Electronic Supplementary Information for

Control of consistent ordering in π-conjugated polymer films for organic field-effect transistor applications

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Experimental Section

Synthesis of 1,4-bis(bromomethyl)-2,5-bis(dodecyloxy)benzene

A mixture of 1,4-bis(dodecyloxy)benzene (10.0 g, 0.022 mol), paraformaldehyde (13.4 g, 0.045 mol), glacial acetic (100 mL) were added in a flask stirring for 1 h, then hydrobromic acid (6.12 mL) and isochoric glacial acetic acid were dropped into the flask slowly. The system was stirring for 1 h at 25 °C, after that it was slowly enhancing temperature to 80 °C for 8 h. The system was then cooled till 25 °C and poured into distilled water, and then filtration washed with water till neutral point. The crude product was recrystallized from hot acetone and dried under vacuum to give white powder. Yield: 13.3 g (94%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.86 (s, 2H), 4.54 (s, 4H), 4.02-3.98 (t, 4H), 1.85−1.80 (m, 4H), 1.51−1.48 (m, 4H), 1.34−1.28 (br, 32H), 0.92−0.87 (t, 6H).

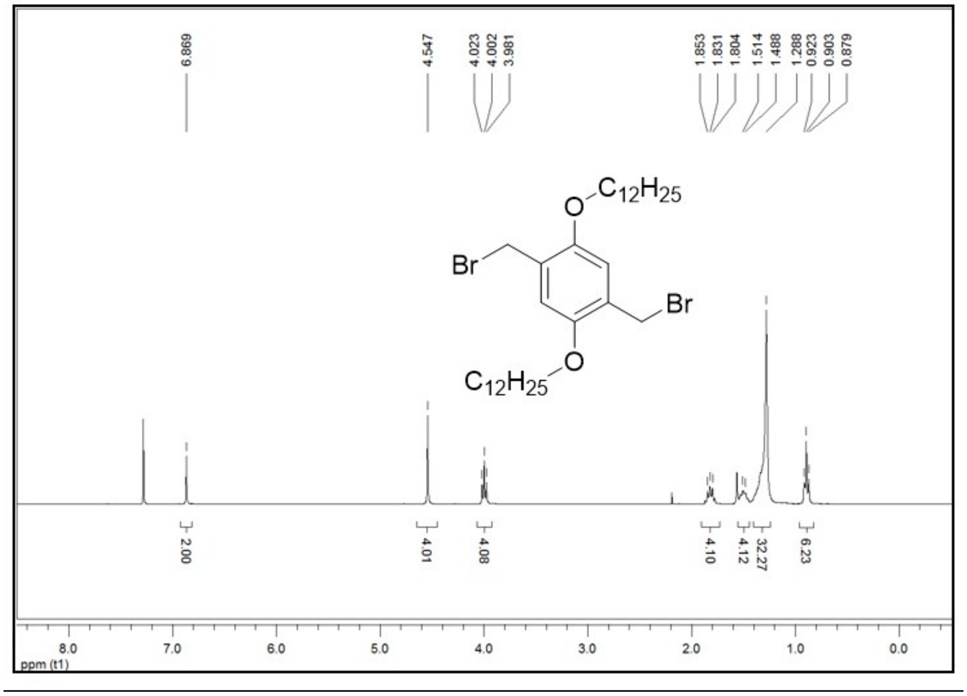


Fig. S1. ^{1}H NMR spectrum of 1,4-bis(bromomethyl)-2,5-bis(dodecyloxy)benzene.

Synthesis of tetraethyl(2,5-bis(dodecyloxy)-1,4-phenylene)bis(methylene)diphosphonate

1,4-Bis(bromomethyl)-2,5-bis(dodecyloxy)benzene (6.6 g, 0.010 mol) and triethyl phosphite (3.81 g, 0.023 mol) were stirred for 5 h at 170 °C. Excess triethyl phosphite was removed by applying high vacuum and the product was obtained as a colorless crystalline solid. Yield: 7.50 g (97%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.93 (s, 2H), 4.05-4.01 (m, 8H), 3.5–3.90 (t, 4H), 3.27–3.20 (d, 4H), 1.79–1.74 (m, 4H) 1.47–1.43 (m, 4H), 1.28 (br, 32H), 1.27–1.22 (t, 12H), 0.92–0.87 (t, 6H).

