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Supporting Information for

A Systematic Study on Molecular Planarity and D-A conformation in Thiazolothiazole- and Thienylenevinylene-based Copolymers for Organic Field-Effect Transistors

*Dae-Hee Lim, Soo-Young Jang, Minji Kang, Sehyun Lee, Yeong-A Kim, Youn-Jung Heo, Min-Hye Lee and Dong-Yu Kim**

Synthetic procedures

Synthesis of 3-dodecylthiophene (1) Distilled ether (80 ml) was poured into dried magnesium (4.47 g, 0.18 mol) in two-neck flask. Under 0 °C, 1-bromododecane (45.87 g, 0.18 mol) diluted with distilled ether was injected into the flask and refluxed at 40 °C for 3 hours. The color became dark gray while the Grignard reagent was synthesized. Another two-neck flask was prepared and mixture of 3-bromothiophene (20 g, 0.12 mol) and $Ni(dppp)Cl_2$ (0.66 g, 2 mol%) was stirred 10 minutes. Then synthesized Grignard reagent was injected dropwise into the second two-neck flask under 0 °C. After reflux at 40 °C overnight, the reaction mixture was quenched by adding of 1M HCl under 0 °C .The reaction mixture was extracted with ether and organic layer was dried over $MgSO_4$. After removal of the solvent under reduced pressure, the crude product was purified by column chromatography (silica gel, hexane) to afford 22.48g (yield: 72.7 %) as colorless oil. ^{1}H NMR ($CDCl_3$, 400MHz) : δ 7.21 (dd, ^3J = 5 and ^4J = 3 Hz, 1H), 6.89-6.92 (m, 2H), 2.61 (t, J = 7.7 Hz, 2H), 1.37-1.63 (m, 2H), 1.26-1.30 (m, 18H), 0.88 (t, J = 6.8 Hz, 3H)

Synthesis of 2-bromo-3-dodecylthiophene (2) 3-dodecythiophene (6.21 g, 0.025 mol) was diluted with 100 ml chloroform/acetic acid cosolvent (5:1 v/v). Stirring under 0 °C and dark condition, N-bromosuccinimide (4.38 g, 0.025 mol) dissolved in 15 ml dimethylformamide was dropped into the flask slowly. After 2 hours, the reaction mixture was poured into water and extracted with methylene chloride, and its organic layer was dried over $MgSO_4$. After removal of the solvent under reduced pressure, the crude product was purified by column chromatography (silica gel, hexane) to afford 5.55g (yield: 68 %) as colorless oil. ^{1}H NMR ($CDCl_3$, 400MHz) : δ 7.19 (d, J = 5.3 Hz, 2H), 6.79 (d, J = 5.3 Hz, 2H), 2.58 (t, J = 7.5 Hz, 2H), 1.64-1.57 (m, 2H), 1.36-1.20 (m, 18H), 0.88 (t, J = 5.0 Hz, 3H)

Synthesis of 2-formyl-3-dodecylthiophene (3) Dried Magnesium (1.08 g, 0.044 mol) was mixed with distilled THF 50 ml and 2-bromo-3-dodecylthiophene (7.4 g, 0.022 mol) was added dropwise and stirred at 70 °C for 3 hours. The color became dark gray while the Grignard reagent was synthesized. After the reaction mixture was cooled down to room temperature, N,N-dimethylformamide (3.24g, 0.044 mol) was dropped into the flask and stirred at 70 °C overnight. Under 0 °C, the reaction mixture was quenched with HCl (1M solution) and extracted with ether. Organic layer was dried over $MgSO_4$, and solvent was removed. The crude product was purified by column chromatography (silica gel, hexane:ethylacetate = 9.5:0.5) to afford 3.9g (yield: 63 %) as colorless oil. ^{1}H NMR ($CDCl_3$, 400MHz) : δ 9.98 (s, 1H), 7.62 (d, 1H), 6.98 (d, 1H), 2.84 (t, 2H), 1.68 (m, 20H), 0.90 (t, 3H)

