

β -Alkyl substituted Dithieno[2,3-*d*;2',3'-*d'*]benzo[1,2-*b*;4,5-*b'*]dithiophene (DTBDT) Semiconducting Materials and Their Application to Solution-Processed Organic Transistors

Jonggi Kim,^{†,Ψ} A-Reum Han,^{‡,Ψ} Jung Hwa Seo,[§] Joon Hak Oh^{*,‡} and Changduk Yang^{*,†}

[†]Interdisciplinary School of Green Energy, KIER-UNIST Advanced Center for Energy (K-U ACE), Low Dimensional Carbon Materials Center, Ulsan National Institute of Science & Technology (UNIST), Ulsan 689-798, South Korea.

[‡]School of Nano-Bioscience and Chemical Engineering, KIER-UNIST Advanced Center for Energy (K-U ACE), Low Dimensional Carbon Materials Center, Ulsan National Institute of Science & Technology (UNIST), Ulsan 689-798, South Korea.

[§]Department of Materials Physics, Dong-A University, Busan 604-714, South Korea.

^ΨThe first two authors contributed equally to this work

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1. ^1H and ^{13}C NMR spectra

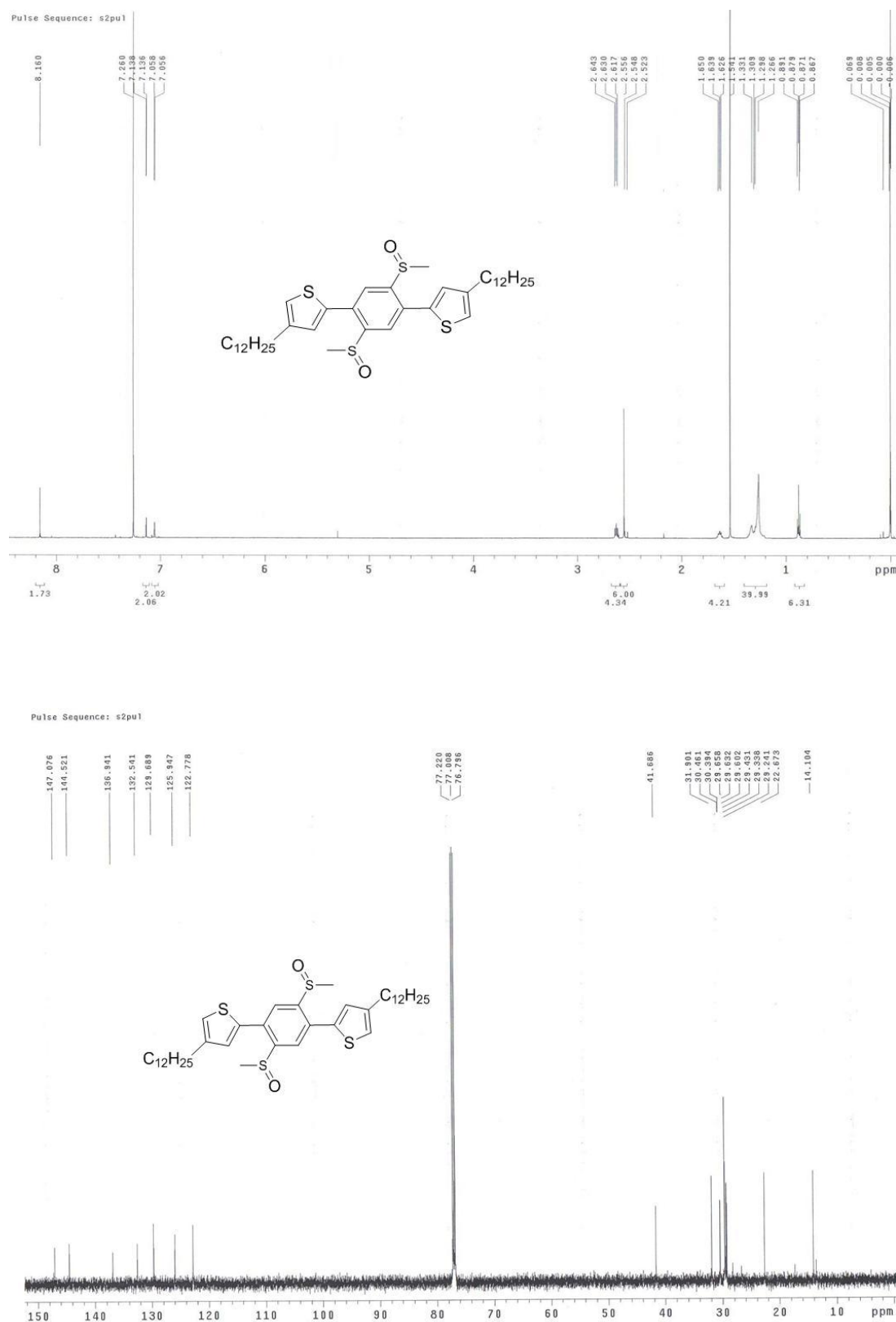


Figure S1. ^1H and ^{13}C NMR spectra of **4**

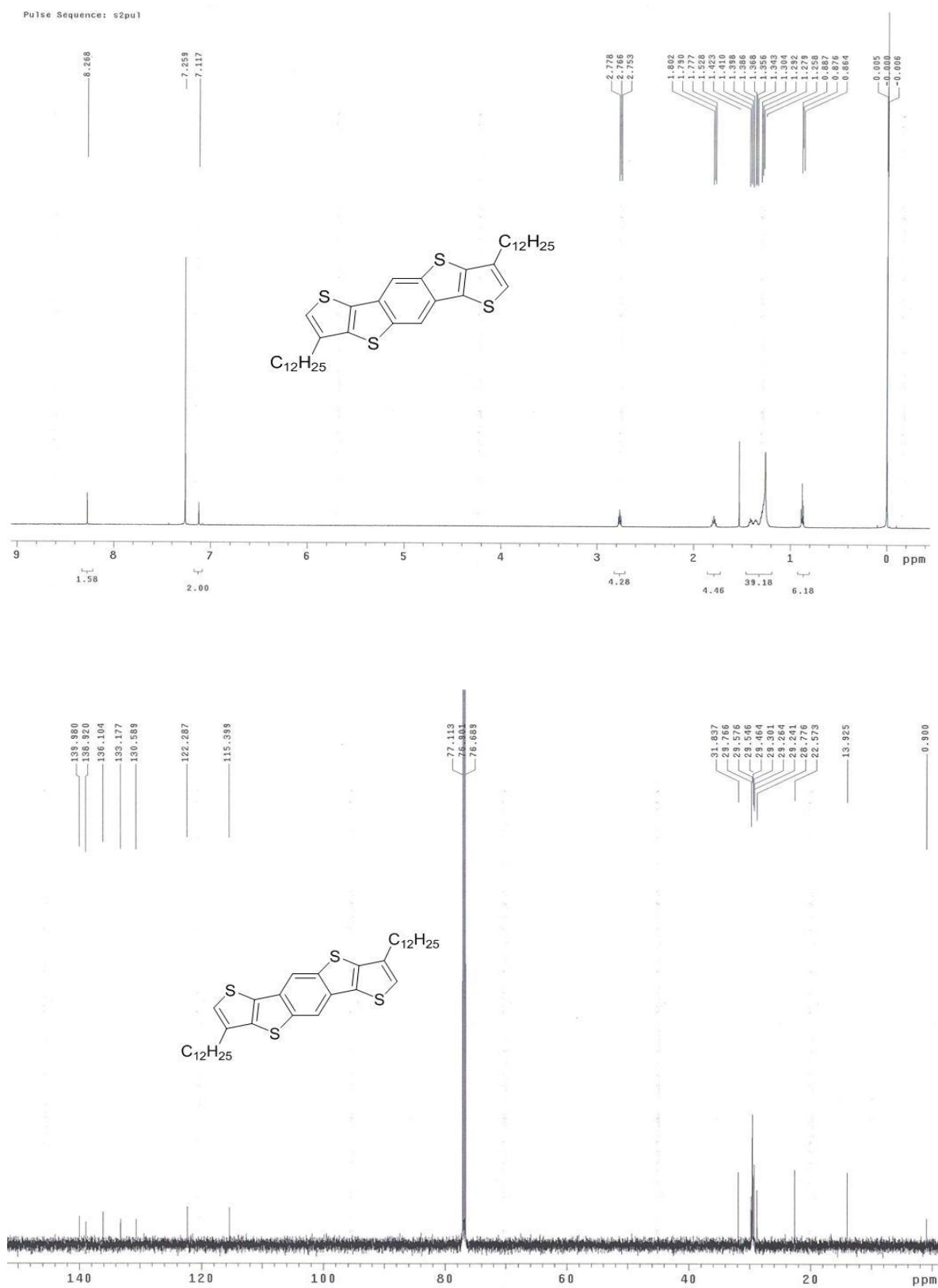