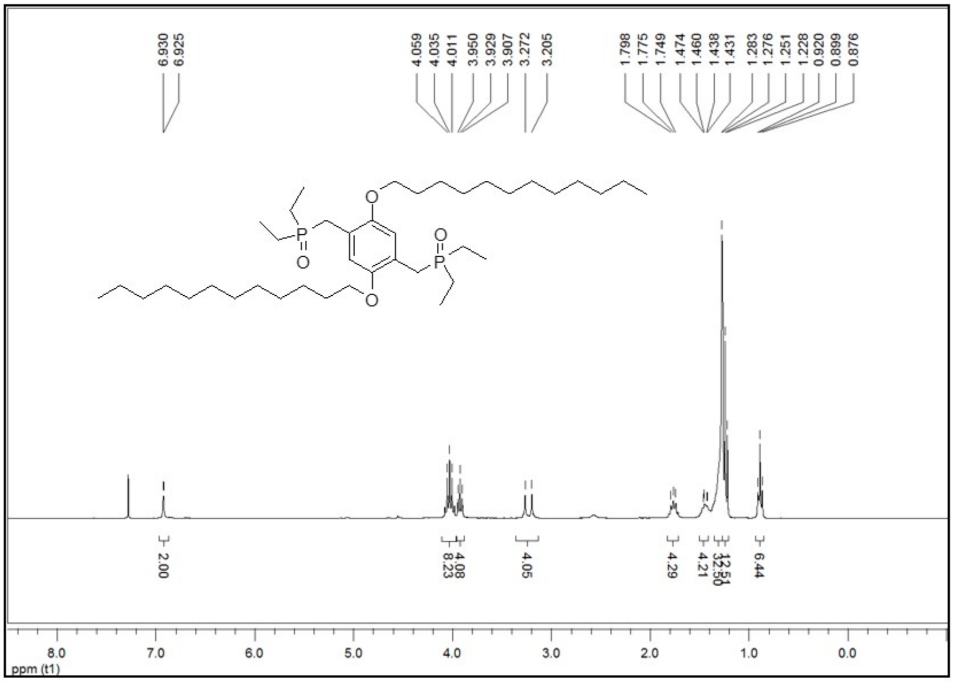


Fig. S2 ^{1}H NMR spectrum of tetraethyl(2,5-bis(dodecyloxy)-1,4-phenylene)bis(methylene) diphosphonate.

Synthesis of 2,2′-(1E,1′E)-2,2′-(2,5-bis(dodecyloxy)-1,4-phenylene)bis(ethene-2,1-diyl)dithiophene

Tetraethyl(2,5-bis(dodecyloxy)-1,4-phenylene)bis(methylene)diphosphonate (5.0 g, 0.008 mol) and thiophene-2-carbaldehyde (1.9 g, 0.016 mol) were dissolved in 100 mL of THF. To this solution potassium *tert*-butoxide was added and stirred for 2 h at room temperature. The reaction mixture was quenched by the addition of distilled water, and the mixture was extracted with ethyl acetate. The combined extracts were dried with anhydrous $MgSO_4$ and then evaporated. The crude product was purified by column chromatography on silica gel with hexane. Further purification by recrystallization with methanol. Yield: 2.77 g (53%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.35–7.30 (d, 2H), 7.28–7.23 (d, 2H), 7.21–7.19 (d, 2H), 7.09–7.08 (d, 2H), 7.05 (s, 2H), 7.03–7.01 (t, 2H), 4.07–4.03 (t, 4H), 1.92–1.83 (m, 4H), 1.61-1.51 (m, 4H), 1.44–1.28 (br, 32H), 0.92–0.87 (t, 6H1 ^{13}C-NMR (500 MHz, $CDCl_3$): 151, 143.8, 127.5, 126.4, 125.6, 124.1, 123.4, 122.1, 110.7, 69.5, 31.9, 29.6,29.3, 26.2, 22.6, 14.1, HR-Mass: Calcd $C_{42}H_{62}O_2S_2$: 662.4191, Found : 662.4189.

