Supporting Information

Acene-containing Donor-acceptor Conjugated Polymers: Correlation between the Structure of Donor Moiety, Charge Carrier Mobility, and Charge Transport Dynamics in Electronic Devices.

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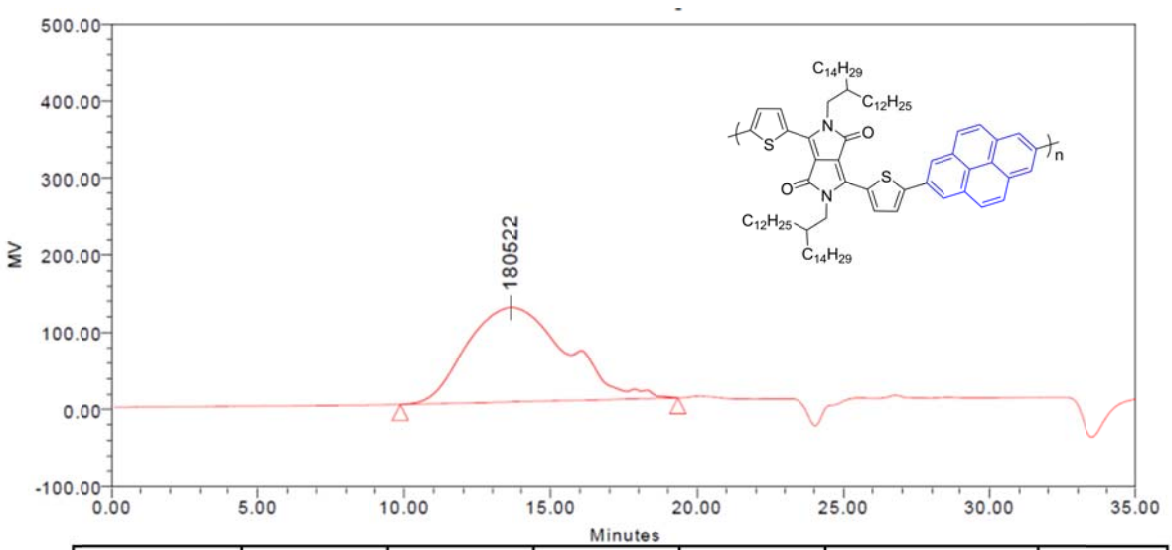
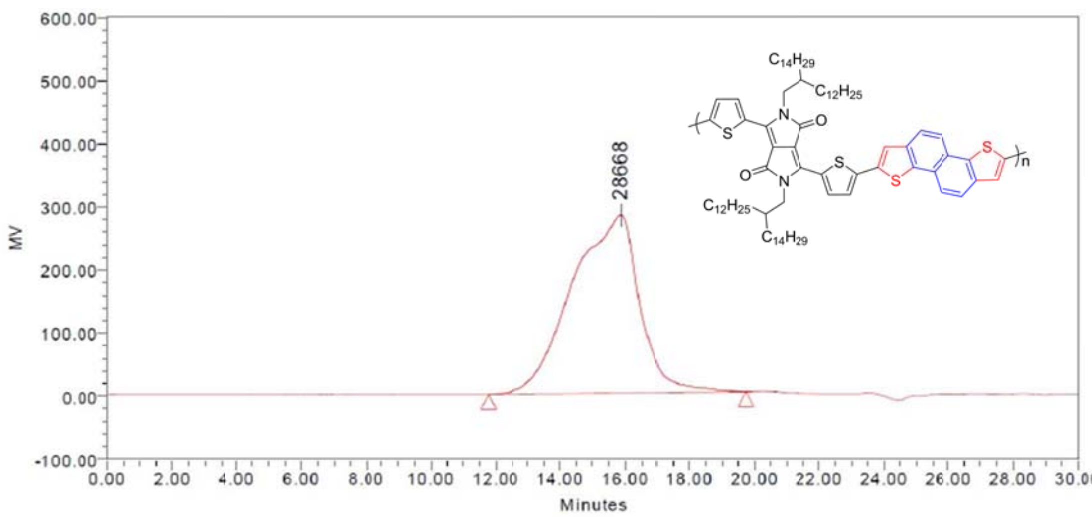
KEYWORDS acene, conjugated copolymer, thin film transistor, charge transport dynamics, inverter