Figure S2. ¹H and ¹³C NMR spectra of **5**

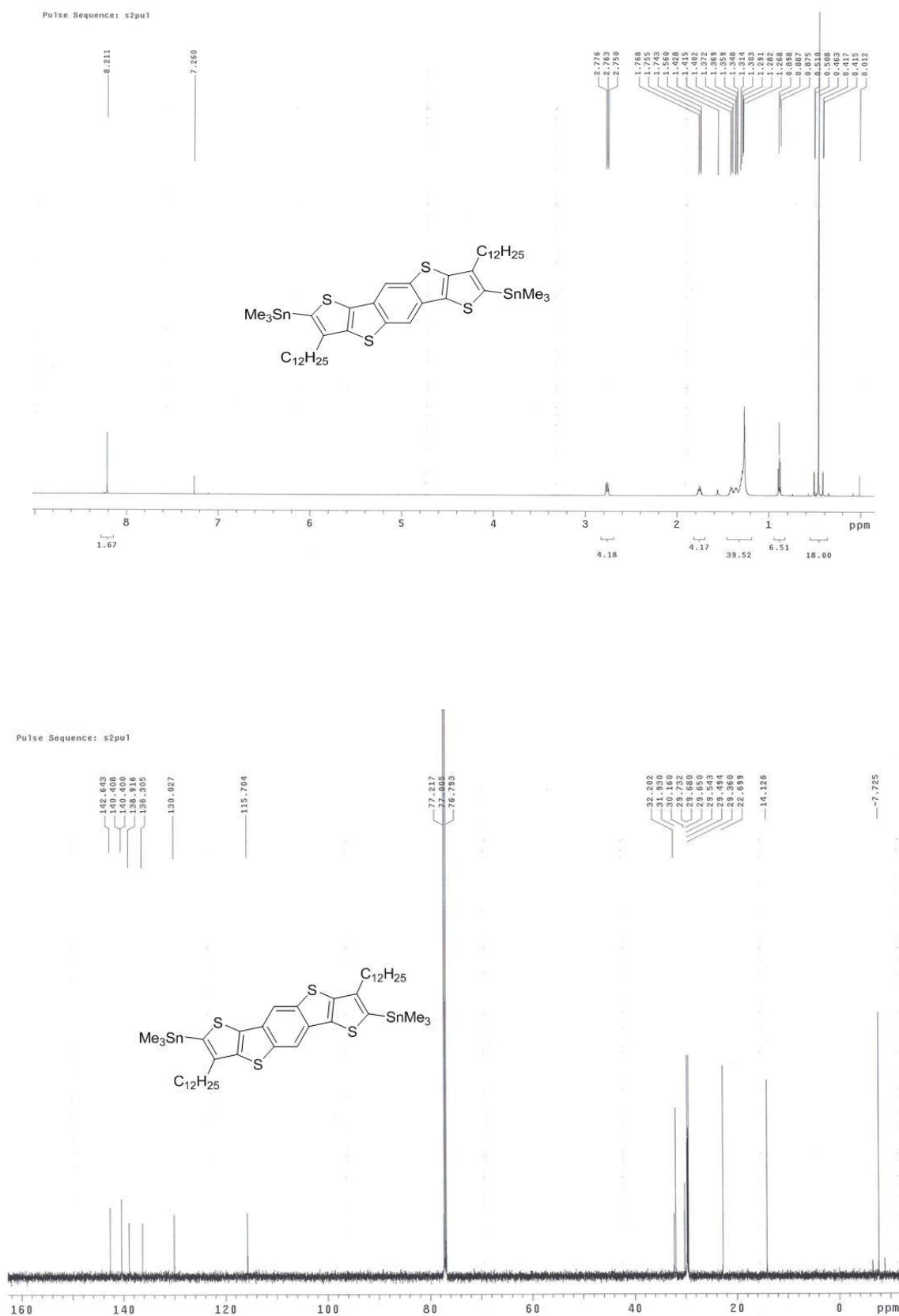


Figure S3. ¹H and ¹³C NMR spectra of 6

2. TGA and DSC

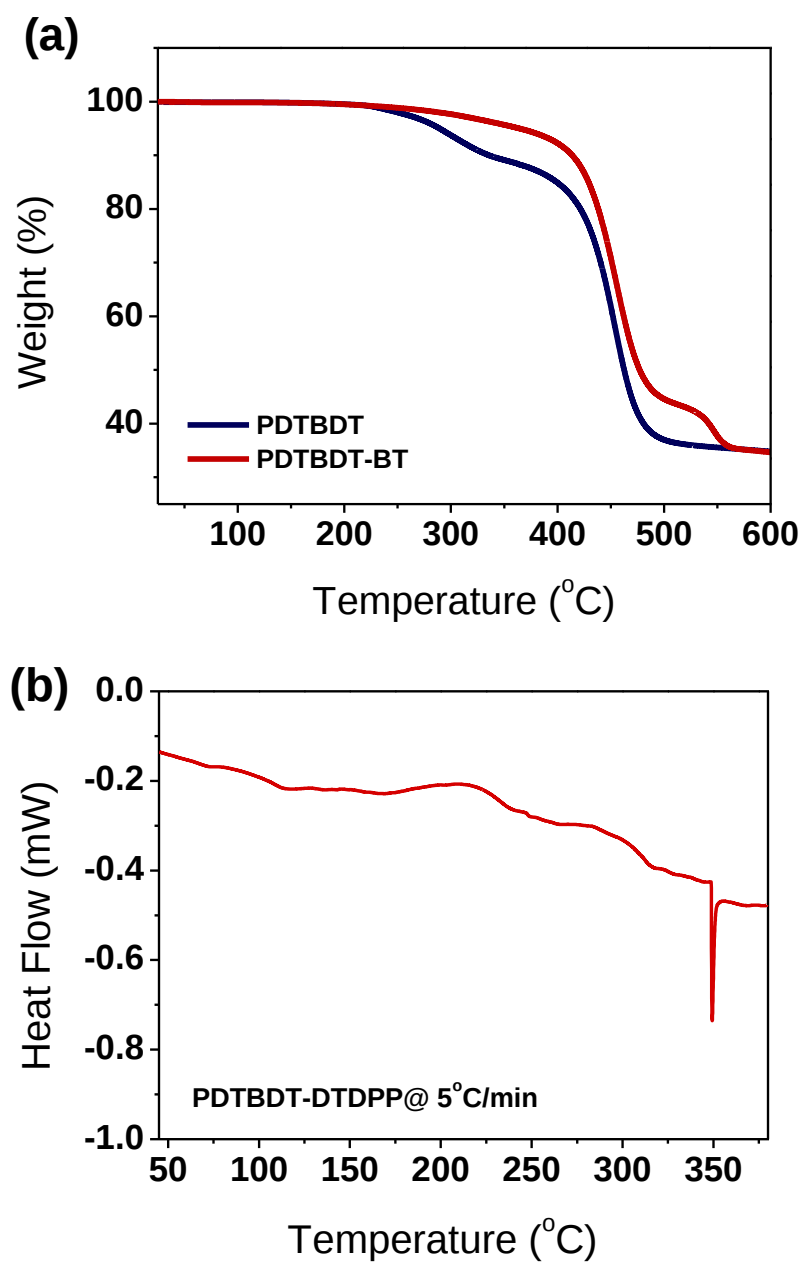


Figure S4. (a) TGA of **PDTBDT** and **PDTBDT-BT** with heating rate of 10 °C/ min under nitrogen atmosphere. (b) DSC data of **PDTBDT-DTDPP** with heating rate of 5 °C/ min under nitrogen atmosphere.