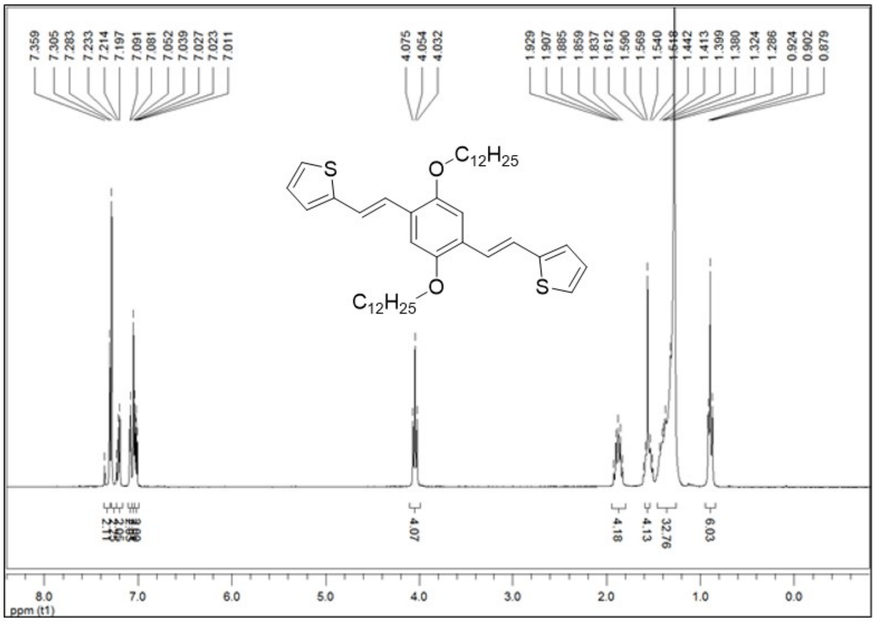


Fig. S3 ^{1}H NMR spectrum of 2,2′-(1*E*,1′*E*)-2,2′-(2,5-bis(dodecyloxy)-1,4-phenylene)bis(ethene-2,1-diyl)dithiophene.

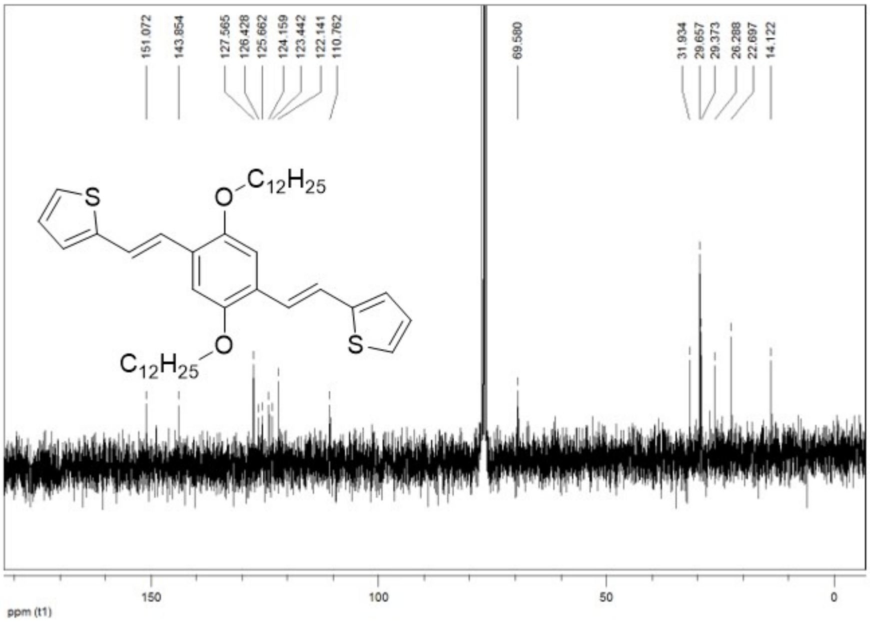


Fig. S4 ^{13}C NMR spectrum of 2,2′-(1*E*,1′*E*)-2,2′-(2,5-bis(dodecyloxy)-1,4-phenylene)bis(ethene-2,1-diyl)dithiophene.

Synthesis of (((1E,1′E)-(2,5-bis(dodecyloxy)-1,4-phenylene)bis(ethene-2,1-diyl))bis(thiophene-5,2-diyl))bis(trimethylstannane)