Synthesis of 2,5-Bis(3-dodecylthiophene-2-yl)thiazolo[5,4-d]thiazole (4) A mixture of 2-formyl-3-dodecylthiophene (5.48 g, 0.02 mol) and dithiooxamide (1.12 g, 0.009 mol) in a two neck flask was stirred at 200 °C for overnight. The color turned from dark red to dark brown while the reflux. Then, reaction mixture was cooled to room temperature and extracted with chloroform and water. Organic layer was dried over $MgSO_4$, and solvent was removed. The brown oil was purified by column chromatography (silica gel, hexane:chloroform = 5:1) and resulting dark yellow solid was recrystallized from isopropyl alcohol to give 1.25g of yellow powder (yield: 21 %). ^{1}H NMR ($CDCl_3$, 400MHz) : δ 7.38 (d, J = 5.1 Hz, 2H), 7.02 (d, J = 5.1 Hz, 2H), 3.00 (t, J = 7.8 Hz, 4H), 1.74 (q, J = 7.8 Hz, 4H), 1.29 (bs, 36H), 0.90 (t, J = 6.7 Hz, 6H)

Synthesis of 2,5-Bis(3-dodecyl-5-(trimethylstannyl)thiophene-2-yl)thiazolo[5,4-d]thiazole (5). 2,5-Bis(3-dodecylthiophene-2-yl)thiazolo[5,4-d]thiazole (0.6 g, 0.94 mmol) was diluted with 50 ml THF. 1.6N solution of n-butyllithium in hexane (2.34 ml, 3.75 mmol) was added dropwise at -78 °C. The solution was stirred at 0 °C for 1 hour, then the color became dark red-brown to nearly black. The solution cooled down again at -78 °C and 1.0 M solution of trimethyltin chloride in THF (2.8 ml, 2.8 mmol) was added in one portion. The solution was warmed to room temperature and stirred overnight. The reaction mixture was extracted with ethyl acetate and water. The organic layer was dried over $MgSO_4$. After removing the solvent, the crude product was recrystallized from isopropyl alcohol to give 0.65 g of yellow powder (yield: 74.9 %). m.p.= 70 °C, ^{1}H NMR ($CDCl_3$, 400 MHz) : δ 7.03 (s, 2H), 2.96 (t, J = 7.9 Hz, 4H), 1.55 (q, J = 7.6 Hz, 4H), 1.26 (br, 36H), 0.87 (t, J = 6.7 Hz, 6H), 0.40 (s, 18H)

Synthesis of E-1,2-(3,3'-didodecyl-2,2'-dithienyl)ethylene (6) TiCl4 (2.4 ml, 0.022 mol) was slowly dropped into 100 ml of distilled THF. After stirring 10 minutes under 0 °C, Zn (divided into the three times, 2.86 g, 0.044 mol) was added and mixture was stirred at 70 °C 1hour. The color changed from green into dark blue. Then prepared 2-formyl-3-dodecylthiophene (6.13 g, 0.022mol, should be dried) and pyridine (1.73 g, 0.022 mol) was added under 0 °C. After refluxing 2 hours, the reaction mixture was quenched with ice and extracted with methylene chloride. The organic layer was dried over $MgSO_4$. After removing the solvent, the crude product was purified by column chromatography (silica gel, hexane) and recrystallization from isopropyl alcohol into several times to give 4 g of pale yellow powder (yield: 69 %). ^{1}H NMR ($CDCl_3$, 400MHz) : δ 7.08 (d, J = 5.3 Hz, 2H), 7.00 (s, 2H), 6.85 (d, J = 5.1 Hz, 2H), 2.66 (t, J = 7.5 Hz, 4H), 1.30-1.6 (m, 40H), 0.88 (t, 6H)

Synthesis of 1,2-bis(5-bromo-3-dodecylthiophen-2-yl)ethene (7). E-1,2-(3,3'-didodecyl-2,2'-dithienyl)ethylene (2 g, 3.8 mmol) was diluted with 50 ml chloroform/acetic acid cosolvent (5:1 *v/v*). Stirring under 0 °C and dark condition, N-bromosuccinimide (1.35 g, 7.6 mmol) dissolved in 5 ml dimethylformamide was dropped into the flask slowly. After 2 hours, the reaction mixture was extracted with methylene chloride and water. The organic layer was dried over $MgSO_4$. After removal of the solvent under reduced pressure, the crude product was purified by column chromatography (silica gel, hexane) and recrystallization from isopropyl alcohol into several times to give 2.3 g of pale yellow powder (yield: 87.7 %). m.p.= 65 °C, ^{1}H NMR ($CDCl_3$, 400 MHz) : δ 6.79 (s, 2H), 6.75 (s, 2H), 2.56 (t, J = 7.8 Hz, 4H), 1.25 (m, 40H), 0.87 (t, J = 6.7 Hz, 6H)