3. AFM

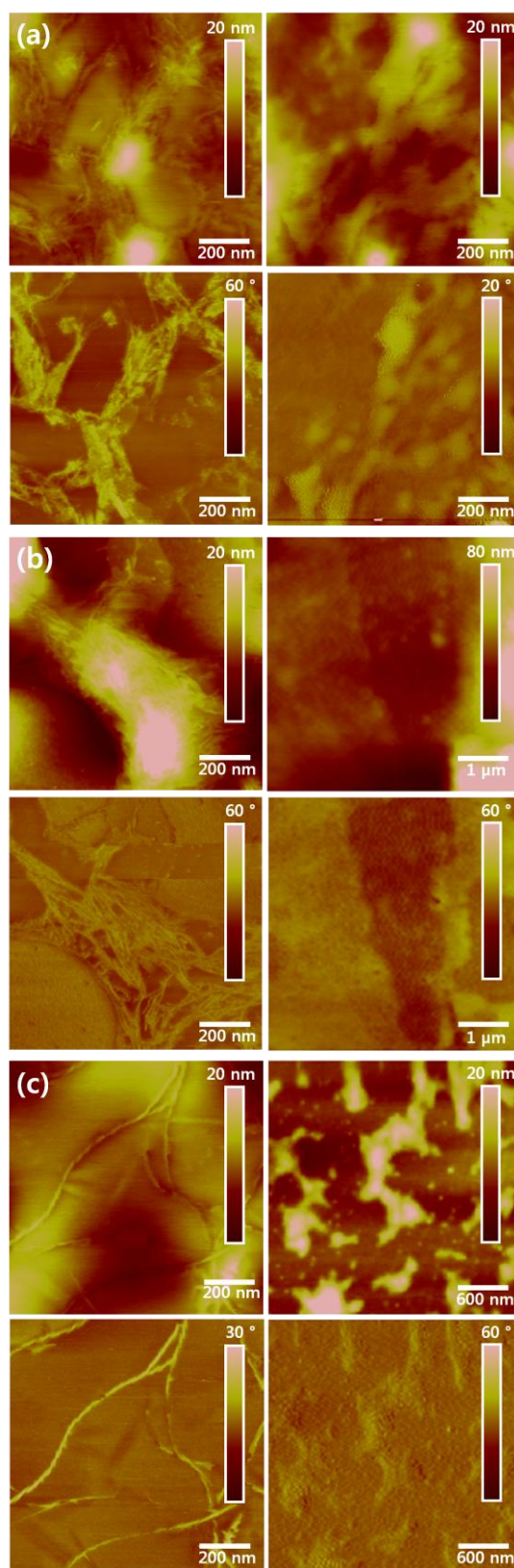


Figure S5. AFM height(up) and phase(down) images of DTBBDT-based polymer thin films as-cast (left) and annealed at 150 °C (right); (a) **PDTBBDT**, (b) **PDTBBDT-BT** and (c) **PDTBBDT-DTBT**.