In a dry three-neck 100 mL nitrogen purged flask, 2,2′-(1*E*,1′*E*)-2,2′-(2,5-bis(dodecyloxy)-1,4-phenylene)bis(ethene-2,1-diyl)dithiophene (1.0 g, 0.0015 mol) was dissolved in 40 mL of anhydrous THF. The solution was cooled to −50 °C, and a solution of *n*-BuLi (1.24 mL, 2.5 M in hexane, 0.0031 mol) was added dropwise with stirring, after which the reaction mixture was stirred for 1 h at room temperature. Next, the reaction mixture was cooled to −78 °C and 1 M chlorotrimethylstannane (3.09 mL, 0.0031 mol) was added in one portion. The reaction mixture was stirred at room temperature for 2 h. Subsequently, the reaction mixture was quenched by the addition of distilled water, and the mixture was extracted with diethyl ether. Finally, the combined organic phase was dried with anhydrous $MgSO_4$ and then recrystallization with ethanol. Yield: 0.75 g (51%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 7.43−7.37 (d, 2H), 7.29−7.24 (d, 2H), 7.21−7.30 (d, 2H), 7.14−7.13 (d, 2H), 7.08 (s, 2H), 4.09−4.05 (t, 4H), 1.94−1.85 (m, 4H), 1.63−1.53 (m, 4H), 1.46-1.30 (br, 32H), 0.93-0.88 (t, 6H), 0.51−0.32 (t, 18H).

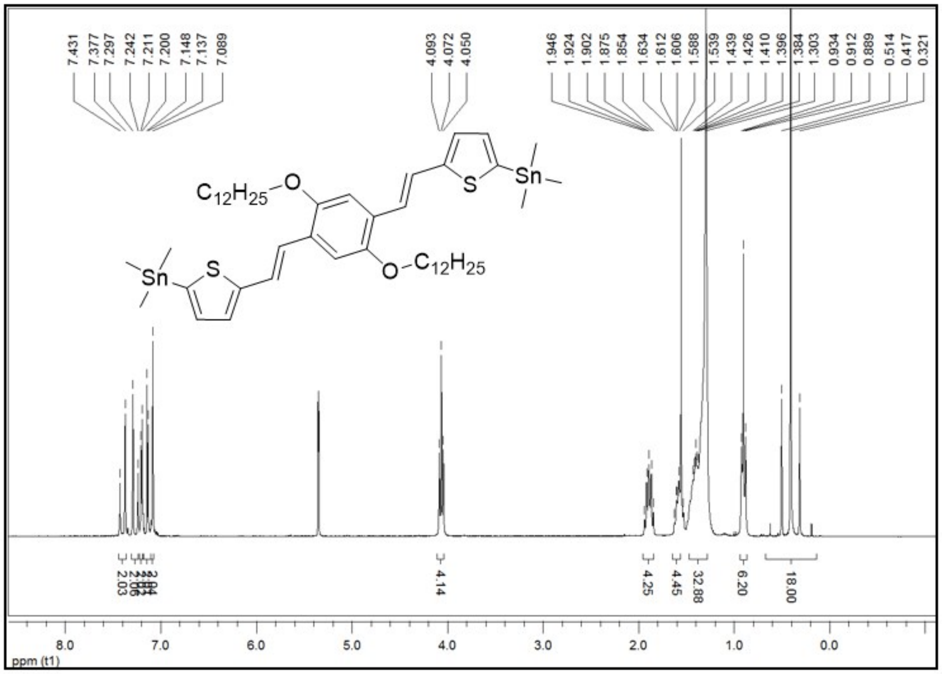


Fig. S5 ^{1}H NMR spectrum of (((1*E*,1'*E*)-(2,5-bis(dodecyloxy)-1,4-phenylene)bis(ethene-2,1-diyl))bis(thiophene-5,2-diyl))bis(trimethylstannane).

Synthesis of 24-DPP-Br

Synthesis of 24-DPP-br was followed by literature method.[18]

^{1}H NMR (300 MHz, CD_2Cl_2): δ = 8.66–8.65 (d, 2H), 7.28–7.23 (t, 2H), 3.95–3.92 (d, 4H), 1.7 (m, 2H), 1.23 (m, 80H), 0.91–0.87 (t, 12H)