Synthesis of 3,3'-dibromo-2,2'-bithiophene (8) 2M solution of LDA in THF/heptane/ethylbenzene (56 ml, 0.1 mol) was added dropwise to a solution of 3-bromothiophene (16.3 g, 0.1 mol) in 100 ml distilled THF at 0 °C. After the solution was stirred for 1 hour, $CuCl_2$ (1.05 equiv, 14.11 g, 0.105mol) was added in one portion. The mixture became very dark and then orange-brown precipitation. The solution was warmed to room temperature and treated with aqueous HCl (1M solution). The reaction mixture was extracted with diethyl ether and dried over $MgSO_4$. After removing the solvent, brown solid was purified by short column chromatography (silica gel, hexane/methylene chloride) and recrystallization from hexane into several times to give 4.7 g of white solid (yield: 29 %). ^{1}H NMR ($CDCl_3$, 400MHz) : δ 7.42 (d, J = 5.4 Hz ,2H), 7.09 (d, J = 5.4 Hz, 2H)

Synthesis of 3,3'-dodecyl-2,2'-bithiophene (9) Distilled ether (25 ml) was poured into dried magnesium (1.1 g, 0.043 mol) in two-neck flask. Under 0 °C, 1-bromododecane (10.84 g, 0.043 mol) diluted with distilled ether (10 ml) was injected into the flask and refluxed at 40 °C for 3 hours. The color became dark gray while the Grignard reagent was synthesized. Another two-neck flask was prepared and mixture of 3,3'-dibromo-2,2'-bithiophene (4.7 g, 0.015 mol) and Ni(dppp)Cl2 (0.078 g, 2 mol%) in distilled ether (50 ml) was stirred 10 minutes. Then synthesized Grignard reagent was injected dropwise into the second two-neck flask under 0 °C. The mixture was stirred at 70 °C overnight, then cooled down room temperature. The reaction mixture was extracted with ether and saturated aqueous NH_4Cl solution. The organic layer was dried over $MgSO_4$. After removal of the solvent under reduced pressure, the crude product was purified by column chromatography (silica gel, hexane) to afford 3.83 g (yield: 52.7 %) as light yellow oil. ^{1}H NMR ($CDCl_3$, 400MHz) : δ 7.28-7.26 (d, J = 8.00 Hz, 2H), 6.96-6.94 (d, J = 8.00 Hz, 2H), 2.50-2.47 (t, J = 12.00 Hz, 4H), 1.54-1.22 (m, 16H), 0.84-0.82 (t, J = 8.00 Hz, 6H)

Synthesis of 5,5'-dibromo-3,3'-dodecyl-2,2'-bithiophene (10). 3,3'-dodecyl-2,2'-bithiophene (3.8 g, 7.6 mmol) was diluted with 100 ml chloroform/15 ml acetic acid cosolvent. Stirring under 0 °C and dark condition, N-bromosuccinimide (2.72 g, 15.3 mmol) dissolved in 10 ml dimethylformamide was dropped into the flask slowly. After 2 hours, the reaction mixture was extracted with methylene chloride and water. The organic layer was dried over $MgSO_4$. After removal of the solvent under reduced pressure, the crude product was purified by column chromatography (silica gel, hexane) and recrystallization from isopropyl alcohol into several times to give 4.7 g of yellowish powder (yield: 94.8 %). m.p.= 60 °C, ^{1}H NMR ($CDCl_3$, 400MHz) : δ 6.90 (s, 2H), 2.57-2.48 (t, J = 8.00 Hz, 4H), 1.31-1.22 (m, 16H), 0.90-0.85 (t, J = 6.7 Hz, 6H)