4. XRD

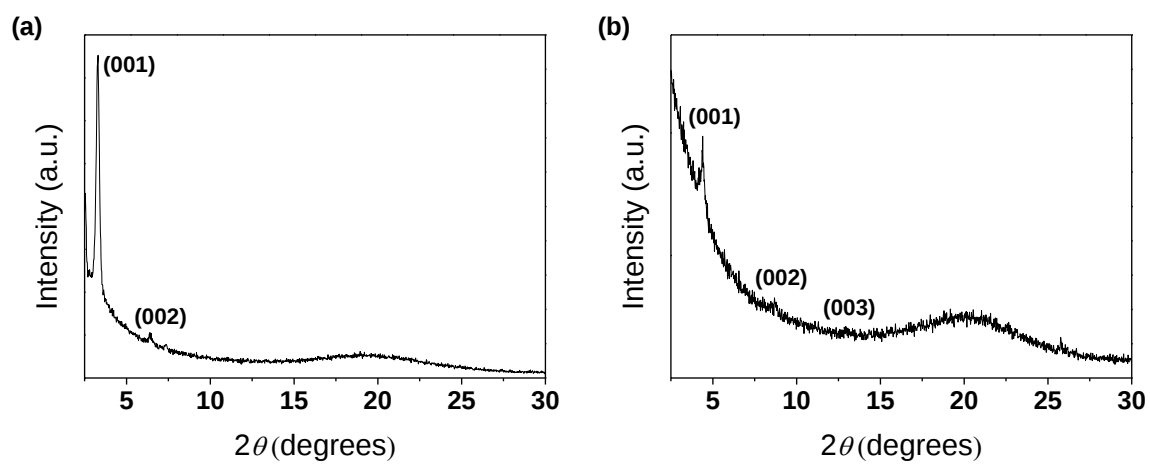


Figure S6. XRD patterns obtained from **PDTBDT** thin films (a) as-cast, (b) annealed at 150 °C.

Table S1. Peak assignments for the out-of-plane XRD patterns obtained from DTBDT-based polymers.

Polymer	(00n)	As-cast		Annealed at 150 °C	
		2θ (°)	$d(001)$ - spacing (Å)	2θ (°)	$d(001)$ - spacing (Å)
PDTBDT	(001)	3.28	26.92	4.38	20.16
	(002)	6.42	-	8.72	-
	(003)	-	-	12.92	-
PDTBDT-BT	(001)	3.22	27.42	4.44	19.89
	(002)	6.68	-	8.74	-
PDTBDT-DTBT	(001)	3.74	23.61	4.32 ^a	20.43
	(002)	7.40	-	-	-
	(003)	12.22	-	12.37	-
PDTBDT-DTDPP	(001)	3.16	27.94	3.24	27.25
	(001)* ^b	3.98	22.19	3.94	22.41
	(002)	-	-	6.44	-
	(002)*	-	-	7.84	-
	(003)	9.04	-	9.66	-
	(003)*	11.01	-	11.83	-
	(004)	-	-	12.92	-
	(004)*	16.04	-	-	-
	(005)	15.70	-	16.20	-
	(005)*	20.04	-	20.50	-
	(006)	19.06	-	19.34	-

^aThe annealed thin film of **PDTBDT-DTBT** exhibited relatively weak XRD peaks. This is probably due to the segregation of annealed thin film as shown by AFM analysis. The (005) XRD peak was observed at $2\theta = 21.54^\circ$ with relatively stronger intensity compared with other higher order XRD peaks.

^bThe secondary phase (P2) with different molecular orientations in contrast with the primary phase (P1) for **PDTBDT-DTDPP** thin film.

5. FET

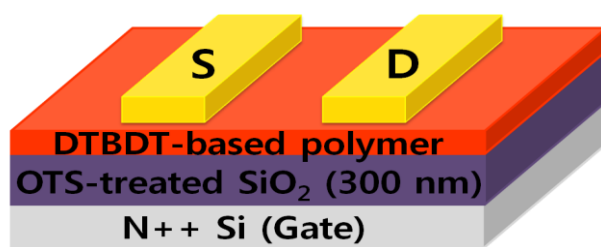


Figure S7. OFET device configuration used in this study.