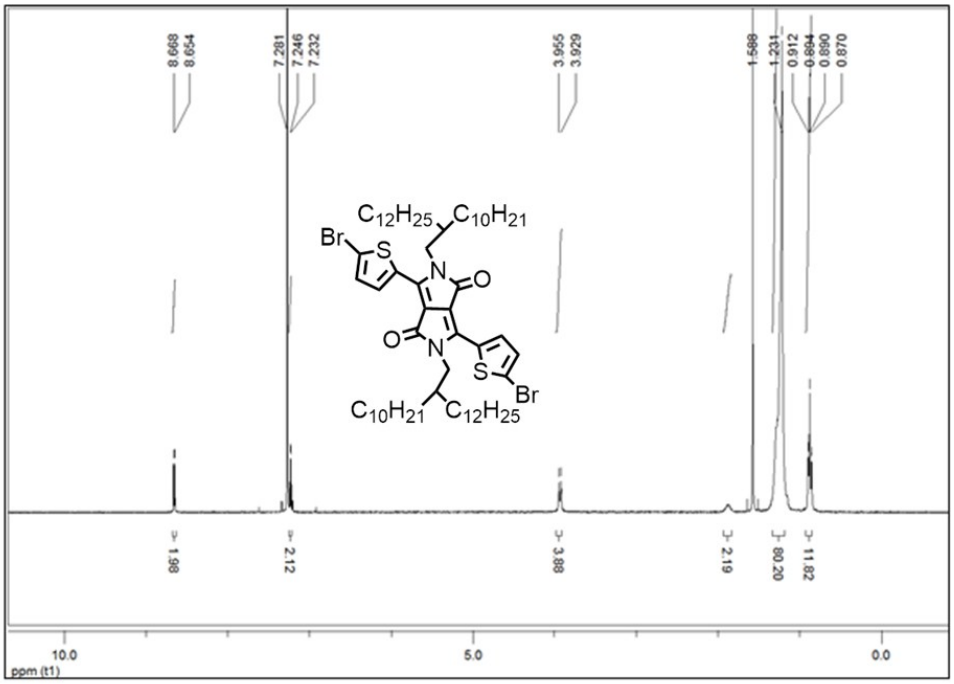


Fig. S6 ^{1}H NMR spectrum of 24-DPP-Br.

Polymerization of pDPP- (TV)$_2$B-2DO

In a Schlenk flask 24-DPP-Br[1] (0.40 g, 0.35 mmol) and (((1*E*,1′*E*)-(2,5-bis(dodecyloxy)-1,4-phenylene)bis(ethene-2,1-diyl))bis(thiophene-5,2-diyl))bis(trimethylstannane) (0.349 g, 0.35 mmol) were dissolved in dry chlorobenzene (6.0 mL). After degassing under nitrogen for 30 min, $Pd_2(dba)_3$ (6.5 mg, 0.007 mmol) and P(*o*-Tol)$_3$ (8.6 mg, 0.028 mmol) were added to the mixture, which was then stirred for 48 h at 110 °C. Tributyl(thiophen-2-yl)stannane and 2-bromothiophene were injected sequentially into the reaction mixture for end-capping, and the solution was stirred for 6 h after each addition. The polymer was precipitated in methanol. The crude polymer was collected by filtration and purified by Soxhlet extraction with methanol, acetone, hexane, and chloroform, successively. The final product, pDPP-(TV)$_2$B-2DO was obtained by precipitation in methanol. Yield: 0.26 g. ^{1}H-NMR (500 MHz, CDCl$_3$): δ = 8.97 (b, 4H) 7.21–6.8 (b, 10H), 4.07 (b, 8H), 1.953 (b, 6H), 1.5–0.5 (b,134)

