

# Supporting Information for

## Liquid-crystalline semiconducting copolymers with intramolecular donor-acceptor building blocks for high-stability polymer transistors

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### Experimental Section

#### *Materials and Methods*

Bis(1,5-cyclooctadiene)nickel  $\text{Ni}(\text{cod})_2$ , and Tetrakis(triphenylphosphine)palladium  $\text{Pd}(\text{PPh}_3)_4$ , were purchased from Acros Organics Co. and 3-dodecylthiophene from TCI Co., LTD. Solvents were dried, distilled, and stored under nitrogen atmosphere. The following compounds were prepared by modifying a reported method: 2-bromo-3-dodecylthiophene,<sup>1</sup> 5,5'-bis(trimethylstannyl)-2,2'-bithiophene,<sup>2</sup> and 1-chloro-2-butadecanone.<sup>3</sup>  $^1\text{H}$  NMR spectra (Fig. S1-S3) and FT-IR spectra (Fig. S4) were measured with a Bruker NMR 300 MHz (DPX 300) and FT-IR (EXCALIBUR) spectrometers, respectively. UV-vis measurements were carried out using a UV-Vis-Near IR spectrophotometer (Varian, Cary-5000). (Fig. S5) Thermal behavior of **PQTBtz-C12** was measured using a differential scanning calorimeter (DSC, Perkin-Elmer DSC 7). (Fig. S6-S7)

We used highly doped n-type (100) Si wafers ( $< 0.004 \Omega \text{ cm}$ ) with a 300 nm dry thermal oxide gate dielectric (capacitance  $C_i = 10 \text{ nF cm}^{-2}$ ). These wafers were cleaned in piranha solution (CAUTION: highly corrosive and oxidizing 7:3 mixture of  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{O}_2$ ) for 30 min, rinsed with

dionized water and dried under a nitrogen stream. For OTS treatment, a 0.1 % solution of octadecyltrimethoxysilane, OTS (Gelest Inc., Morrisville, PA) in trichloroethylene (EMD Chemicals Inc., Darmstadt, Germany) was spin-coated on the cleaned wafers, allowed to react overnight at room temperature in the presence of ammonia vapor. Excess silane was removed by ultrasonication in toluene, followed by rinsing with toluene, acetone and isopropyl alcohol, and drying under a stream of nitrogen. OTS-treated wafers typically showed contact angle  $\sim 102^\circ$ . These OTS molecular substrates were imaged with AFM and were found to have an RMS roughness of about 0.2 nm.

In order to confirm the nano-morphology and molecular orientation, PQTBTz-C12 thin films (thickness: 70nm) were spin-coated from 1wt% solution in chlorobenzene on OTS-treated SiO<sub>2</sub> substrates, and annealed at 100 °C, 150 °C and 180 °C for 1 hr under N<sub>2</sub>. Atomic Force Microscope (Digital Instruments Multimode) operating in tapping mode with a silicon cantilever was used to characterize the surface morphologies of the samples. The grazing-incidence X-ray diffraction measurements were performed at the 4C2 and 8C1 beamline (wavelength  $\sim 1.54 \text{ \AA}$ ) at the Pohang Accelerator Laboratory (PAL). The measurements were obtained in a scanning interval of  $2\theta$  between  $3^\circ$  and  $32^\circ$ . UV-vis measurements were carried out using a UV-Vis-Near IR spectrophotometer (Varian, Cary-5000).

The electrical properties (field-effect mobility and bias-stability) of PQTBTz-C12 based OTFT devices were measured by using a top-contact geometry. A 300nm thick silicon oxide gate dielectric (capacitance  $C_i = 10 \text{ nFcm}^{-2}$ ) was thermally grown on a highly doped silicon wafer. PQTBTz-C12 thin films were spin-coated from 1wt% solution in chlorobenzene on OTS-treated SiO<sub>2</sub> substrates, and annealed at 100 °C, 150 °C and 180 °C for 1 hr under N<sub>2</sub>. Finally, source-drain electrodes (Au: thickness  $\sim 70\text{nm}$ ) were evaporated through shadow masks. The standard channel

length ( $L$ ) and width ( $W$ ) are 100  $\mu\text{m}$  and 1000  $\mu\text{m}$ , respectively. A Keithley 4200-SCS semiconductor parameter analyzer was used to conduct all of the measurements of current-voltage characteristics under ambient conditions. We compared the environmental and electrical stability of all devices under the same condition. In other words, when we evaluated the TFT characteristics, the ambient condition represented the 29~32% relative humidity.

