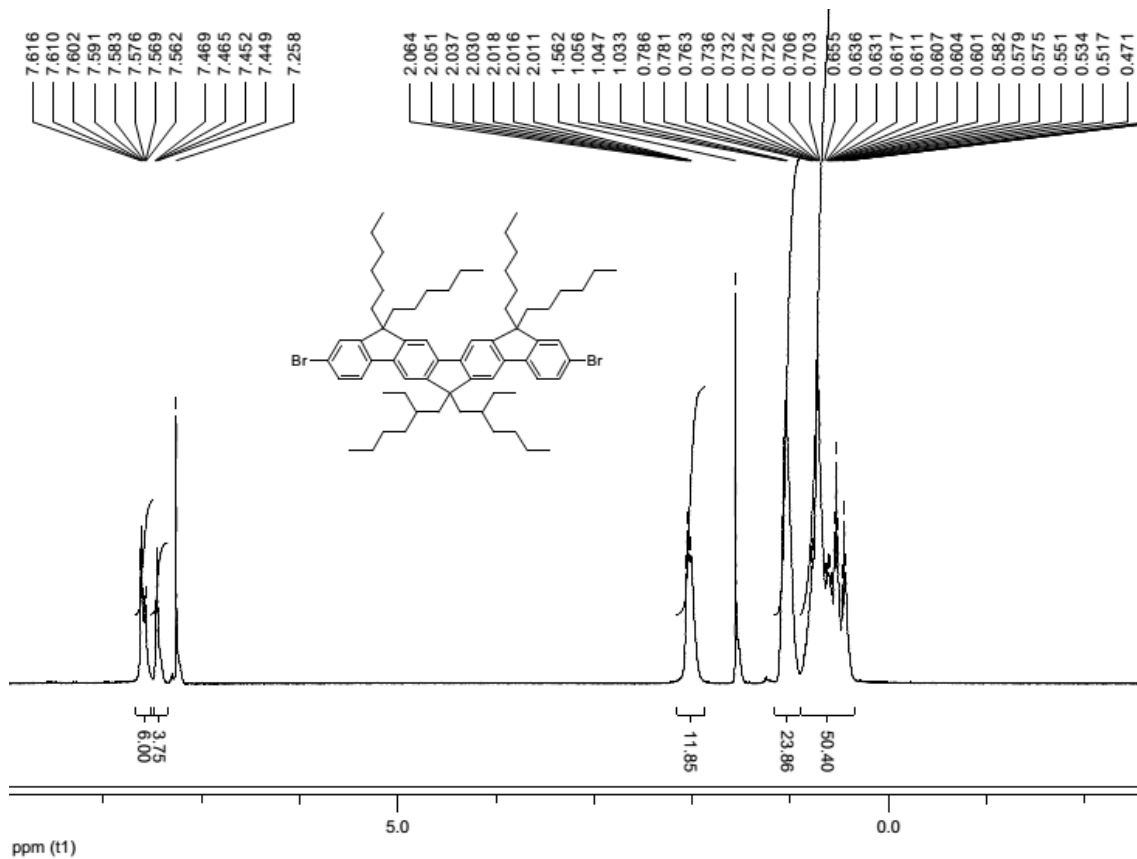




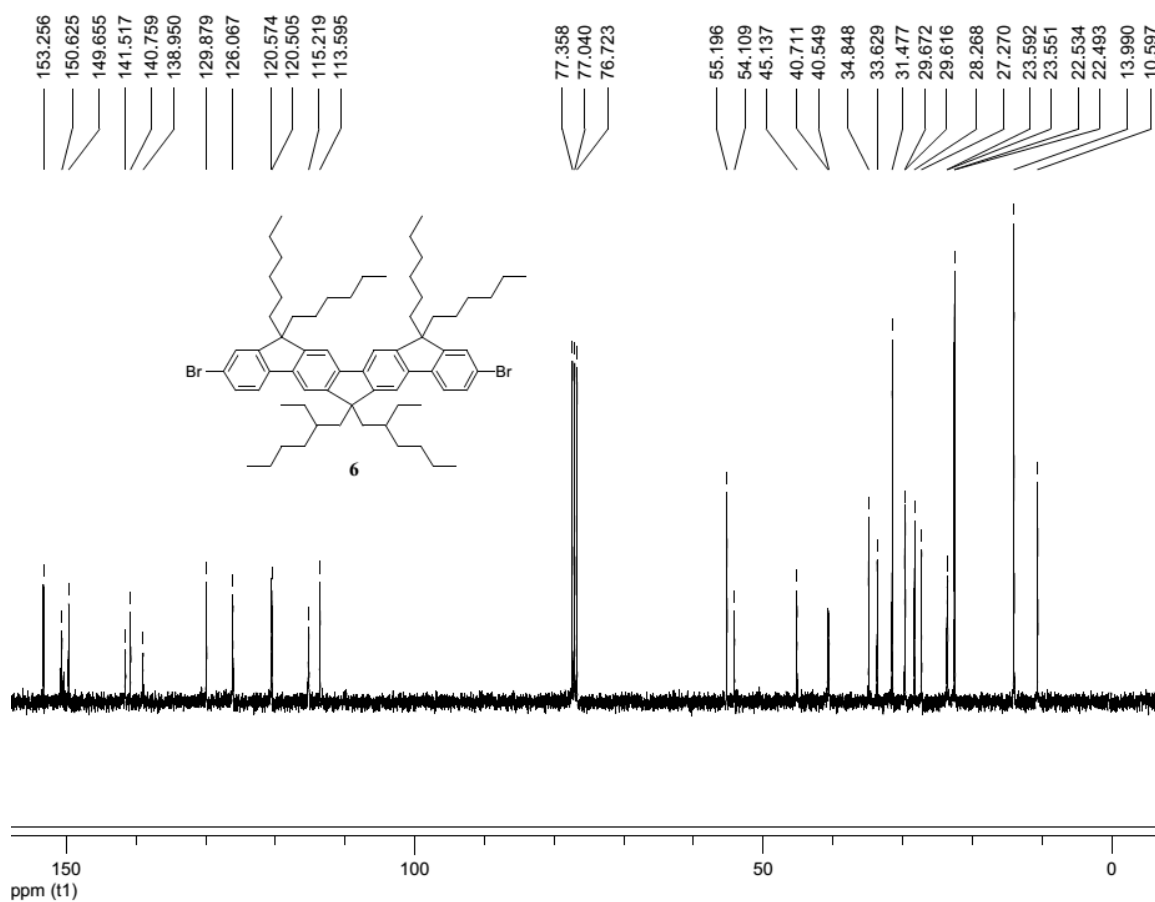
$^1\text{H}$  NMR of compound **5** in  $\text{CDCl}_3$



$^{13}\text{C}$  NMR of compound **5** in  $\text{CDCl}_3$



<sup>1</sup>H NMR of compound **6** in CDCl<sub>3</sub>



<sup>13</sup>C NMR of compound **6** in CDCl<sub>3</sub>