

# Supporting Information

## Development of High Crystalline D-A-Type Random Polymers for High Performance Large-Area Organic Solar Cells

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### General

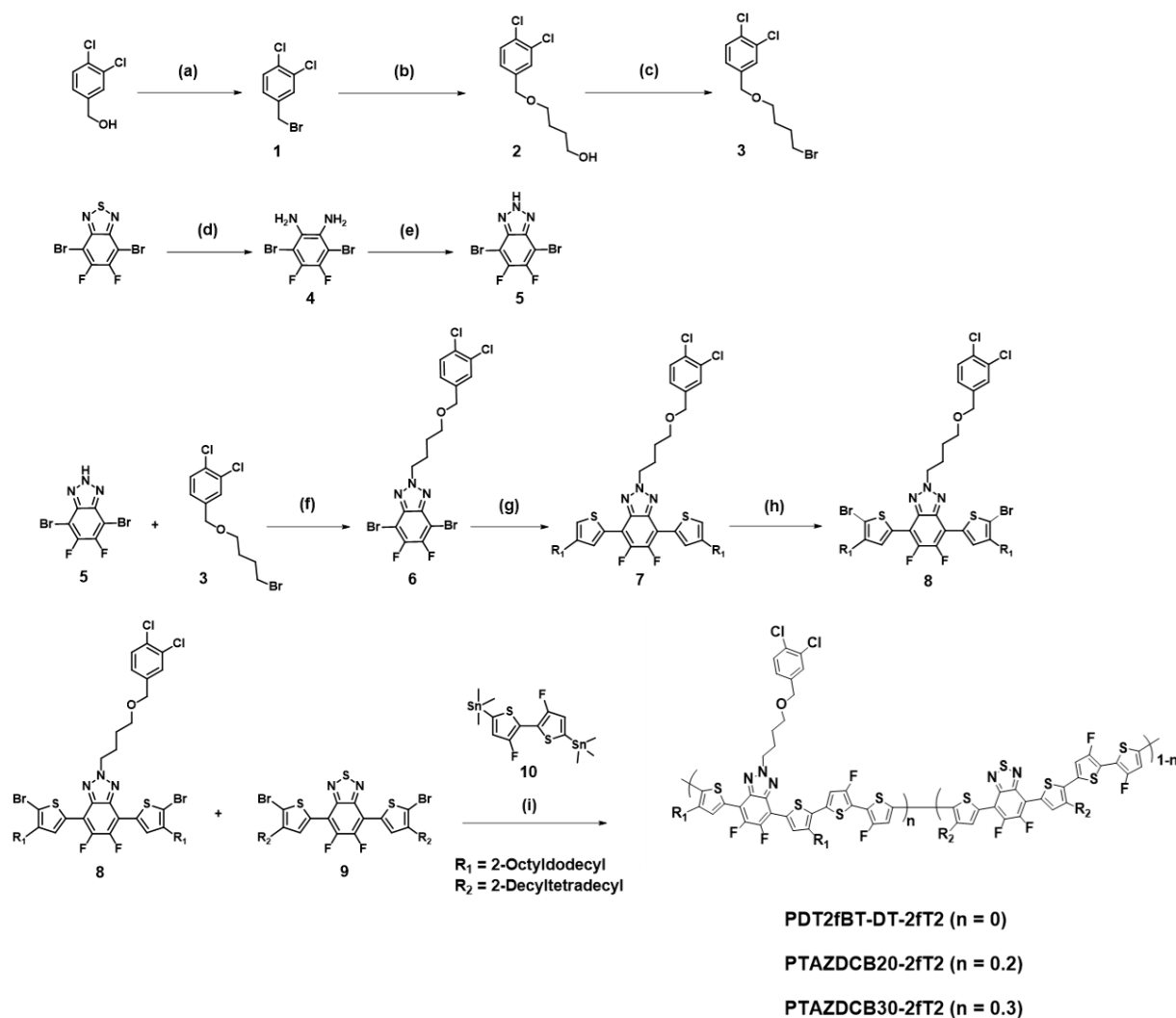
All of the chemicals were purchased from Aldrich and used without further purification unless mentioned otherwise. Tetrahydrofuran (THF) was distilled before use with sodium metal using benzophenone as an indicator. PC<sub>71</sub>BM was purchased from Sunatech. 4,7-bis(5-bromo-4-(2-decyltetradecyl)thiophen-2-yl)-5,6-difluorobenzo[*c*][1,2,5]thiadiazole (9) was synthesized using a method in the literature.<sup>1</sup> 3-(2-octyldodecyl)thiophene, 4,7-dibromo-5,6-difluorobenzo[*c*][1,2,5]thiadiazole, and (3,3'-difluoro-[2,2'-bithiophene]-5,5'-diyl)bis(trimethylstannane) (10) were synthesized according to previous reports.<sup>2-4</sup>

### Characterization methods

$^1\text{H}$  (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) spectra were conducted by a Bruker Ascend 400 spectrometer. The NMR peaks of each compound were assigned with chemical shifts ( $\delta$ : ppm) and spectral splitting patterns are designated as singlet (s), doublet (d), triplet (t), quartet (q), and multiplet (m). The number-average molecular weights ( $M_n$ ), weight-average molecular weights ( $M_w$ ) and polydispersity index (PDI) of the polymers were recorded on a Waters Gel-Permeation Chromatography (GPC) system using chlorobenzene as the eluent at 80 °C and polystyrene as the standard. UV-visible (UV-vis) absorption spectra were carried out by using an UV/vis spectrometer (Lambda 35, PerkinElmer) in the range from 300 nm to 900 nm. Microwave reactions were accomplished by a microwave initiator (Biotage). The cyclic voltammetry (CV) was performed using a CH instruments electrochemical analyzer to investigate electrochemical properties. Glassy carbon electrode was used as a working electrode and a platinum (Pt) wire as a counter electrode. A 0.1 M deoxygenated tetra-butylammonium hexafluorophosphate ( $\text{Bu}_4\text{NPF}_6$ ) solution in acetonitrile was used as an electrolyte solution. All potentials were obtained versus  $\text{Ag}/\text{Ag}^+$  (Ag in 0.1 M  $\text{AgNO}_3$  solution) reference electrode. The HOMO energy levels of polymers were estimated by using the equation:  $\text{HOMO (V)} = - [E_{\text{ox}} - E_{1/2}(\text{ferrocene}) + 4.8]$ , where  $E_{\text{ox}}$  is the onset oxidation potential of the polymer and  $E_{1/2}(\text{ferrocene})$  is the onset oxidation potential of ferrocene versus  $\text{Ag}/\text{Ag}^+$ . Differential scanning calorimetry (DSC) analysis (TA instruments Q600 thermal analysis) was measured with heating from 25 °C to 350 °C at a scan rate of 10 °C min under  $\text{N}_2$  atmosphere. The thermal properties were obtained by thermogravimetric analysis (TGA, TA instruments Q50 thermal analysis). Transmission electron microscopy (TEM) images were obtained by a FEI (Tecnai F20 G<sup>2</sup>). TEM samples were prepared from spin coating the blend solution on ITO/PEDOT:PSS substrate, followed by floating the film in water and then lifting on a carbon-coated square mesh copper grid. Atomic force microscopy (AFM) image was recorded on using an XE-100 (Park system) in non-contact mode. Two-dimensional grazing incidence wide-angle X-ray diffraction (GI-WAXD) were measured by the PLS-II 9A U-SAXS beamline of PAL. The X-rays coming from the in-vacuum undulator (IVU) were monochromated (wavelength  $\lambda=1.111 \text{ \AA}$ ) using a double crystal monochromator and

focused both horizontally and vertically (FWHM 300  $\mu\text{m}$  (H) x 30 (V)  $\mu\text{m}$  at sample position) using K-B type mirrors. Matrix assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) was performed with trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) as a matrix.