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- (2) Pham, C. V.; Macomber, R. S.; Mark, H. B. Jr.; Zimmer, H. *J. Org. Chem.* **1984**, 49, 5250.
- (3) Politis, J. K.; Curtis, M. D.; Gonzales, L.; Martin, D. C. ; He, Y. ; Kanicki, J. *Chem. Mater.* **1998**, 10, 1713.

## Synthesis

The polycondensation using a zerovalent palladium catalyst  $\text{Pd}(\text{PPh}_3)_4$ , the Stille coupling reaction,<sup>4</sup> from the tetramer constituted of thiophene and thiazole rings gives the corresponding copolymer, **PQTBTz-C12**, with unsubstituted bithiophene unit as shown in Scheme 1, and a series of soxhlet extractions with acetone, methylene chloride, and chloroform, in this order, were carried out for purification, according to the reported analogous polycondensation.<sup>6-8</sup> In addition, the molecular weight was controlled using both the soxhlet extraction and the adjustment of the polymerization time. The number average molecular weight ( $M_n$ ) of **PQTBTz-C12**, estimated from GPC ( $\text{CHCl}_3$ , vs polystyrene standards), is in the range from 13,000 to 41,000 g/mol (polydispersity of about 1.4~1.7). The copolymer with 5,5'-bithiazole moieties shows good solubility in common organic solvents such as chloroform, chlorobenzene, THF, toluene, dichlorobenzene, etc.

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- (5) Bao, Z.; Chen, W. K.; Yu, L. *J. Am. Chem. Soc.* **1995**, 117, 12426.

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**Compound (1).** N-bromosuccinimide (NBS) (4.22 g, 23.7 mmol) was added into a chloroform solution of 3-dodecylthiophene (6.0 g, 23.7 mmol) and stirred at room temperature. The reaction mixture was quenched with water, and then extracted with chloroform/water twice. Column chromatography on a SiO<sub>2</sub> using hexane gave the compound **1** [yield = 92 %, <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  0.87 (t, 3H), 1.25 (m, 18H), 1.56 (m, 2H), 2.55 (t, 2H), 6.78 (d, 1H), 7.17 (d, 1H)].

**Compound (2).** A mixture of compound **1** (19.0 g, 57.5 mmol) and copper cyanide (CuCN) (10.3 g, 115.0 mmol) was stirred in 100 mL of *N*-methyl-2-pyrrolidone (NMP) at 140°C for 2 days. After cooling to room temperature, ethyl ether was added to the reaction mixture, which was then filtered. The filtrate was washed with dilute HCl<sub>(aq)</sub>, water, and saturated NaHCO<sub>3</sub>(aq) (in this order). Compound **2** (yield= 71%) was separated by means of column chromatography [SiO<sub>2</sub>, eluent: hexane/ethylacetate = 10/1, <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  0.87 (t, 3H), 1.29 (m, 18H), 1.64 (m, 2H), 2.78 (t, 2H), 6.95 (d, 1H), 7.46 (d, 1H)].

**Compound (3).** Compound **2** (14.0 g, 50.5 mmol) and diethylamine (0.42 mL, 4.0 mmol) were added to dimethylformamide (DMF) in a round flask equipped with a dry-ice condenser at room temperature. After bubbling with H<sub>2</sub>S gas for 40 min (at -70 °C), the reaction mixture was stirred for 2 h (at 60°C). The addition of ethyl acetate and the subsequent extraction with water and a dilute HCl solution gave the organic phase. The solids remained after evaporation and drying were then washed with hexane in order to obtain the yellow compound **3** [yield= 88%, <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  0.88 (t, 3H), 1.25 (m, 18H), 1.67 (m, 2H), 2.91 (t, 2H), 6.95 (d, 1H), 7.36 (d, 1H)].

**Compound (4).** This compound was prepared by modifying a reported procedure for bithiazole.<sup>9</sup>

Compound **3** (13.5 g, 43.3 mmol) and 1-chloro-2-butadecanone (10.7 g, 43.3 mmol) were dissolved in ethanol. After reaction at 85°C (for 12 h), the cooled reaction mixture was concentrated under vacuum. Then, a dilute HCl solution was added and the washing with chloroform/water was carried out. The obtained organic phase was finally dried with MgSO<sub>4</sub> and the product (compound **4**) was obtained by means of column chromatography; a high yield of about 95% was reached [<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 0.88 (t, 6H), 1.25 (m, 36H), 1.66 (m, 4H), 2.78 (t, 2H), 2.89 (t, 2H), 6.84 (s, 1H), 6.93 (d, 1H), 7.24 (d, 1H)].