Synthesis of 2,5-dibromothieno[3,2-b]thiophene (11) Thieno[3,2-b]thiophene (3.4 g, 0.036 mol) was diluted with 300 ml chloroform/acetic acid cosolvent (5:1 v/v). Stirring under 0 °C and dark condition, N-bromosuccinimide (12.7 g, 0.072 mol) dissolved in 30 ml dimethylformamide was dropped into the flask slowly. After 2 hours, the reaction mixture was extracted with chloroform and water. The organic layer was dried over $MgSO_4$. After removal of the solvent under reduced pressure, the crude product was purified by column

chromatography (silica gel, hexane) to give 9.6 g of white solid (yield: 90 %). ^{1}H NMR ($CDCl_3$, 400MHz) : δ 6.31 (s, 2H)

Synthesis of 2,5-Bis(3-dodecylthiophene-2-yl)thieno[3,2-b]thiophene (12) $PdCl_2(PPh_3)_2$ (0.282 g, 3 mol%) was dissolved in 75 ml dimethylformamide and 2,5-dibromothieno[3,2-b]thiophene (2.42 g, 8 mmol) was added. The 2-tributylstannyl-3-dodecylthiophene (13.22 g, 0 024 mol) was added into the solution and stirring 110 °C 2 days. The color turned deep green-blue while the reflux. The solution was then allowed to cool, quenched with water, and extracted methylene chloride. The organic layer was dried over $MgSO_4$. After removal of the solvent under reduced pressure, the crude product was purified by column chromatography (silica gel, hexane:methylene chloride = 5:1) and recrystallization from isopropyl alcohol into several times to give 2.1 g of yellow powder (yield: 40 %). ^{1}H NMR ($CDCl_3$, 400MHz) : δ 7.20 (s, 2H), 7.04 (d, J = 7.6 Hz, 2H), 6.83 (d, J = 7.6 Hz, 2H), 2.59 (t, J = 7.60 Hz, 2H), 1.65-1.60 (m, 2H), 1.42-1.26 (m, 18H), 0.88 (t, J = 7.2 Hz, 3H)

Synthesis of 2,5-Bis(3-dodecyl-5-(trimethlystannyl)thiophene-2-yl)thieno[3,2-b]thiophene (13). 2,5-Bis(3-dodecylthiophene-2-yl)thieno[3,2-b]thiophene (0.6 g, 0.94 mmol) was diluted with 30 ml THF. 1.6N solution of n-butyllithium in hexane (2.34 ml, 3.75 mmol) was added dropwise at -78 °C. The solution was stirred at 0 °C for 1hour, then the color became dark brown nearly black. The solution cooled down again at -78 °C and 1.0M solution of trimethyltin chloride in THF (2.8 ml, 2.8 mmol) was added in one portion. The solution was warmed to room temperature and stirred overnight. The reaction mixture was extracted with ethyl acetate and water. The organic layer was dried over $MgSO_4$. After removing the solvent, brown oil (0.65 g) was obtained (yield: 74.9 %). ^{1}H NMR (CDCl3, 400MHz): δ 7.21-7.20 (s, 1H), 7.02-7.00 (s, 1H), 3.77-3.72 (t, 4H), 1.26-1.24 (m, 36H), 0.86 (t, 6H), 0.46-0.29 (m, 18H)

Synthesis of poly[(4,4'-didodecyl-5'-(2-(3-dodecyl-5-methylthiophen-2-yl)vinyl)-[2,2'-bithiophen]-5-yl)-5-(3-dodecyl-5-methylthiophen-2-yl)thiazolo[5,4-d]thiazole] (P1) In 20 ml of anhydrous chlorobenzene, 2,5-Bis(3-dodecyl-5-(trimethylstannyl)thiophene-2-yl)thiazolo[5,4-d]thiazole (0.65 g, 0.67 mmol), 5,5'-di-br-2,2'-dithienylethylene (0.46 g, 0.67 mmol), tris(dibenzylideneacetone)dipalladium (0.012 g, 2 mol%), and Tri(o-tolyl)phosphine (0.016 g, 8 mol%) was dissolved. After stirring at 150 °C 3 days, the color became dark blue nearly black. The reaction mixture was poured into 250 ml of methanol and filtered. The polymer was purified with methanol, hexane and methylene chloride using soxhlet extraction and finally, the polymer was obtained into chloroform. The solution was precipitated into 200 ml methanol and filtered to afford 0.163 g of polymer. M_n = 10,300 g/mol, PDI 2.123. Anal. Calcd (%): C, 71.74; H, 9.46; N, 2.39; S, 16.41. Found (%): C, 71.97; H, 9.41; N, 2.24; S, 16.31.