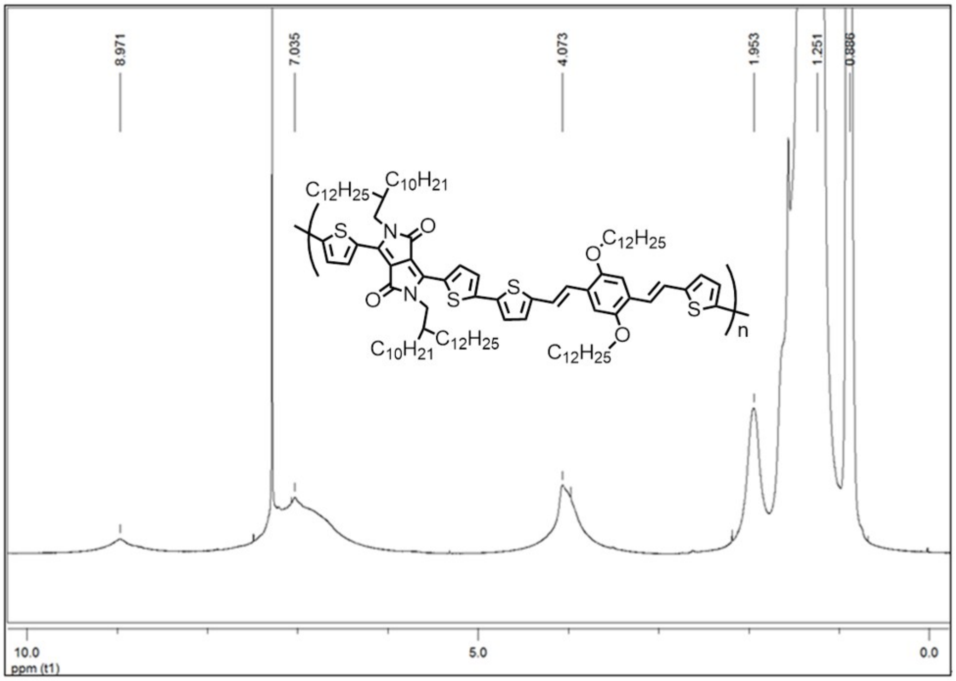
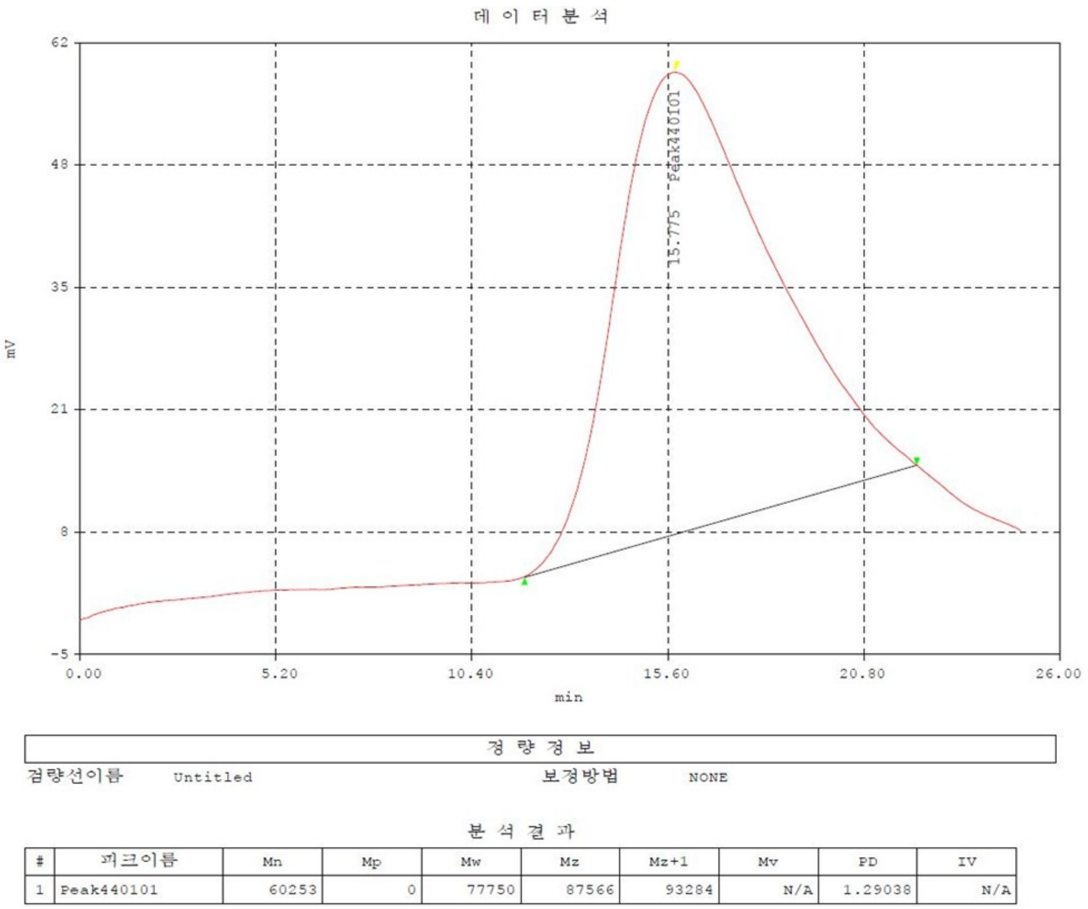


Fig. S7 ^{1}H NMR spectrum of pDPP-(TV)$_2$B-2DO.