## Synthesis



**Scheme S1.** Reagents and conditions: (a)  $\text{Br}_2$ ,  $\text{PPh}_3$ ,  $\text{CH}_2\text{Cl}_2$ , 99%; (b) butane-1,4-diol,  $\text{NaH}$ , THF, 96%; (c) NBS,  $\text{PPh}_3$ ,  $\text{CH}_2\text{Cl}_2$ , 87%; (d)  $\text{Zn}_{(\text{dust})}$ ,  $\text{AcOH}/\text{H}_2\text{O}$ ; (e)  $\text{NaNO}_2$ ,  $\text{AcOH}/\text{H}_2\text{O}$ , 75%; (f)  $\text{K}_2\text{CO}_3$ , DMF, 55%; (g) trimethyl(4-(2-octyldodecyl)thiophen-2-yl)stannane,  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ , THF, 70%; (h) NBS,  $\text{CHCl}_3$ ,

90%; (i) 9, 10, Pd<sub>2</sub>dba<sub>3</sub>, P(*o*-tolyl)<sub>3</sub>, chlorobenzene, microwave heating at 170 °C, for PFBT-FTh, 55%; for PTAZDCB20, 75%; for PTAZDCB30, 65%.

#### **(4-(2-Octyldodecyl)thiophen-2-yl)trimethylstannane**

Diisopropylamine (0.40 ml, 3.53 mmol) was dissolved in anhydrous THF (2 ml) and then cooled to -78 °C. After adding *n*-BuLi (1.6 M in hexane, 2.1 ml, 3.37 mmol) dropwise, the solution warmed up to 0 °C for 30 min to complete the lithium diisopropylamide (LDA) solution. Then, 3-(2-octyldodecyl)thiophene (1.16 g, 3.18 mmol) was dissolved in anhydrous THF (22 ml). Prepared LDA was added dropwise to the mixture at -78 °C and kept the solution temperature at -78 °C for 1 h. Trimethyltinchloride solution (1.0 M in hexane, 3.65 ml, 3.65 mmol) was then rapidly injected to the solution. The reaction mixture was stirred overnight to reach room temperature. Then, the reaction was quenched with D.I. water and extracted with diethyl ether. The organic layer was dried over anhydrous MgSO<sub>4</sub> and filtered and concentrated under reduced pressure. After vacuum drying, yellow oil compound was obtained (1.63 g, 97%). The compound was used in the next reaction without further purification.

<sup>1</sup>H NMR (CDCl<sub>3</sub>), δ (ppm) : 7.15–7.17 (m, 1H), 6.90–6.98 (m, 1H), 2.57 (d, 2H), 1.54–1.60 (m, 1H), 1.20–1.32 (m, 32H), 0.86–0.89 (m, 6H), 0.28–0.41 (m, 9H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>), δ (ppm) : 143.30, 137.34, 136.90, 126.70, 126.62, 39.16, 34.52, 33.58, 32.11, 30.20, 29.87, 29.86, 29.84, 29.81, 29.53, 26.80, 22.86, 14.28, -9.92.

#### **4-(Bromomethyl)-1,2-dichlorobenzene (1)**

To a suspension of PPh<sub>3</sub> (15.41 g, 58.75 mmol) in dichloromethane (300 ml), Br<sub>2</sub> (2.98 ml, 58.18 mmol) was slowly added to the mixtures at 0 °C. Then, (3,4-dichlorophenyl)methanol (10 g, 56.49 mmol) dissolved in dichloromethane (100 ml) was added to the mixtures and stirred for 24 h at room temperature. The reaction was then quenched by aqueous sodium bisulfite. The reaction mixture was washed with

aqueous 5% NaHCO<sub>3</sub> and extracted with dichloromethane. The organic layer was dried over anhydrous MgSO<sub>4</sub> and filtered. The reaction mixture was concentrated in vacuo to give the crude product that was purified by column chromatography using a hexane/dichloromethane (1:1) to give a colorless oil compound (1) (13.42 g, 99%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>), δ (ppm) : 7.48 (d, 1H), 7.40 (d, 1H), 7.20–7.23 (m, 1H), 4.40 (s, 2H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>), δ (ppm) : 137.96, 132.87, 132.68, 131.4, 130.89, 128.42, 31.35.

#### **4-((3,4-Dichlorobenzyl)oxy)butan-1-ol (2)**

To a suspension of NaH (897.7 mg, 37.40 mmol) in anhydrous THF (40 ml) under argon atmosphere at 0 °C, 1,4-butanediol (11.24 g, 124.6 mmol) in THF (14 ml) was quickly added to the suspension. The reaction mixture was stirred for 1 h at room temperature and salt precipitates were then formed. 4-(bromomethyl)-1,2-dichlorobenzene (1) (5.97 g, 24.88 mmol) dissolved in THF (3 ml) was added dropwise to the mixture at 0 °C. After stirring for 12 h at room temperature, the reaction was quenched by D.I. water (50 ml) and extracted with diethyl ether and washed with brine. The organic layer was dried over anhydrous MgSO<sub>4</sub> and filtered. The reaction mixture was concentrated in vacuo to give the crude product that was purified by column chromatography using a hexane/ethyl acetate (2:1) to give a colorless oil compound (2) (6.33 g, 96%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>), δ (ppm) : 7.40–7.43 (m, 2H), 7.15–7.18 (m, 1H), 4.46 (s, 2H), 3.65–3.69 (m, 2H), 3.51–3.54 (m, 2H), 1.87 (t, 1H), 1.64–1.77 (m, 4H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>), δ (ppm) : 137.68, 131.42, 130.42, 129.37, 128.37, 125.76, 70.49, 69.65, 61.46, 28.75, 25.39.

#### **4-((4-Bromobutoxy)methyl)-1,2-dichlorobenzene (3)**

A solution of PPh<sub>3</sub> (4.4 g, 16.44 mmol) in dichloromethane (21 ml) was added to a stirred mixture of N-bromosuccinimide (NBS) (2.93 g, 16.78 mmol) in dichloromethane (35 ml) at -78 °C in dark. After

reaction mixture was dissolved, 4-((3,4-dichlorobenzyl)oxy)butan-1-ol (2) (3.50 g, 14.05 mmol) in dichloromethane (14 ml) was added dropwise at -78 °C. The reaction mixture was then stirred overnight to reach room temperature. The reaction was quenched with D.I. water and extracted with dichloromethane and washed with brine. The crude product was then concentrated in vacuo, followed by column chromatography using a hexane/dichloromethane (2:1) to give a colorless oil compound (3) (3.81 g, 87%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>), δ (ppm) : 7.40–7.43 (m, 2H), 7.14–7.17 (m, 1H), 4.44 (s, 2H), 3.51 (t, 2H), 3.44 (t, 2H), 1.94–2.01 (m, 2H), 1.74–1.81 (m, 2H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>), δ (ppm) : 137.88, 131.59, 130.55, 129.48, 128.43, 125.74, 70.59, 68.76, 32.72, 28.71, 27.37.

#### **3,6-Dibromo-4,5-difluorobenzene-1,2-diamine (4)**

4,7-Dibromo-5,6-difluorobenzo[c][1,2,5]thiadiazole (1.98 g, 6.00 mmol) and zinc<sub>(dust)</sub> (3.92 g, 60.0 mmol) were dissolved in acetic acid (30 ml) and D.I. water (7 ml) under argon protection and stirred for 2 h at 90 °C. After removing zinc<sub>(dust)</sub> through filtration, the reaction mixture was extracted with diethyl ether and washed with 5% NaOH for three times. The organic layer was then dried over anhydrous MgSO<sub>4</sub> and filtered and concentrated under reduced pressure. Compound (4) was used crude upon concentration immediately in the next step without further purification to avoid fast decomposition.

#### **4,7-Dibromo-5,6-difluoro-2H-benzo[d][1,2,3]triazole (5)**

3,6-Dibromo-4,5-difluorobenzene-1,2-diamine (4) was dissolved in acetic acid (10 ml) and D.I. water (5 ml). A solution of sodium nitrite (NaNO<sub>2</sub>) (537.4 mg, 7.79 mmol) dissolved in D.I. water (2 ml) was slowly added to the reaction mixture and stirred at room temperature for 1 h, followed by ultrasonication of the mixtures until providing the pale brown solid precipitate in the solution. Finally, the reaction mixture was cooled to 0 °C and stirred for additional 30 min to have solid precipitate effectively formed.

The solid was then filtered and washed with D.I. water thoroughly to give a pale brown solid compound (5) for two steps. (1.41 g, 75%). The compound was used in the next reaction without further purification.