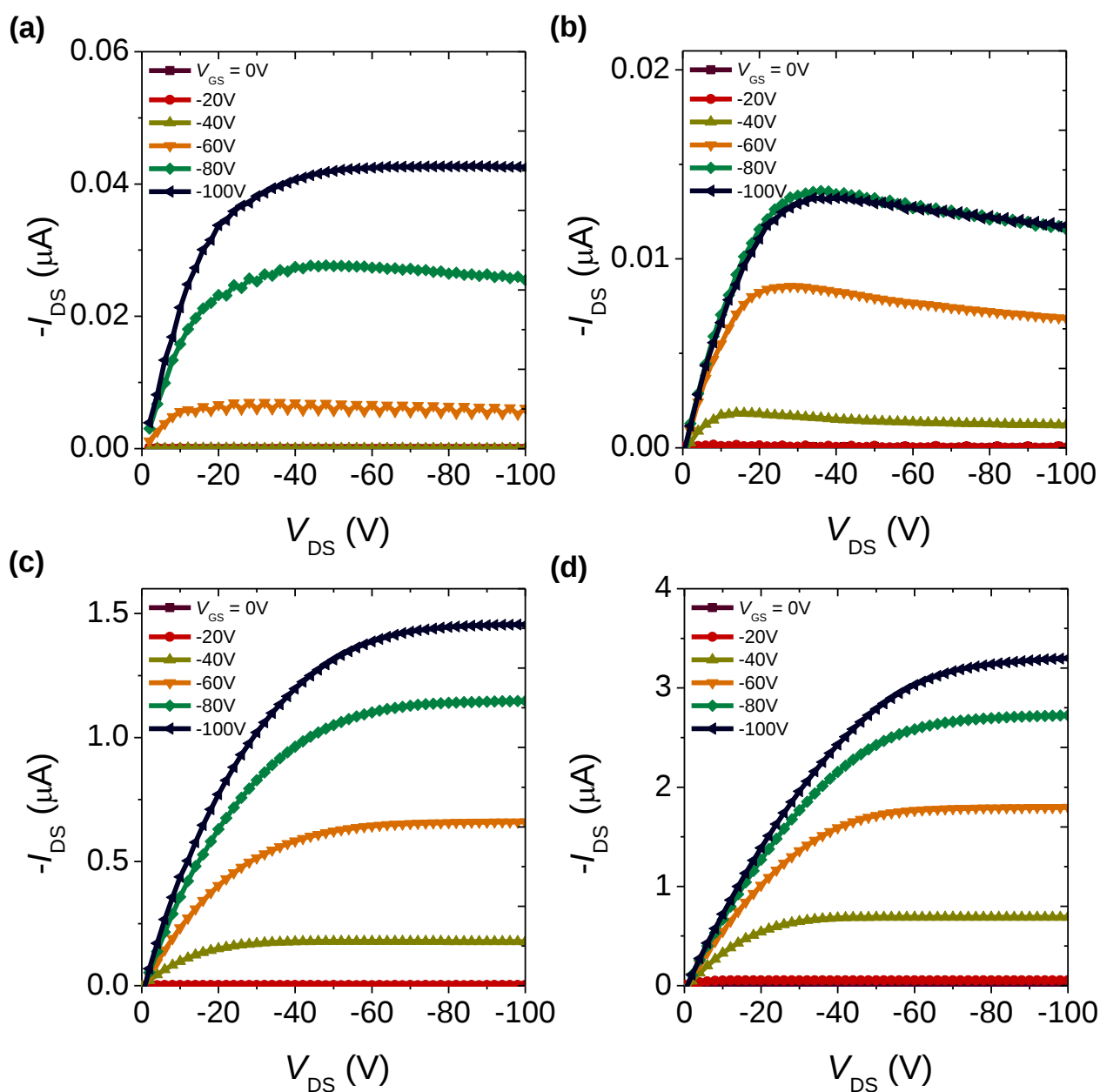


Figure S8. Output characteristics of OFET devices of DTBDT-based polymers annealed at 150 °C; (a) PDTBDT, (b) PDTBDT-BT, (c) PDTBDT-DTBT, and (d) PDTBDT-DTDPP.

Table S2. OFET performance of as-cast DTBDT-based polymers.

Polymer	$\mu_{\max}$ [cm ² V ⁻¹ s ⁻¹]	μ_{avg} [cm ² V ⁻¹ s ⁻¹]	$I_{\text{on}}/I_{\text{off}}$	V_{T} [V]
PDTBDT	2.90×10^{-7}	2.25×10^{-7}	6.91×10^1	-25.1
PDTBDT-BT	2.24×10^{-7}	8.36×10^{-8}	8.43×10^3	-40.8
PDTBDT-DTBT	1.14×10^{-3}	6.04×10^{-4}	1.42×10^4	-29.6
PDTBDT-DTDPP	2.28×10^{-3}	2.16×10^{-3}	3.82×10^3	-19.2