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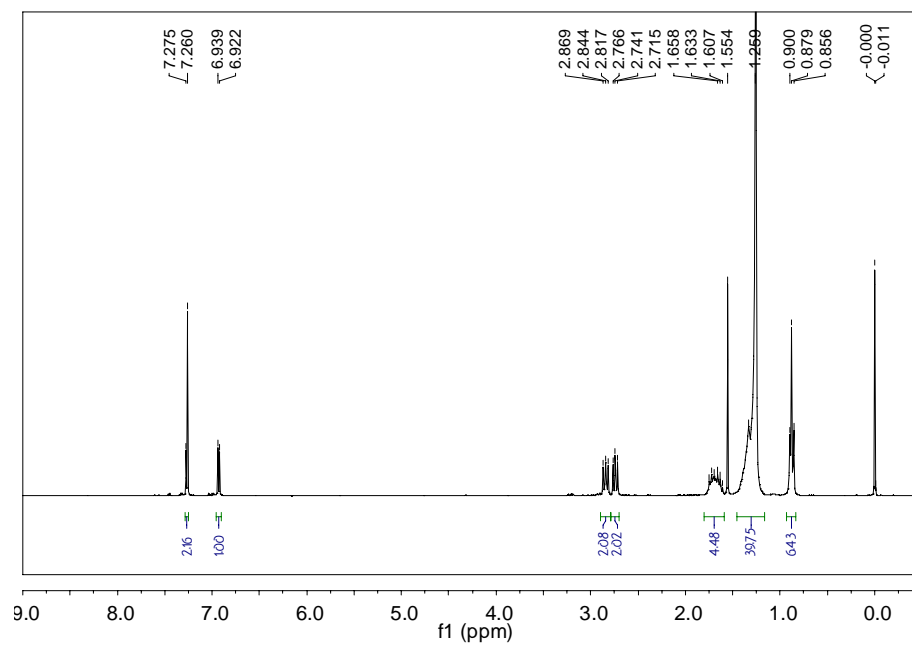
**Compound (5).** NBS was added—under stirring and at room temperature—to a chloroform solution of the obtained thiophene–thiazole dimer (compound **4**). The reaction mixture was quenched with water and then extracted twice with chloroform/water. Column chromatography on SiO<sub>2</sub> using hexane gave compound **5** [yield= 91%, <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 0.88 (t, 6H), 1.25 (m, 20H), 1.63 (m, 4H), 2.74 (t, 2H), 2.84 (t, 2H), 6.92 (d, 1H), 7.27 (d, 1H)]. (Fig. S1)

**Compound (6).** Compound **5** (5.0 g, 8.58 mmol) was added upon stirring to a solution containing 0.75 eq of the zerovalent nickel complex Ni(cod)<sub>2</sub> (1.77 g, 6.43 mmol), cyclooctadiene (cod, 0.7 mL, 6.43 mmol), and bipyridine (bpy, 1.01 g, 6.43 mmol). The reaction mixture was stirred at 80°C for 1~2 days and then quenched with a dilute aqueous HCl. Extraction with chloroform/water (2–3 times) and column chromatography (SiO<sub>2</sub>, eluent: CHCl<sub>3</sub>/hexane = 8/2) gave the product (compound **6**) in the form of an organic solid [yield= 68%, <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 0.86 (t, 6H), 1.32 (m, 20H), 1.69 (m, 4H), 2.68 (t, 2H), 2.92 (t, 2H), 6.96 (d, 1H), 7.28 (d, 1H)].