**4,7-Dibromo-2-(4-((3,4-dichlorobenzyl)oxy)butyl)-5,6-difluoro-2*H*-benzo[*d*][1,2,3]triazole (6)**

4,7-Dibromo-5,6-difluoro-2*H*-benzo[*d*][1,2,3]triazole (5) (1.48 g, 4.74 mmol), 4-((4-bromobutoxy)methyl)-1,2-dichlorobenzene (3) (1.74 g, 5.30 mmol), and K<sub>2</sub>CO<sub>3</sub> (1.31 g, 9.49 mmol) were dissolved in anhydrous N, N-dimethylformamide (DMF) (30 ml) and stirred for 24 h at 90 °C under argon atmosphere. After reaction was completed, the reaction was quenched by aqueous 1 M HCl solution (10 ml). The reaction mixture was then extracted by diethyl ether and washed with D.I. water. The crude product was then concentrated in vacuo, followed by column chromatography using a chloroform/methanol (0.25% v/v) to give a green solid compound (6) (1.42 g, 55%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>), δ (ppm) : 7.39–7.42 (m, 2H), 7.14–7.17 (m, 1H), 4.80 (t, 2H), 4.43 (s, 2H), 3.53 (t, 2H), 2.23–2.27 (m, 2H), 1.68–1.73 (m, 2H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>), δ (ppm) : 150.47, 150.26, 147.94, 147.73, 138.97, 138.71, 132.44, 131.40, 130.36, 129.23, 126.61, 96.41, 96.28, 96.20, 96.13, 96.04, 95.92, 71.52, 69.70, 57.26, 27.09, 26.69.

**2-(4-((3,4-Dichlorobenzyl)oxy)butyl)-5,6-difluoro-4,7-bis(4-(2-octyldodecyl)thiophen-2-yl)-2*H*-benzo[*d*][1,2,3]triazole (7)**

(4-(2-Octyldodecyl)thiophen-2-yl)trimethylstannane (509.9 mg, 0.97 mmol), 2-(4-((3,4-dichlorobenzyl)oxy)butyl)-5,6-difluoro-4,7-bis(4-(2-octyldodecyl)thiophen-2-yl)-2*H*-benzo[*d*][1,2,3]triazole (7) (202.3 mg, 0.37 mmol), and Pd[PPh<sub>3</sub>]<sub>2</sub>Cl<sub>2</sub> (46 mg, 0.07 mmol) were dissolved in anhydrous THF (3 ml) under argon atmosphere. The reaction mixture was refluxed for 48 h to complete the reaction. The reaction mixture was concentrated in vacuo to give the crude product that was purified by column chromatography using a hexane/toluene (3:2) to give an green oil compound (7) (290 mg, 70.2%).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ),  $\delta$  (ppm) : 8.04 (d, 2H), 7.40 (d, 1H), 7.37 (d, 1H), 7.12–7.14 (m, 1H), 7.10 (d, 2H), 4.83 (t, 2H), 4.43 (s, 2H), 3.55 (t, 2H), 2.64 (d, 4H), 2.26–2.34 (m, 2H), 1.73–1.80 (m, 2H), 1.65–1.71 (m, 2H), 1.24–1.31 (m, 64H), 0.84–0.88 (m, 12H).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ),  $\delta$  (ppm) : 148.71, 148.52, 146.20, 146.00, 142.36, 138.83, 137.93, 137.89, 132.61, 132.02, 131.55, 130.45, 129.33, 126.63, 123.95, 110.16, 110.07, 71.61, 69.88, 56.64, 39.04, 34.99, 33.47, 32.07, 30.19, 29.86, 29.82, 29.52, 26.95, 26.87, 26.80, 22.83, 14.25.

**4,7-Bis(5-bromo-4-(2-octyldodecyl)thiophen-2-yl)-2-(4-((3,4-dichlorobenzyl)oxy)butyl)-5,6-difluoro-2H-benzo[d][1,2,3]triazole (8)**

Under avoiding any light source, 2-(4-((3,4-dichlorobenzyl)oxy)butyl)-5,6-difluoro-4,7-bis(4-(2-octyldodecyl)thiophen-2-yl)-2H-benzo[d][1,2,3]triazole (7) (283 mg, 0.25 mmol) and a small portion of silica gel was dissolved in chloroform (4.2 ml). The solution was cooled to 0 °C in an ice bath and NBS (99.6 mg, 0.56 mmol) was added by small portions. After removing the ice bath, the reaction was stirred for 24 h at room temperature. After the reaction was completed, the mixture was extracted with chloroform and washed with brine and water. Organic phase was dried over anhydrous  $\text{MgSO}_4$  and the solvent was evaporated under reduced pressure. The crude product then was purified by column chromatography using a hexane/toluene (2:1) to give a green oil compound (8) (291 mg, 90%).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ),  $\delta$  (ppm) : 7.87 (s, 2H), 7.37–7.40 (m, 2H), 7.12–7.15 (m, 1H), 4.83 (t, 2H), 4.44 (s, 2H), 3.55 (t, 2H), 2.58 (d, 4H), 2.26–2.33 (m, 2H), 1.72–1.79 (m, 4H), 1.23–1.31 (m, 64H), 0.83–0.87 (m, 12H).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ),  $\delta$  (ppm) : 148.67, 148.47, 146.15, 145.95, 141.84, 138.80, 137.56, 137.52, 132.66, 131.67, 131.62, 131.59, 130.51, 129.36, 126.67, 113.89, 113.85, 109.62, 109.53, 109.49, 71.69, 69.87, 56.80, 38.67, 34.27, 33.51, 32.07, 30.17, 29.86, 29.82, 29.79, 29.51, 26.98, 26.89, 26.71, 22.83, 14.25.

HRMS (MALDI+) Calcd for  $\text{C}_{65}\text{H}_{97}\text{Br}_2\text{Cl}_2\text{F}_2\text{N}_3\text{OS}_2$  ( $\text{M}^+$ ): 1269.3; found: 1269.5



### Synthesis of PFBT-FTh

4,7-Bis(5-bromo-4-(2-decyltetradecyl)thiophen-2-yl)-5,6-difluorobenzo[*c*][1,2,5]thiadiazole (9) (103.7 mg, 0.088 mmol), 3,3'-difluoro-[2,2'-bithiophene]-5,5'-diylbis(trimethylstannane) (10) (46.8 mg, 0.088 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (0.81 mg, 0.0009 mmol), P(*o*-tolyl)<sub>3</sub> (1.08 mg, 0.004 mmol), and degassed chlorobenzene (0.44 ml) were placed in a microwave vial under argon protection. The reaction mixture was heated to 170 °C for 2 h and cooled down to room temperature. The solution was precipitated into methanol, filtered and purified by Soxhlet extraction. The polymer was then extracted successively with methanol, ethyl acetate, hexane, dichloromethane, chloroform and chlorobenzene. The chlorobenzene fraction was concentrated in vacuo, and then precipitated in methanol. After filtration, the polymer was dried under vacuum over 24 h to give a dark green solid (71 mg, 55%).  $M_n = 138$  kDa, PDI = 2.58

<sup>1</sup>H NMR (C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>),  $\delta$  (ppm) : 8.00–8.26 (br, 2H), 7.04–7.51 (br, 2H), 2.51–3.01 (br, 4H), 1.80–2.01 (br, 2H), 1.11–1.58 (br, 80H), 0.86–0.89 (br, 12H).

### Synthesis of PTAZDCB20

Compound (8) (73.3 mg, 0.057 mmol), compound (9) (269.6 mg, 0.231 mmol), compound (10) (152.3 mg, 0.288 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (2.6 mg, 0.03 mmol), P(*o*-tolyl)<sub>3</sub> (3.5 mg, 0.01 mmol) and degassed chlorobenzene (1.4 ml) were placed in a microwave vial under argon protection. PTAZDCB20 was then prepared using the same procedure for the synthesis of PFBT-FTh polymer to give a green solid (320 mg, 75.3%).  $M_n = 149$  kDa, PDI = 2.51

<sup>1</sup>H NMR (C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>),  $\delta$  (ppm) : 7.27–7.39 (br, 4.6H), 4.80–4.90 (br, 1.2H), 2.59–2.64 (br, 4.4H), 2.03–2.04 (br, 2.4H), 1.16–1.50 (br, 76.8H), 0.81–0.92 (br, 12H).