Synthesis of poly{(3,3'-didodecyl-2,2'-bithiophene-5,50-diyl)-alt-[2,5-bis(3-dodecyl-thiophen-2-yl)thiazolothiazole-5,5'-diyl]} (P2) In 20 ml of anhydrous chlorobenzene, 2,5-Bis(3-dodecyl-5-(trimethylstannyl)thiophene-2-yl)thiazolo[5,4-d]thiazole (0.65 g, 0.67 mmol), 5,5'-dibromo-3,3'-dodecyl-2,2'-bithiophene (0.44 g, 0.67 mmol), tris(dibenzylideneacetone)dipalladium (0.012 g, 2 mol%), and Tri(o-tolyl)phosphine (0.016 g, 8 mol%) was dissolved. After stirring at 150 °C 3 days, the color became bright-red. The reaction mixture was poured into 250 ml of methanol and filtered. The polymer was purified with methanol, hexane and methylene chloride using soxhlet extraction and finally, the polymer was obtained into chloroform. The solution was precipitated into 200 ml methanol and filtered to afford 0.686 g of polymer. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.14 (S, 2H), 7.06 (S, 2H), 0.86-0.88 (m,65H), M_n = 41,600 g/mol, PDI 1.899. Calcd (%): C, 71.27; H, 9.50; N, 2.44; S, 16.79. Found (%): C, 71.36; H, 9.43; N, 2.39; S, 16.82.

Synthesis of poly[(4,4'-didodecyl-5'-(2-(3-dodecyl-5-methylthiophen-2-yl)vinyl)-[2,2'-bithiophen]-5-yl)-5-(3-dodecyl-5-methylthiophen-2-yl)thieno[3,2-b]thiophene] (P3) In 20 ml of anhydrous chlorobenzene, 2,5-Bis(3-dodecyl-5-(trimethlystannyl)thiophene-2-yl)thieno[3,2-b]thiophene (0.65 g, 0.67 mmol), 5,5'-di-br-2,2'-dithienylethylene (0.46 g, 0.67 mmol), tris(dibenzylideneacetone)dipalladium (0.012 g, 2 mol%), and Tri(o-tolyl)phosphine (0.016 g, 8 mol%) was dissolved. After stirring at 150 °C 3 days, the color became light orange-red. The reaction mixture was poured into 250 ml of methanol and filtered. The polymer was purified with

methanol, hexane and methylene chloride using soxhlet extraction and finally, the polymer was obtained into chloroform. The solution was precipitated into 200 ml methanol and filtered to afford 0.2072 g of polymer. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21 (S, 2H), 7.03 (S, 2H), 6.86 (S, 2H), 6.80 (S, 2H), 2.79 (br, 8H), 2.66 (br, 12H), 1.2-1.4 (br, 12H), 0.85-0.88 (m, 24H); M_n = 10,500 g/mol, PDI 1.793. Calcd (%): C, 73.91; H, 9.65; S, 16.44. Found (%): C, 74.05; H, 9.55; S, 16.31.

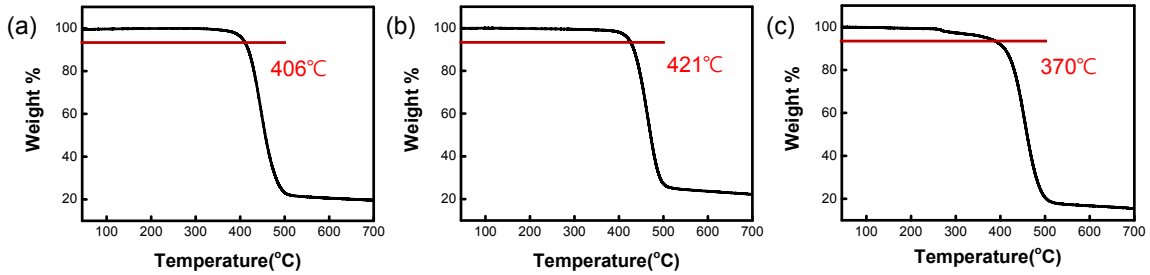

Figure S1. TGA of (a) P1, (b) P2 and (c) P3 in nitrogen atmosphere at a heating rate of 10 °C min^{-1}