정량정보

검량선이름 Untitled

보정방법 NONE

분석결과

#	피크이름	Mn	Mp	Mw	Mz	Mz+1	Mv	PD	IV
1	Peak440101	60253	0	77750	87566	93284	N/A	1.29038	N/A

Fig. S8 GPC trace of pDPP-$(TV)_2$B-2DO eluted with a dilute CB solution.

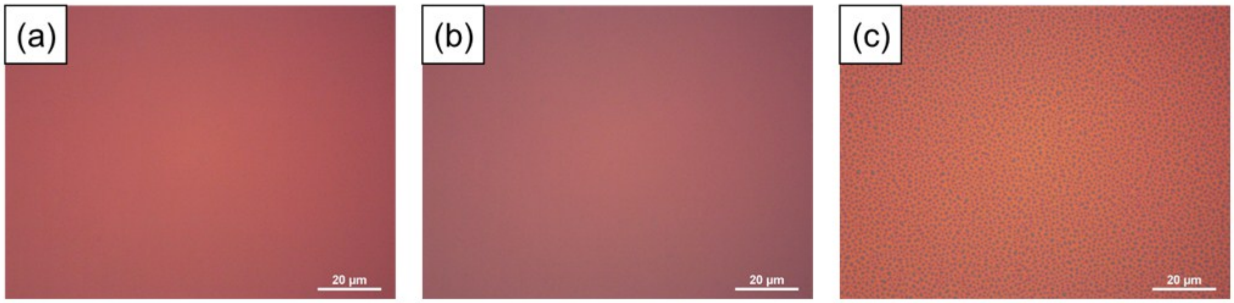


Fig. S9 OM images of the (a) as-spun, (b) 250 °C-annealed and (c) 300 °C-annealed pDPP-$(TV)_2$B-2DO films.

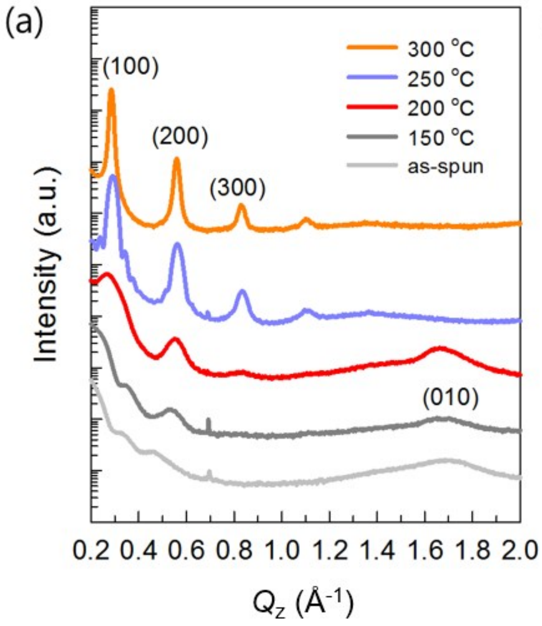


Fig. S10 1D (a) out-of-plane and (b) in-plane X-ray profiles of spun-cast pDPP-(TV)$_2$B-2DO films before and after annealing at different temperatures.

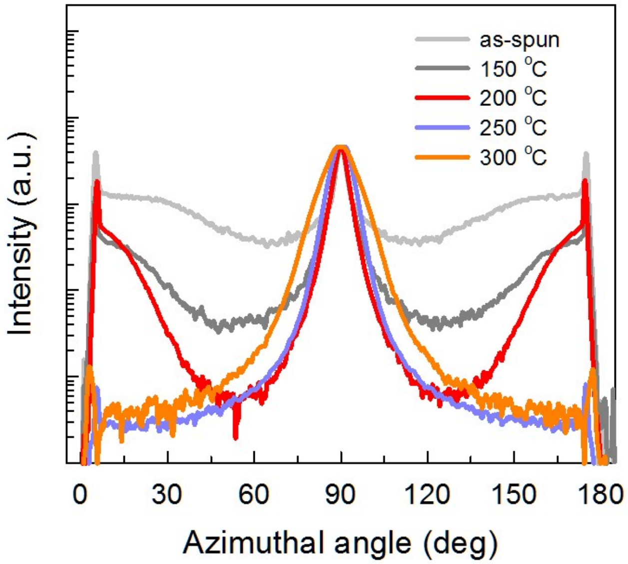


Fig. S11 Azimuthal angles of spun-cast pDPP-(TV)$_2$B-2DO films on gPS-SiO$_2$ dielectrics before and after annealing at different T_As (the intensities were normalized at the maximum peak positions of (100)$_{\text{edge-on}}$.