### Synthesis of PTAZDCB30

Compound (8) (28.7 mg, 0.022 mmol), compound (9) (61.6 mg, 0.052 mmol), compound (10) (39.8 mg, 0.074 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (0.7 mg, 0.0007 mmol), P(*o*-tolyl)<sub>3</sub> (0.95 mg, 0.003 mmol) and degassed chlorobenzene (0.4 ml) were placed in a microwave vial under argon protection. PTAZDCB30 polymer was then prepared using the same procedure for the synthesis of PFBT-FTh polymer except the chloroform fraction was obtained to give a green solid (72.7 mg, 65.1%).  $M_n = 115$  kDa, PDI = 2.96.

<sup>1</sup>H NMR (C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>),  $\delta$  (ppm) : 7.31–7.48 (br, 4.9H), 4.78–4.95 (br, 1.8H), 2.58–2.67 (br, 4.6H), 1.99–2.09 (br, 2.6H), 1.15–1.49 (br, 75.2H), 0.80–0.96 (br, 12H).

### Charge carrier mobility measurement

Space-charge-limited current (SCLC) measurements were conducted by using Keithley model 2400 source measuring unit. The single carrier diode were fabricated utilizing an architecture of ITO/PEDOT:PSS/active layer/Au and ITO/Al/Active layer/Al for hole-only devices and electron only devices, respectively. The *J-V* characteristics of the single carrier devices are estimated from Mott-Gurney law as in following equation,

$$J = \frac{9}{8} \varepsilon_r \varepsilon_0 \mu \frac{V^2}{L^3}$$

,where  $\varepsilon_0$  is the permittivity of a free space;  $\varepsilon_r$  is the relative permittivity of the material;  $\mu$  is the carrier mobility;  $L$  is the film thickness of active layer.  $V$  is the effective voltage determined by  $V = V_{appl} - V_r - V_{bi}$ , where  $V_{appl}$  is the applied voltage to the device,  $V_r$  is the voltage drop due to contact resistance and series resistance across the electrodes, and  $V_{bi}$  is the built-in voltage due to the difference in work function of the two electrodes.<sup>5-6</sup>

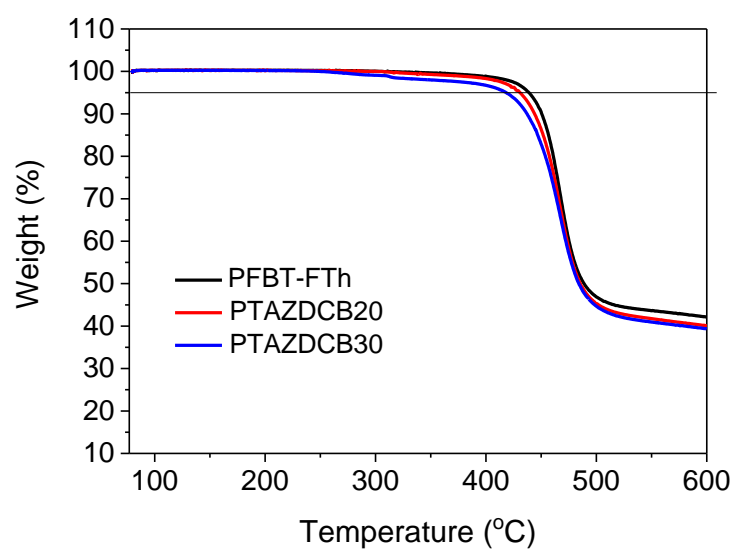
### Solar cell fabrication

Pre-patterned indium tin oxide (ITO) glass substrates were cleaned by ultrasonication in 2-propanol, acetone, and 2-propanol sequentially in each step for 10 min and dried under 90 °C oven for 1 h.

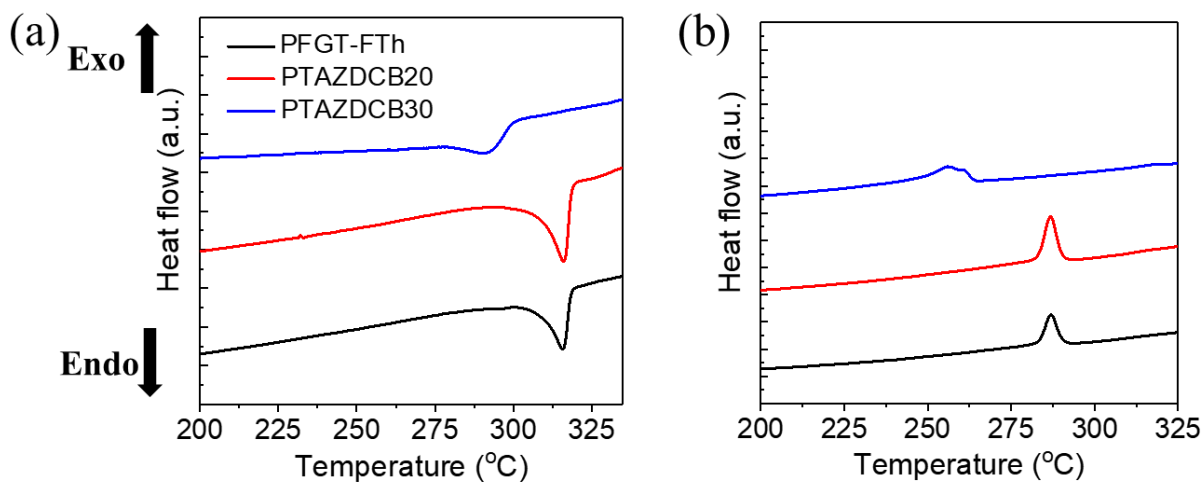
Polyethlenimine ethoxylated (PEIE) solution diluted with 2-methoxyethanol to a 0.2 wt% was spinning on the ITO substrate at 6000 rpm for 25 s in a N<sub>2</sub> filled glovebox after treating the cleaned substrate with an UV/O<sub>3</sub> cleaner for 20 min. Active layer solution (polymer:PC<sub>71</sub>BM=1:2 (w/w)) were prepared by dissolving in a mixture of chlorobenzene (CB) and *o*-dichlorobenzene (DCB) (CB:DCB = 1:1 v/v) with 2.5 vol% of 1-chloronaphthalene (CN) in a polymer concentration of 6.5 mg/ml for PFBT-FTh polymer. Active layer solution of PTAZDCB20 and PTAZDCB30 (polymer:PC<sub>71</sub>BM=1:2 (w/w) and polymer concentration=10 mg/ml) was prepared in CB with 2.5 vol% of CN. The blend solution were stirred at 110 °C for 1 h in order to fully dissolve the active layer materials and then transferred to the N<sub>2</sub> filled glovebox. Both as-prepared ITO/PEIE substrates and the blend solutions were heated in a hot plate at 110 °C before spin coating process while keeping the solution temperature at 110 °C. The active layers were formed by spin coating at around 600 rpm – 1000 rpm on the top of the ITO/PEIE substrate to afford optimum thickness of 250 – 300 nm. A thin layer of MoO<sub>3</sub> (4 nm), followed by Ag (100 nm) was then thermally evaporated through a shadow mask at a high vacuum to complete the devices.

### **Solar cell measurement**

A Keithley model 2400 source meter under AM1.5G at sun light intensity (100 mW/cm<sup>2</sup>) in ambient air was used to measure the devices. A class-A solar simulator with a 1000 W Xenon lamp (Yamashita Denso) was used as a light source. Its light intensity was calibrated by using a NREL-calibrated Si solar cell coupled with KG-5 filter. External quantum efficiencies (EQE) were obtained by incident photon-to-current conversion equipment (Mescience), calibrated by a G425 silicon photodiode.