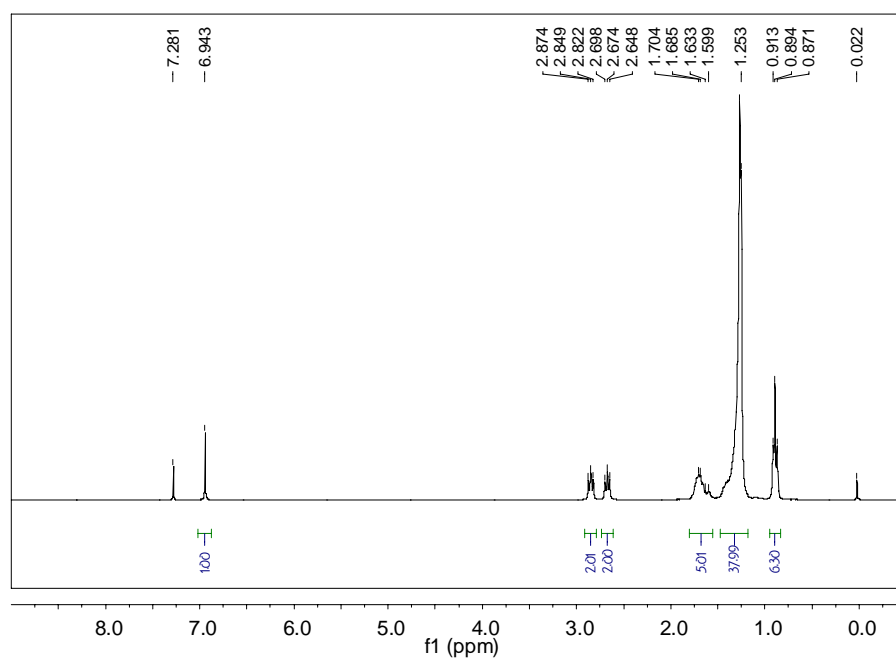
**Compound (7).** Brominated compound **7**—a yellow solid —was obtained by applying a method similar to that described above for the preparation of compound **5** [yield = 75%, <sup>1</sup>H NMR (300MHz,

CDCl<sub>3</sub>)  $\delta$  0.89(t, 12H), 1.25(m, 72H), 1.68(m, 8H), 2.67(t, 4H), 2.85(t, 4H), 6.94(s, 2H). (Fig. S2)  
FT-IR (KBr, cm<sup>-1</sup>) 2920, 2846, 1541, 1446, 1394, 1386, 1253, 1232, 1024, 964, 883, 844, 825, 721, 594. (Fig. S4)]

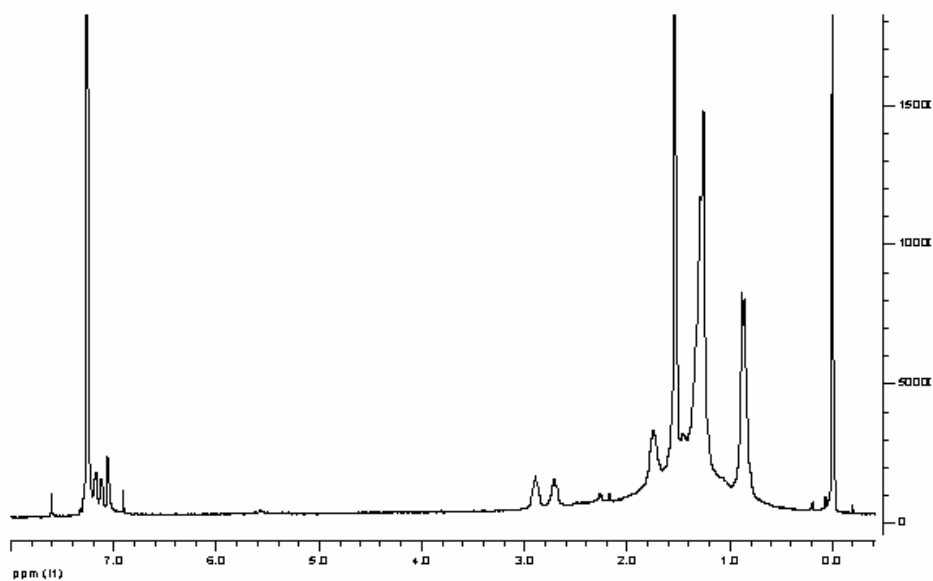
**PQBTz-C12.** Compound **7** (0.5 g, 0.43 mmol) and 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (0.21 g, 0.43 mmol) were dissolved in anhydrous DMF with stirring under nitrogen atmosphere. After adding palladium complex (39 mg, 10 mol% vs. compound **7**), Pd(PPh<sub>3</sub>)<sub>4</sub>, the reaction mixture was stirred at 80°C for about 3~12 h under nitrogen condition. After the reaction was completed, the reaction solution was cooled to room temperature and then filtered to afford dark reddish solid. The obtained polymer solid was dissolved in CHCl<sub>3</sub> and was washed with dilute aqueous HCl solution, NH<sub>4</sub>OH<sub>(aq)</sub>, and distilled water in this order. Organic CHCl<sub>3</sub> part was concentrated and reprecipitated into excess amount of methanol. Subsequently, soxhlet extractions was carried out with acetone, methylene chloride, and chloroform and drying for 1~2 days gave 0.33 g of dark red polymer solid, **PQBTz-C12** [yield = 65 %;  $M_n$  = 22,000, <sup>1</sup>H NMR (300MHz, CDCl<sub>3</sub>)  $\delta$  0.88 (12H, CH<sub>3</sub>), 1.28 (72H, (CH<sub>2</sub>)<sub>9</sub>), 1.74 (4H, CH<sub>2</sub>), 2.70 (4H, Thiophene-CH<sub>2</sub>), 2.87 (4H, Thiazole-CH<sub>2</sub>), 7.06 (2H, Dodecyl-Thiophene-H), 7.12 (2H, Bithiophene-H), 7.18 (2H, Bithiophene-H). FT IR (KBr, cm<sup>-1</sup>) 3066, 2920, 2850, 1556, 1460, 1406, 1377, 1246, 1217, 1029, 817, 779, 721].