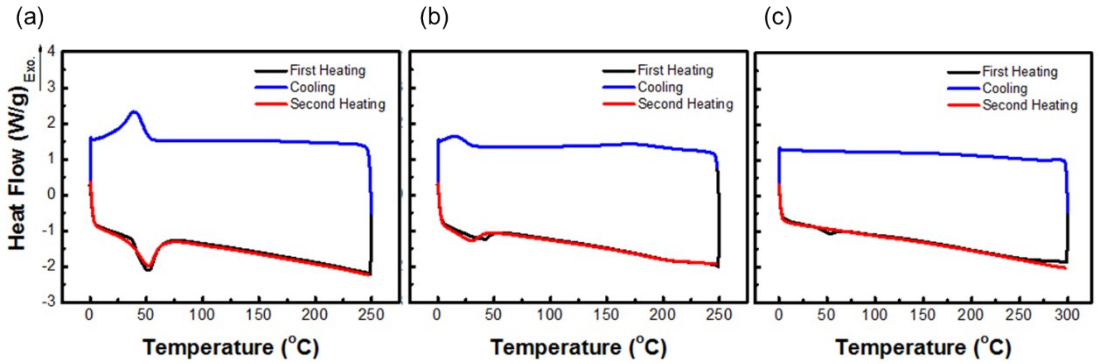

Figure S2. DSC plots showing second scan heating and cooling curves at 10 °C min^{-1} of (a) P1, (b) P2 and (c) P3