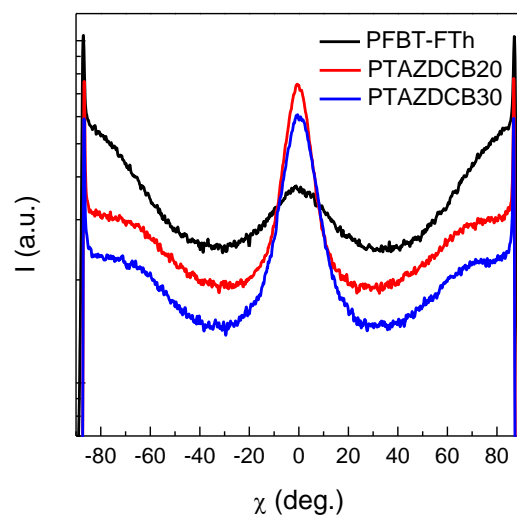
**Figure S1.** TGA curves of polymers



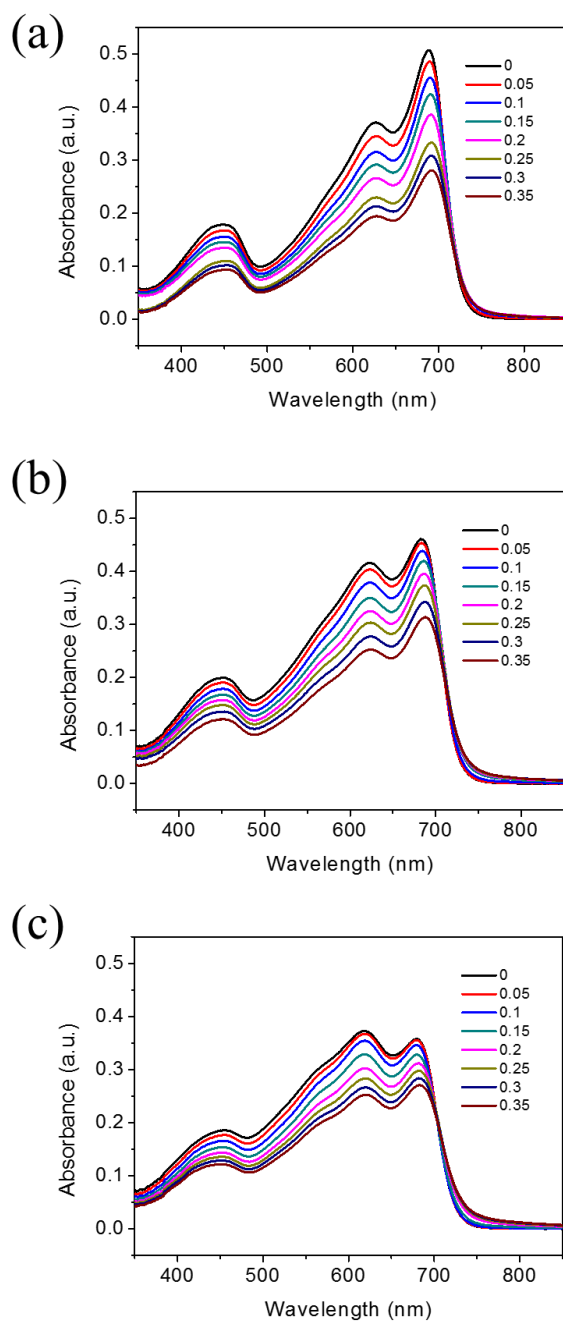
**Figure S2.** Differential scanning calorimetry (DSC) plots of (a) heating and (b) cooling of polymers

**Table S1.** Crystallographic parameter for polymers.

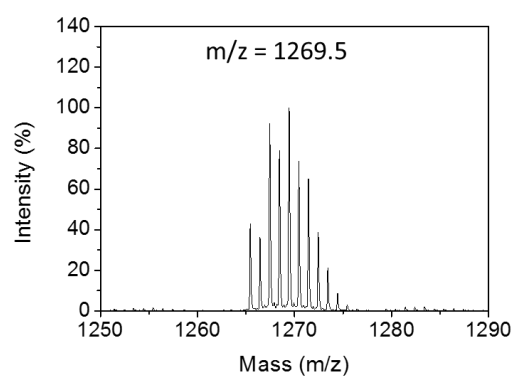
Face-on Properties	PTBT-FTh	PTAZDCB20	PTAZDCB30
$d_{(100)}$ at $q_{xy}$	24.6 Å	24.9 Å	24.5 Å
$d_{(010)}$ at $q_z$	3.60 Å	3.60 Å	3.59 Å
$L_{c(100)}$ at $q_{xy}$	162.4 Å	213.8 Å	214.1 Å
$L_{c(010)}$ at $q_z$	43.0 Å	45.7 Å	44.3 Å



**Figure S3.** Azimuthal intensity plot for (100) diffraction peak.



**Figure S4.** UV–Vis absorption spectra of (a) PFBT-FTh, (b) PTAZDCB20 and (c) PTAZDCB30 dissolved in cosolvents ( $1 \times 10^{-5}$  M) of chlorobenzene and polar acetonitrile with various volume proportions of the acetonitrile in the range 0 to 0.35.