1. Gel permeation chromatograms of acene-containing conjugated polymers



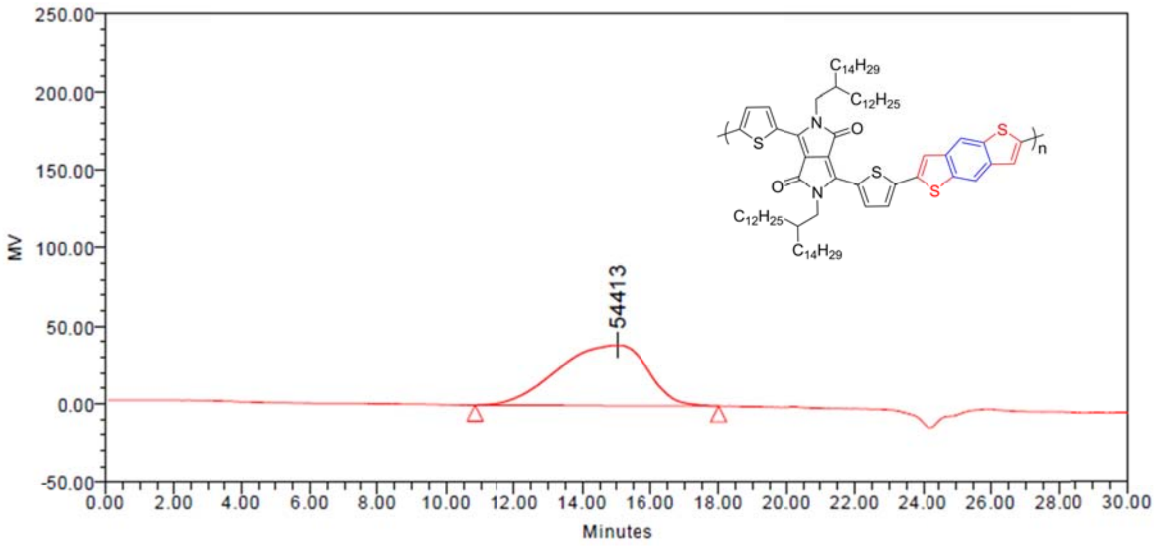
	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Polydispersity	% Area
PDPPPy	48827	265737	180522	681751	5.442463	100.00

Figure S1. GPC chromatogram of PDPPPy..



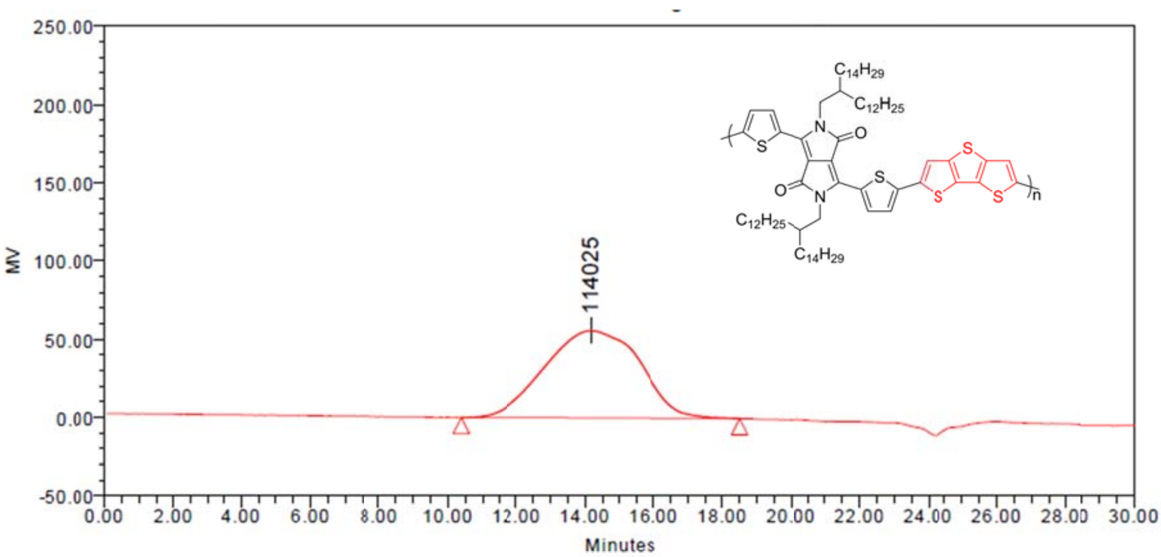
	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Polydispersity	% Area
PDPPNDT	30775	65518	28668	128806	2.128937	100.00

Figure S2. GPC chromatogram of PDPPNDT.



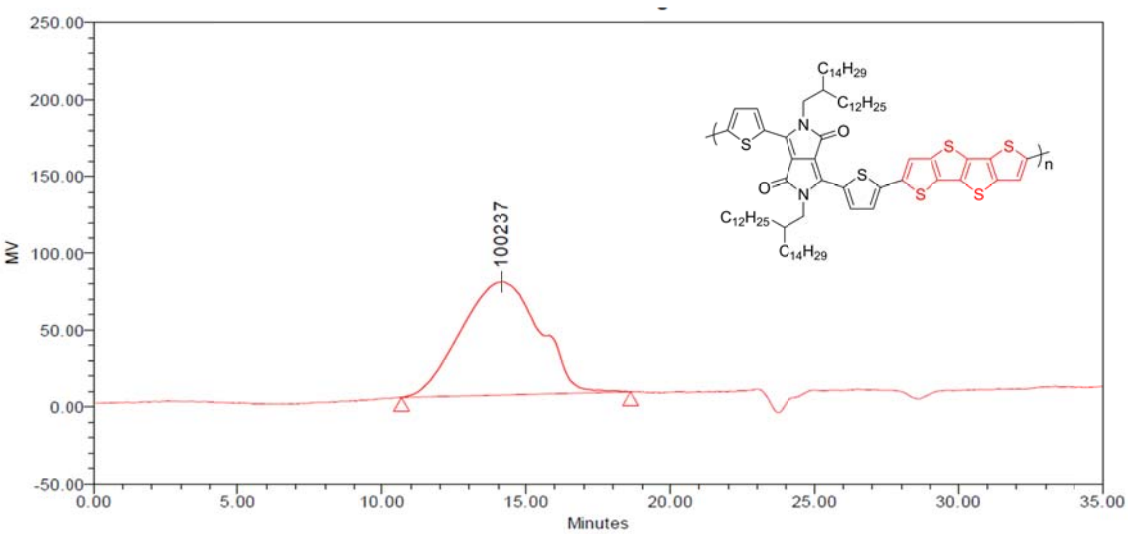
	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Polydispersity	% Area
PDPPBDT	56800	136713	54413	315981	2.406910	100.00