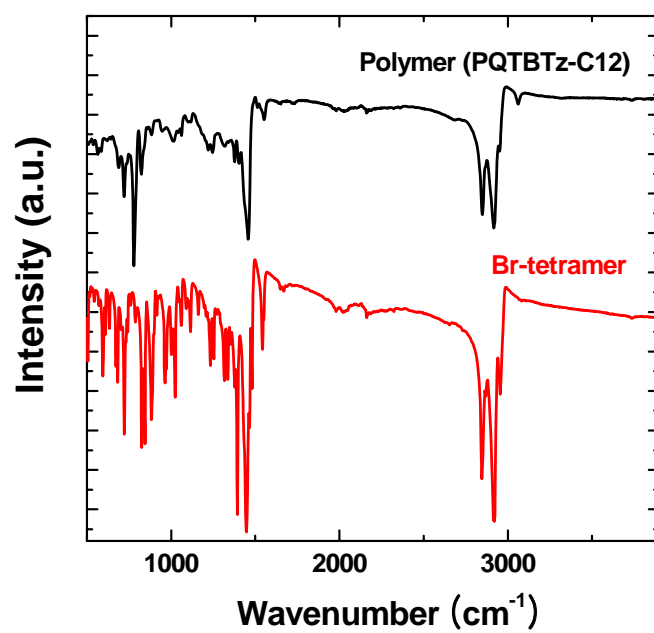
**Figure S1.**  $^1\text{H}$  NMR spectrum of *compound (5)* in  $\text{CDCl}_3$