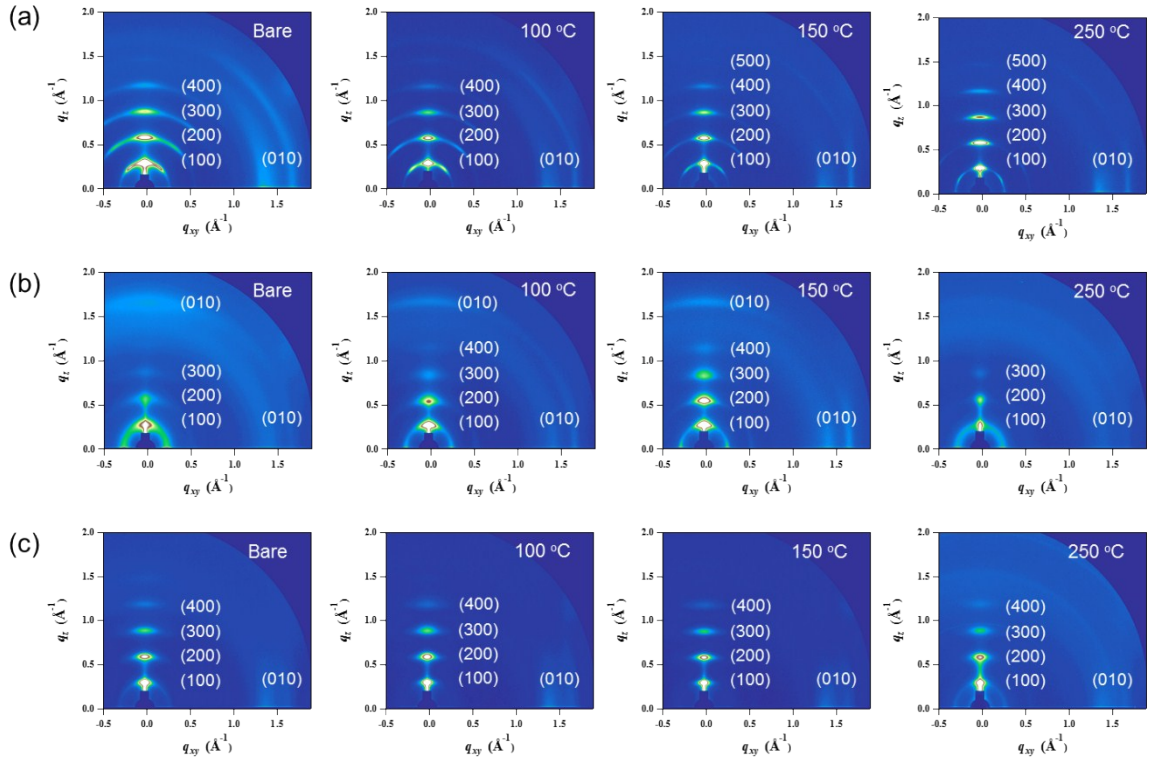

Figure S3. 2D GIXD patterns of the (a) P1, (b) P2 and (c) P3 thin films without and with thermal annealing for various temperature (pristine/100 °C/150 °C/250 °C)

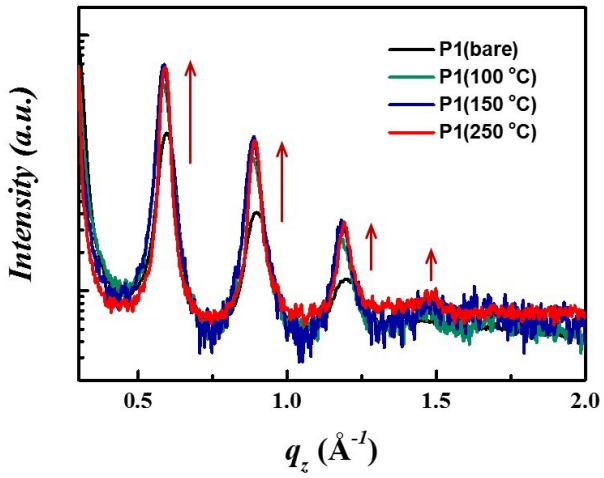

Figure S4. Vertical line cut of 2D GIXD patterns for P1 with thermal annealing for various temperature (pristine/100 °C/150 °C/250 °C)

Table S1. OFET performance of P1.

Condition	Hole Mobility[cm^2/Vs]		Threshold Voltage [V]	On/Off Ratio
	Average[a]	Maximum		
RT	8.3X10^{-2}±0.01	0.087	-41.8	~ 10^5
100°C	7.8X10^{-2}±0.01	0.081	-38.9	
150°C	1.7X10^{-1}±0.04	0.21	-30.8	
250°C	1.13±0.53	1.66	-64.4	

Condition	Electron Mobility[cm^2/Vs]		Threshold Voltage [V]	On/Off Ratio
	Average[a]	Maximum		
RT	-	-	-	
100°C	-	-	-	
150°C	6X10^{-4}±0.00014	0.002	74.9	~ 10^2
250°C	4.3X10^{-2}±0.005	0.05	79.5	

[a] Average mobilities and standard deviations from four different devices.

Table S2. OFET performance of P2.

Condition	Hole Mobility[cm^2/Vs]		Threshold Voltage [V]	On/Off Ratio
	Average[a]	Maximum		
RT	$1.9X10^{-2}\pm0.001$	0.02	-41.1	~ 10^6
100°C	$5.2X10^{-2}\pm0.01$	0.06	-44.2	
150°C	$7.2X10^{-2}\pm0.04$	0.08	-38.8	
250°C	$5.2X10^{-2}\pm0.001$	0.05	-42.0	

Condition	Electron Mobility[cm^2/Vs]		Threshold Voltage [V]	On/Off Ratio
	Average[a]	Maximum		
RT	-	-	-	
100°C	-	-	-	
150°C	$2.3X10^{-3}\pm0.0007$	0.003	79.3	~ 10^3
250°C	$6.7X10^{-3}\pm0.003$	0.01	73.9	

[a] Average mobilities and standard deviations from four different devices.

Table S3. OFET performance of P3.

Condition	Hole Mobility[cm^2/Vs]		Threshold Voltage [V]	On/Off Ratio
	Average[a]	Maximum		
RT	$6.6X10^{-2}\pm0.01$	0.08	-40.0	~ 10^5
100°C	$1.8X10^{-1}\pm0.02$	0.2	-41.6	
150°C	$1.4X10^{-1}\pm0.01$	0.1	-39.9	
250°C	$7X10^{-2}\pm0.001$	0.07	-40.9	

[a] Average mobilities and standard deviations from four different devices.