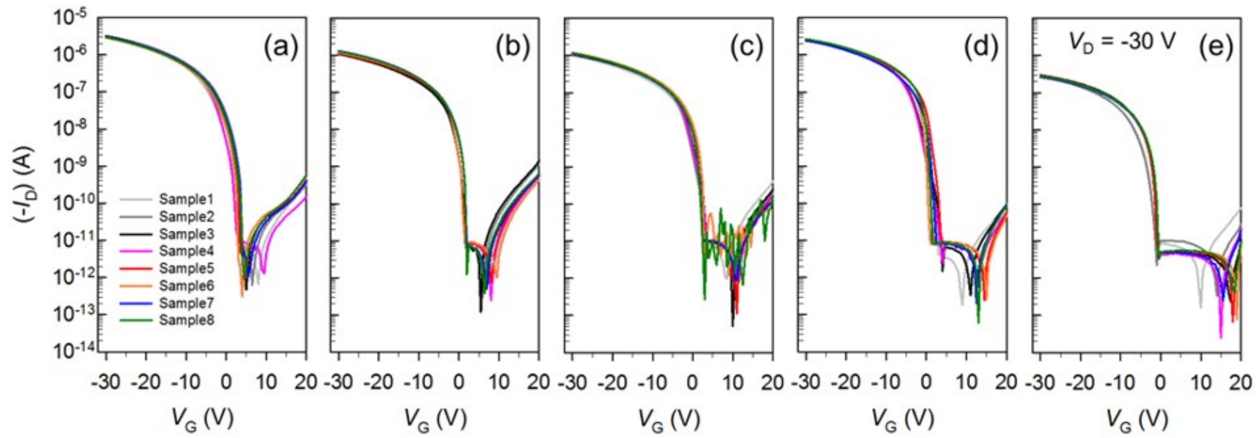


Fig. S12 All the I_D-V_G transfer curves of pDPP-(TV)$_2$B-2DO based OFETs (a) before and (b-e) after annealing at different T_A values: (b) 150, (c) 200, (d) 250, (e) 300 °C (Eight samples for each system were measured and summarized).

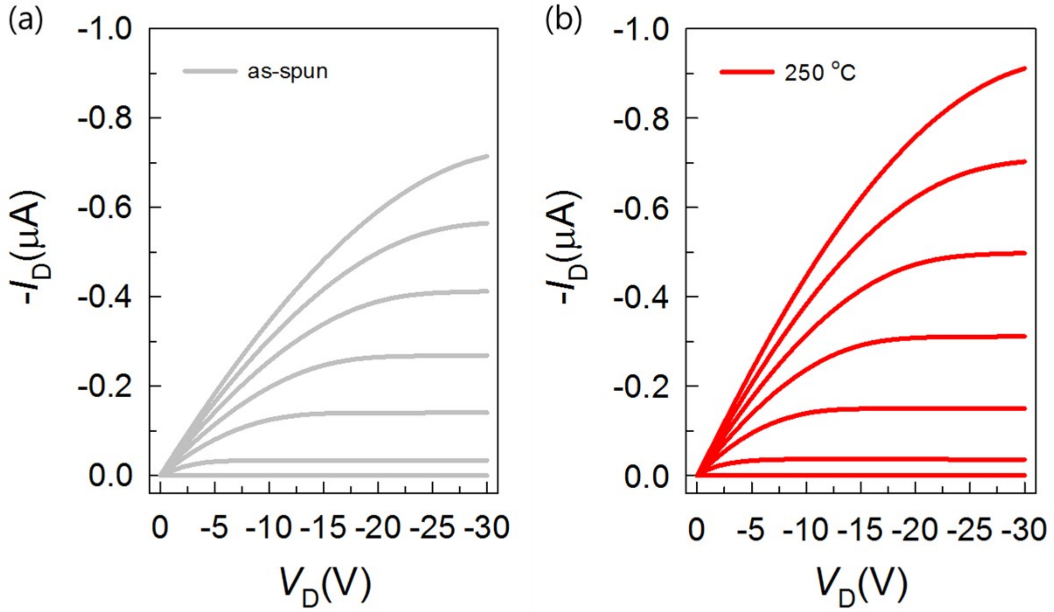


Fig. S13 Typical output curves of (a) the as-spun and (b) 250 °C-annealed pDPP-(TV)$_2$B-2DO OFETs.