**Figure S2.**  $^1\text{H}$  NMR spectrum of *compound (7)* in  $\text{CDCl}_3$

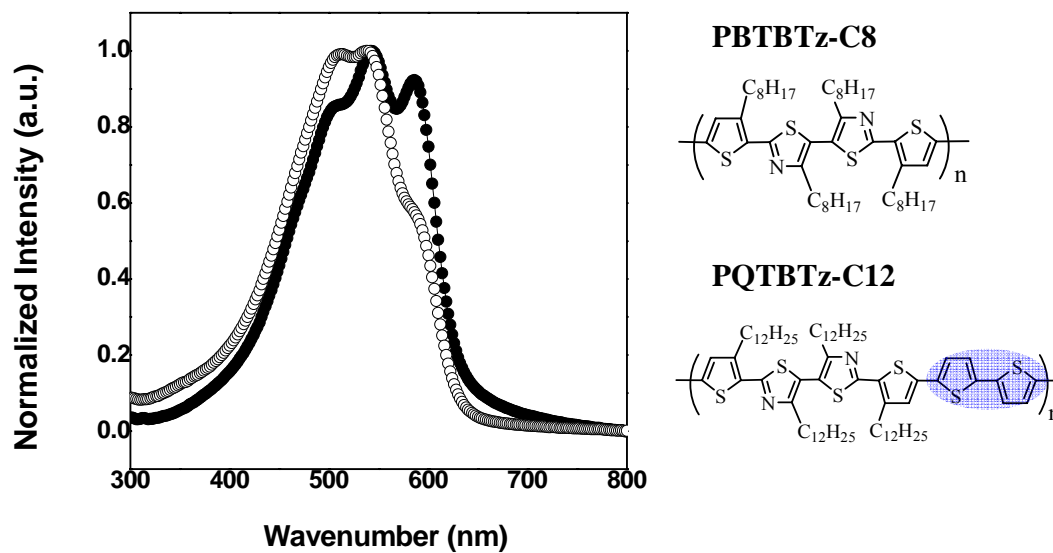


**Figure S3.**  $^1\text{H}$  NMR spectrum of *PQTBTz-C12* in  $\text{CDCl}_3$

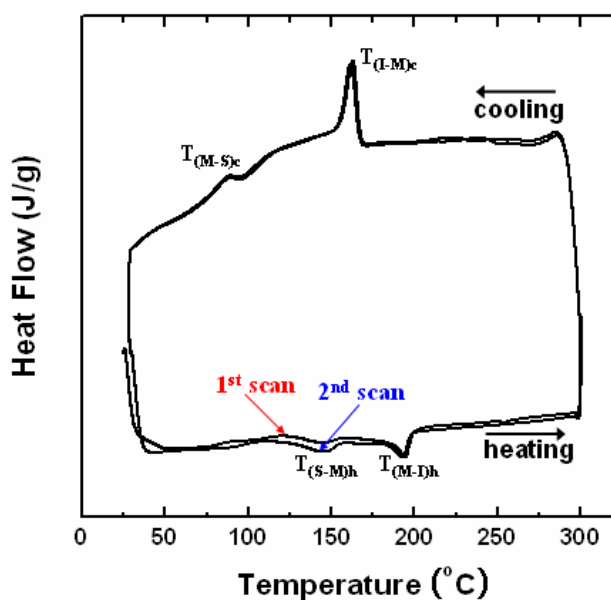


**Figure S4.** FT-IR spectra of *PQTBTz-C12* and its corresponding tetramer (*compound (7)*)

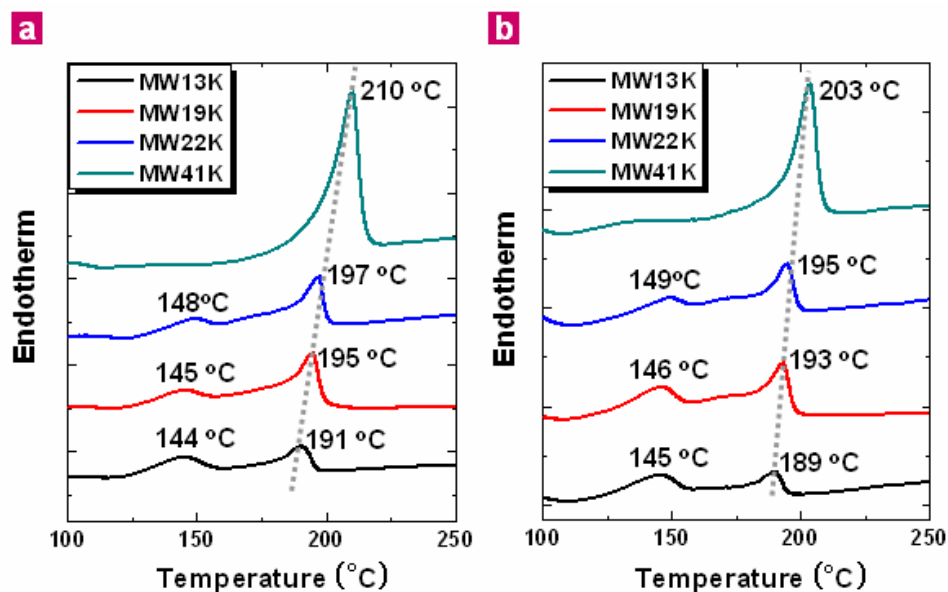




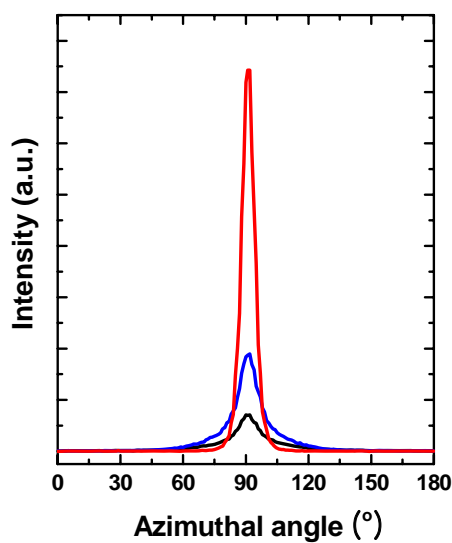
**Figure S5.** UV-vis absorption spectra of **PBTBTz-C8** (open circles) and **PQTBTz-C12** (closed circles) in the solid state.