**Figure S5.** MALDI-TOF mass spectrum of monomer compound (8).



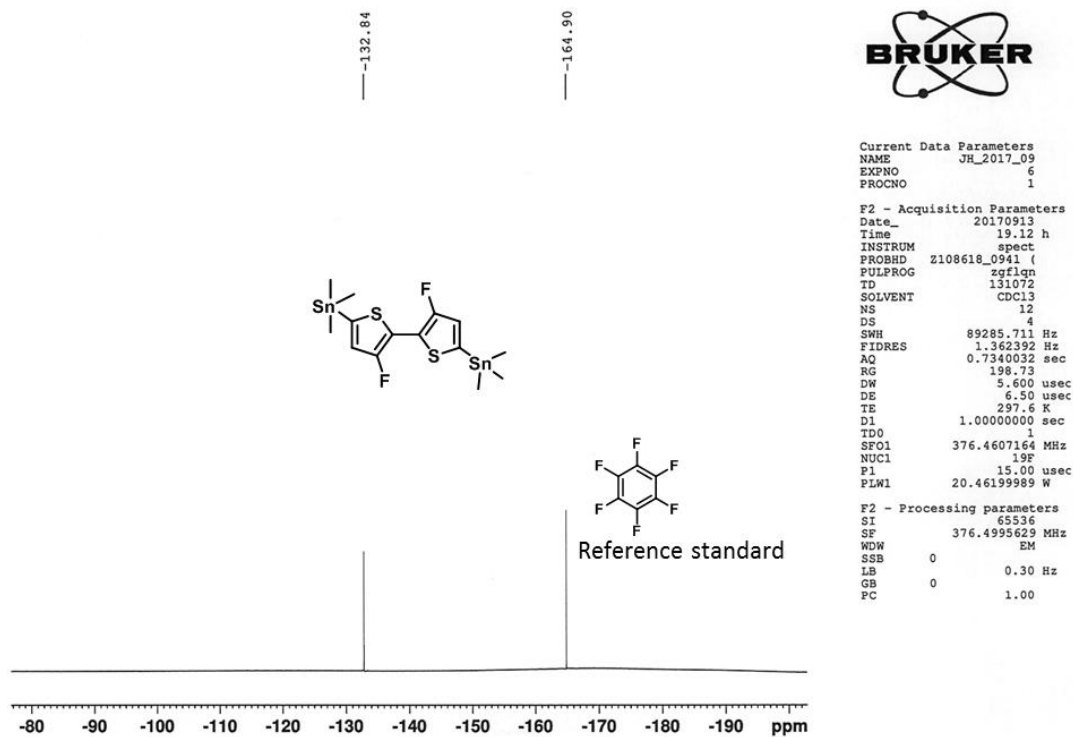
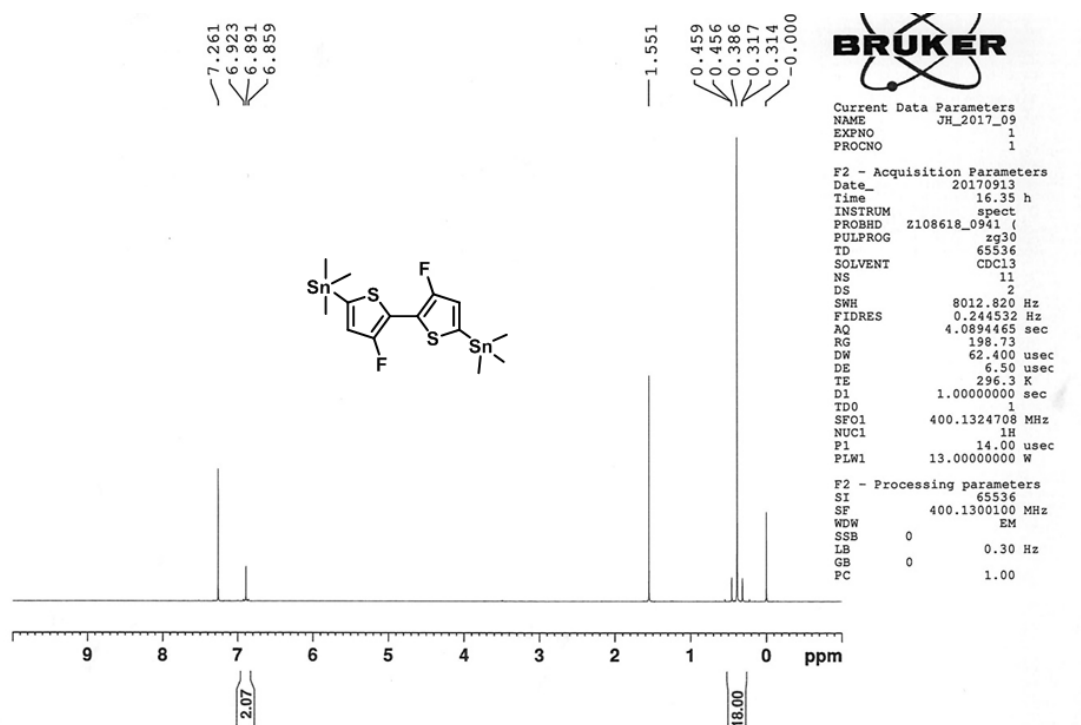
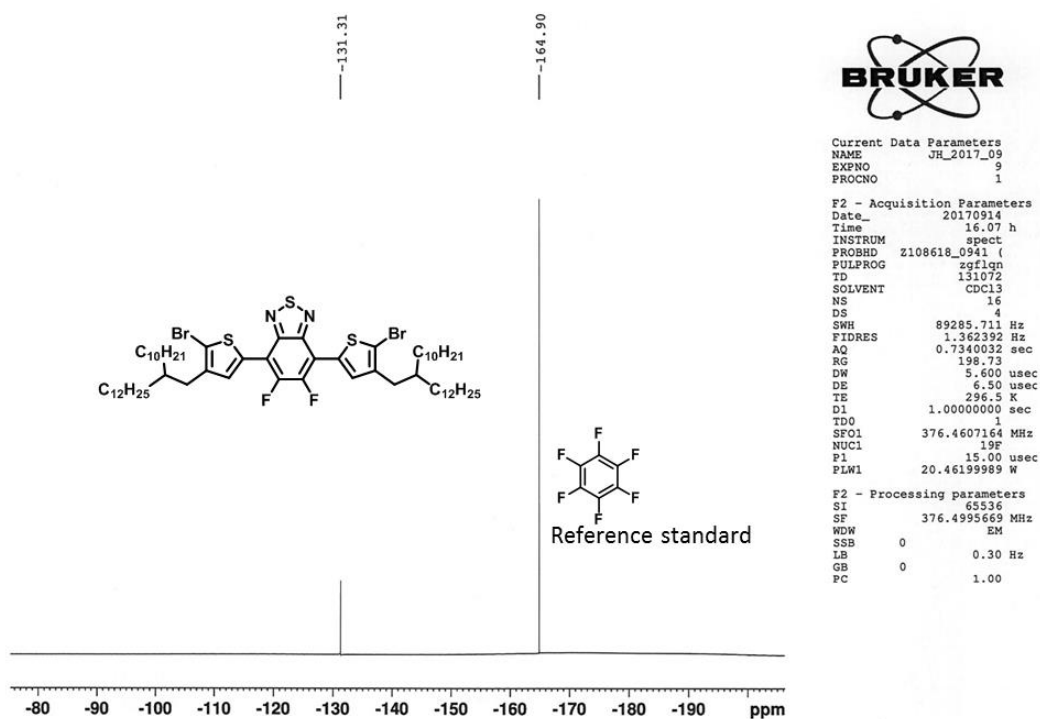


Figure S6. <sup>1</sup>H NMR spectrum of monomer compound (10).

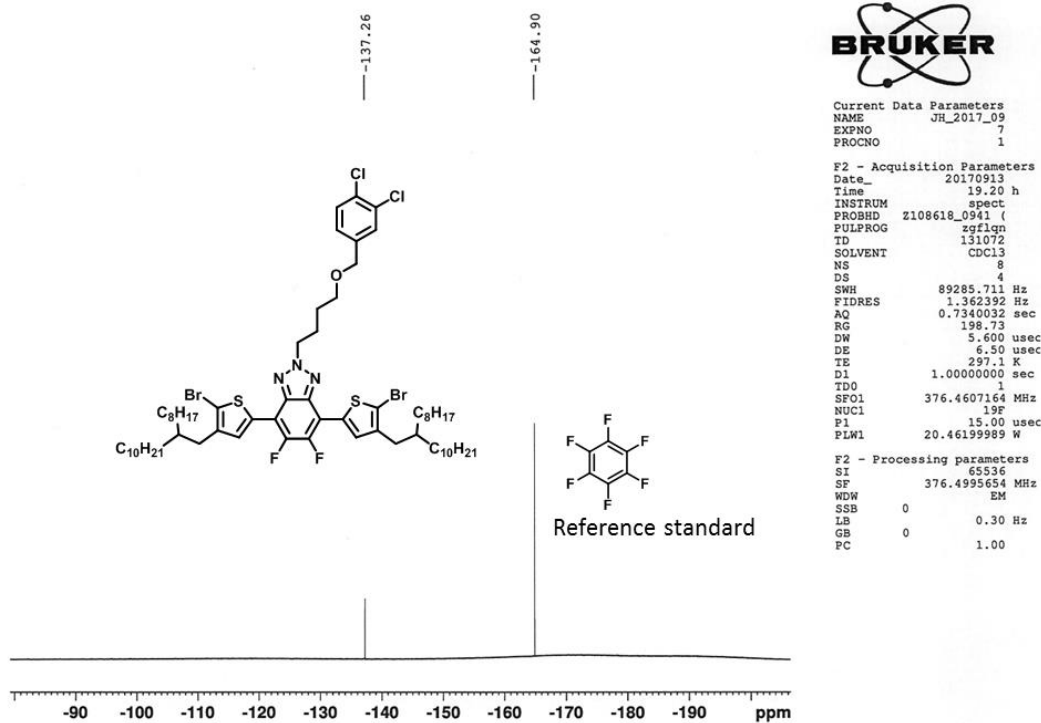
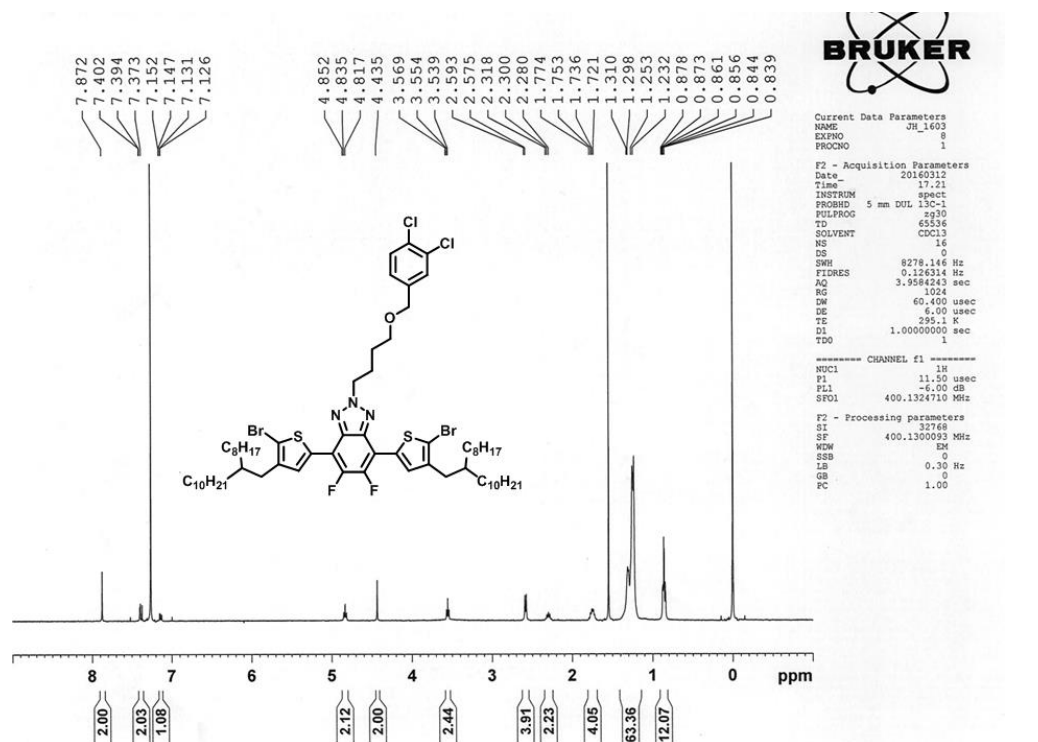
Chemical structure of compound 10 is shown above the spectrum. The structure is a symmetrical molecule with a central benzene ring substituted with two fluorine atoms and two thiophene rings. Each thiophene ring is substituted with a bromine atom and a decyl chain (C<sub>10</sub>H<sub>21</sub>). The decyl chains are labeled C<sub>12</sub>H<sub>25</sub>.

<sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) of compound 10. The x-axis represents chemical shift in ppm, ranging from 0 to 10. The spectrum shows several peaks corresponding to the protons in the molecule. The chemical shift values are listed above the peaks: 7.939, 7.261, 2.605, 2.587, 1.749, 1.548, 1.314, 1.303, 1.236, 0.887, 0.871, 0.865, 0.855, 0.847, and 0.000 ppm. Integration values are shown below the peaks: 2.01, 3.89, 1.98, 80.27, and 12.00.

**Figure S8.**  $^1\text{H}$  NMR spectrum of monomer compound (9).

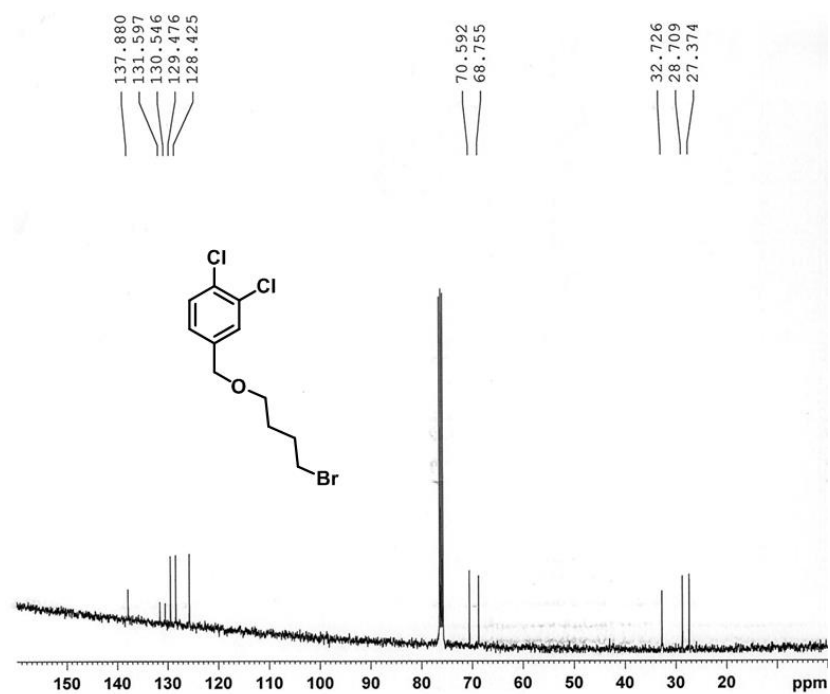


**Figure S9.**  $^{19}\text{F}$  NMR spectrum of monomer compound (9).

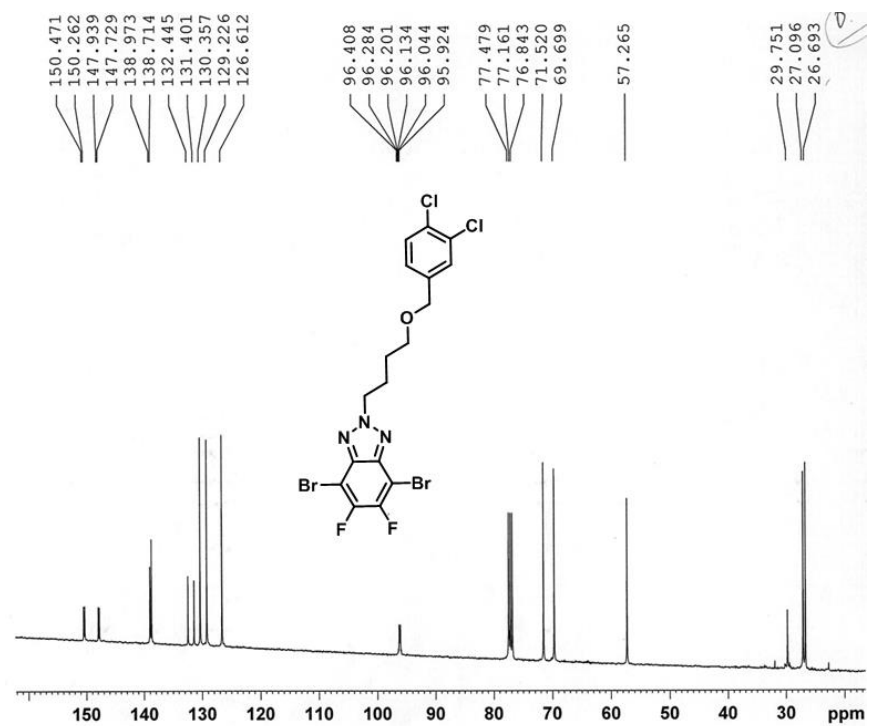