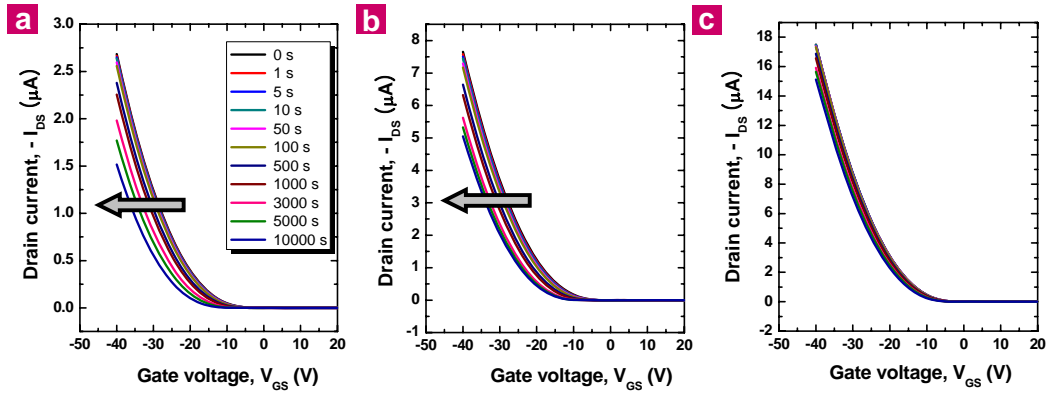
**Figure S6.** DSC curve of **PQTBTz-C12** during the first and second heating/cooling scan at  $10^{\circ}C/min$ .



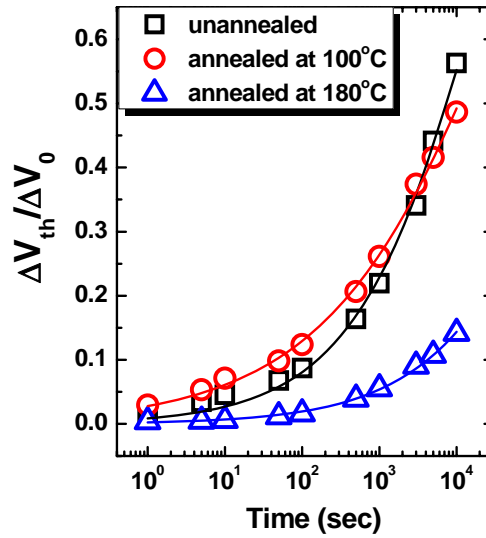
**Figure S7.** Molecular weight dependent thermal behavior of **PQTBTz-C12**, (a) first heating scan and (b) second heating scan.



**Figure S8.** Azimuthal angle scan at  $q(100)$  position of **PQTBTz-C12** thin film according to annealing temperature. (black line: not-annealed, blue line: annealed at 100 °C, and red line: annealed at 180 °C)



**Figure S9.** Linear transfer curves of **PQTBTz-C12**-based OFETs as a function of stress time for various annealing temperatures. **(a)** as-spun (solid-state), **(b)** annealed at 100°C (solid-state), **(c)** annealed at 180°C (mesophase). The gate bias during stress was fixed at -20 V, and the temperature under operation was RT. (Drain bias ~ 0 V) The transfer curves were determined at a drain voltage of -40 V (saturation region) by sweeping the gate bias from 40 V to -40 V.



**Figure S10.** The relative threshold voltages ( $V_{th}^R = \Delta V_{th} / \Delta V_0$ ) obtained from **(a)**, **(b)**, and **(c)** in Figure S9 are presented as functions of stress time on a logarithmic scale. The solid curves are fits with a stretched-exponential time dependence:  $\Delta V_{th}(t) = \Delta V_0(1 - \exp[-(t/\tau)^\beta])$ .  $V_0 = V_g - V_{th,0}$ , where  $V_{th,0}$  is the threshold voltage at the start of the experiment.