**Figure S10.**  $^1\text{H}$  NMR spectrum of monomer compound (8).

**Figure S11.**  $^{19}\text{F}$  NMR spectrum of monomer compound (8).



**Figure S12.**  $^{13}\text{C}$  NMR spectrum of compound (3).



**Figure S13.**  $^{13}\text{C}$  NMR spectrum of compound (6).

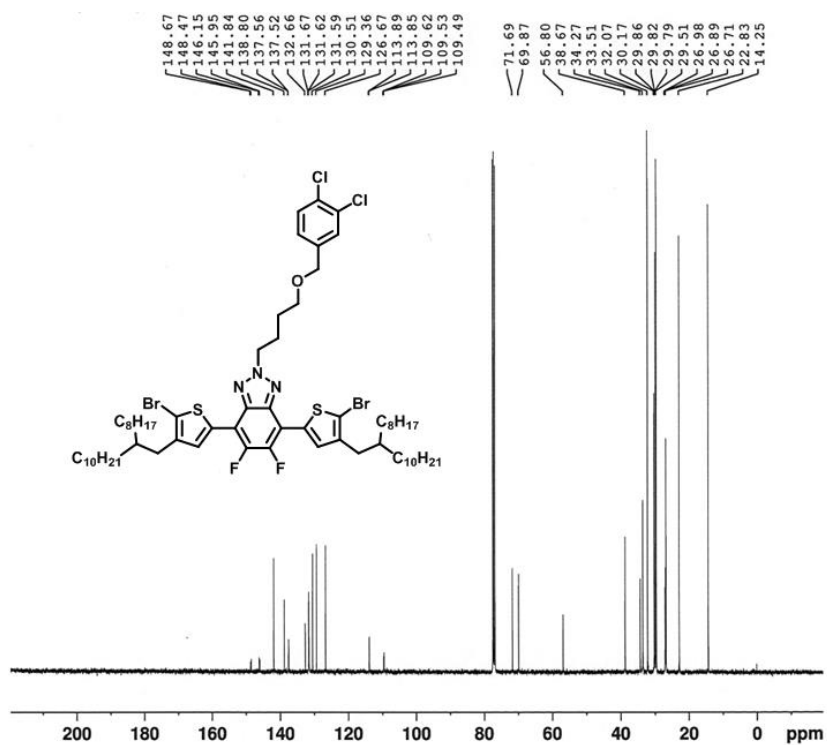
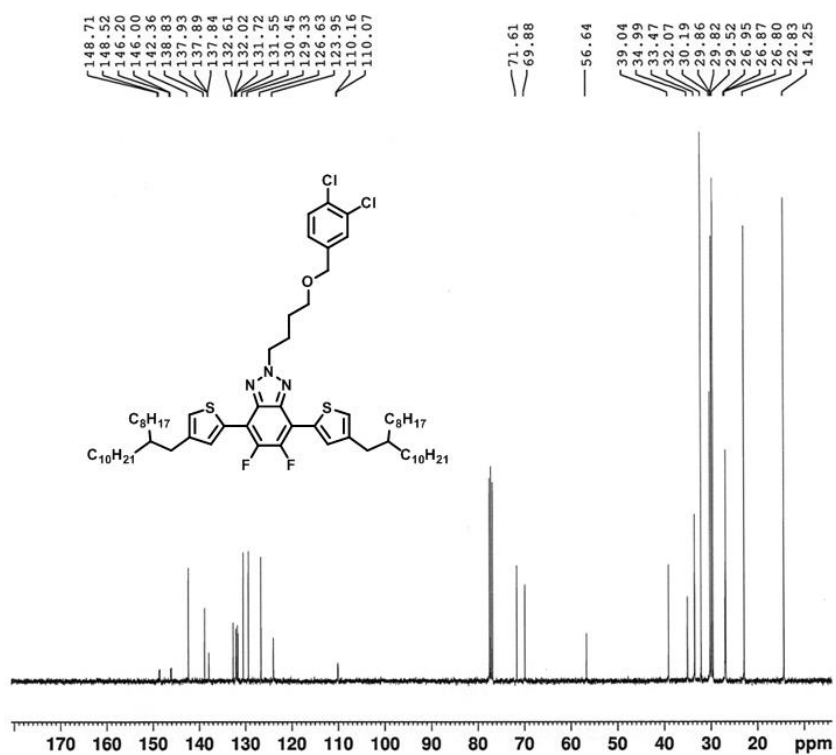
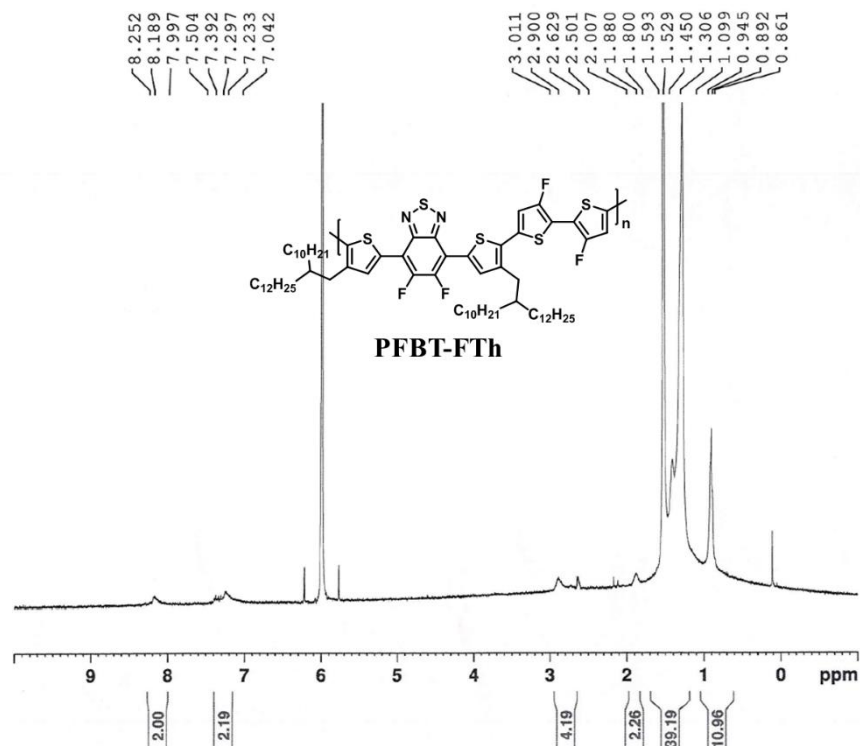


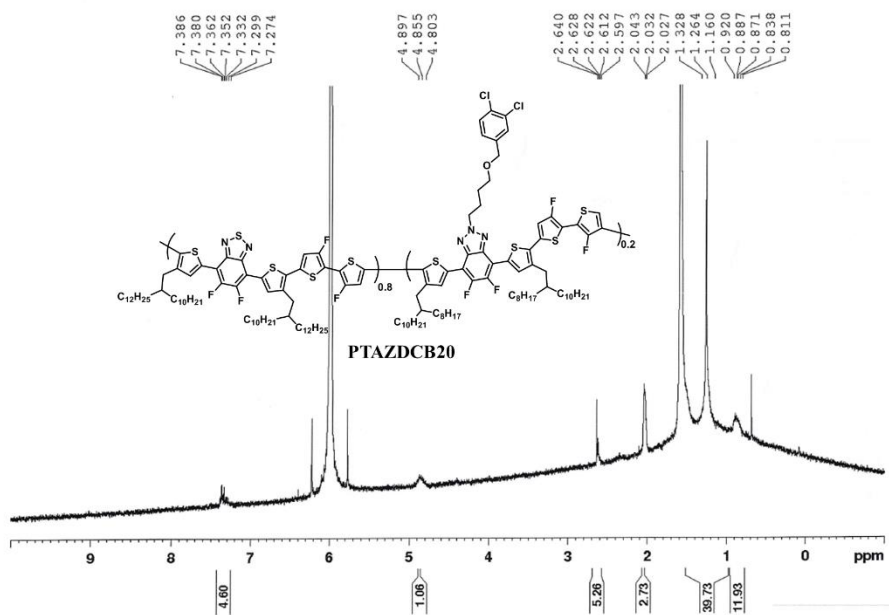
Figure S14. <sup>13</sup>C NMR spectrum of compound (7).

**Figure S15.**  $^{13}\text{C}$  NMR spectrum of compound (8).

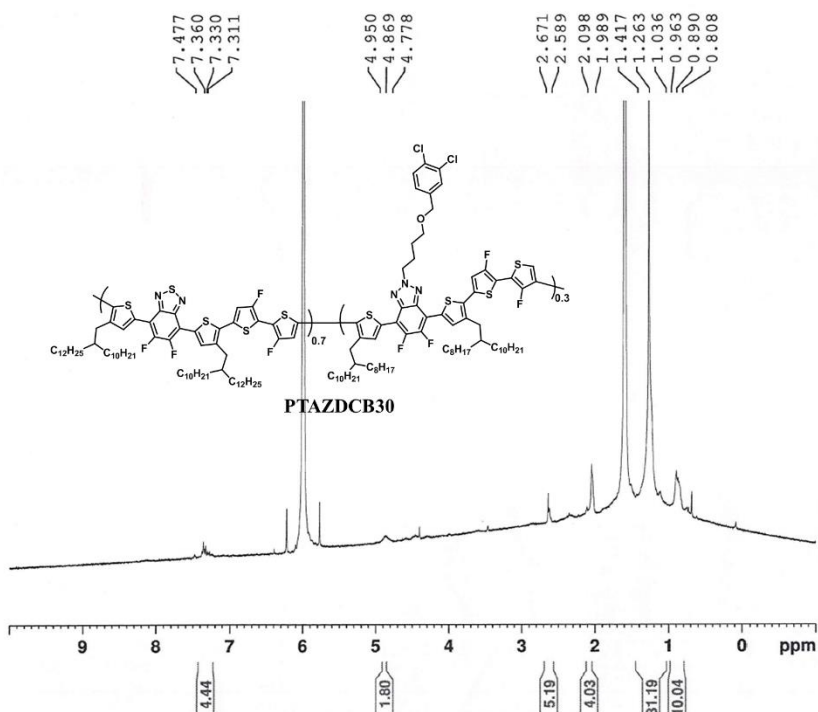


**Figure S16.**  $^1\text{H}$  NMR spectrum of PFBT-FTh polymer.

**Figure S17.**  $^1\text{H}$  NMR spectrum of PTAZDCB20 polymer.







**Figure S14.**  $^1\text{H}$  NMR spectrum of PTAZDCB30 polymer.

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