Figure S3. GPC chromatogram of PDPPBDT.



	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Polydispersity	% Area
PDPPDTT	68027	180343	114025	413754	2.651038	100.00

Figure S4. GPC chromatogram of PDPPDTT.



	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Polydispersity	% Area
PDPPTTTT	58115	171677	100237	396425	2.954088	100.00

Figure S5. GPC chromatogram of PDPPTTTT.

2. Synthesis of acene-containing conjugated polymers

Synthesis of PDPPPy (1)

To a degassed 7 mL toluene solution of 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-pyrene (73 mg, 0.16 mmol), 2,5-di(2-dodecylhexadecyl)-3,6-bis-(5-bromothiophenyl)-1,4-diketopyrrolo[3,4-c]pyrrole (200 mg, 0.16 mmol), K_2CO_3 (1.68 mg, 0.008 mmol), and three drops of Aliquat 336 were added with 0.7 mL of degassed demineralized water. $Pd_2(dba)_3$ (3 mg, 2 mol%) and P(*o*-tolyl)$_3$ (4 mg, 8 mol%) were then added to the reaction mixture. The reaction solution was allowed to stir for 3 h at 90 °C under argon atmosphere. The slightly viscous dark blue solution was cooled down to room temperature. It was poured into a 200 mL methanol/HCl (1 M solution) (9:1 v/v) to obtain polymer precipitates. The crude polymer was collected by filtration and then purified by Soxhlet extraction with acetone, hexane, and chloroform, successively. The polymer was obtained as a dark blue solid (184 mg, 87%). M_n = 48.83 kDa, M_w = 265.7 kDa, and PDI = 5.44. ^{1}H NMR (300MHz); δ(ppm) 0.67-1.68 (br. 108H, aliphatic-H); 8.52-9.23 (br. 12H, aromatic-H). Anal. calcd for $C_{88}H_{132}N_2O_2S_2$: C 80.43, H 10.12, N 2.13, S 4.88; found: C 80.12, H 9.99, N 2.03, S, 4.59. ν_{max} (PDPPPy film on KBr pellet /cm^{-1}) : 2992-2809 (CH stretch), 1660 (C=O), 1552, 1427 (C=C aromatic stretch)

Synthesis of PDPPNDT, (2) [1]

2,5-Di(2-dodecylhexadecyl)-3,6-bis-(5-bromothiophenyl)-1,4-diketopyrrolo[3,4-c]pyrrole (150 mg, 0.012 mmol) and bis(trimethyl-stannyl)NDT (68.3 mg, 0.012 mmol) were dissolved in 15 mL of degassed anhydrous toluene. Subsequently, a catalyst, $Pd_2(dba)_3$ (1.5 mg, 2 mol%) and P(*o*-tolyl)$_3$ (2 mg, 8 mol%), were added to the reaction mixture, and the mixture was kept at 95 °C for 36 h under argon atmosphere. Then, the mixture was cooled down to room temperature, and the polymer precipitated in a 200 mL methanol/HCl (1 M solution) (9:1 v/v). The crude polymer was collected by filtration and then purified by Soxhlet extraction with acetone, hexane, and chloroform, successively. The resulting polymer was obtained as dark green-purple solid (114 mg, 72%). M_n = 30.7 kDa, M_w = 65.5 kDa, and PDI = 2.13. ^{1}H NMR (300MHz, $CDCl_3$); δ(ppm) 0.63-1.66 (br. 108H, aliphatic-H); 8.26-9.25 (br. 10H, aromatic-H). Anal. calcd for $C_{88}H_{134}N_2O_2S_4$: C 76.54, H 9.79, N 2.03, S 9.29; found: C 76.10, H 9.58, N 2.10, S 9.45. ν_{max} (PDPPNDT film on KBr pellet/cm^{-1}) : 2981-2805 (CH stretch), 1663 (C=O), 1551, 1428 (C=C aromatic stretch).

Synthesis of PDPPBDT, (3)

2,5-Di(2-dodecylhexadecyl)-3,6-bis-(5-bromothiophenyl)-1,4-diketopyrrolo[3,4-c]pyrrole (130 mg, 0.01 mmol) and bis(trimethyl-stannyl)BDT (65 mg, 0.01 mmol) were dissolved in 12 mL of degassed anhydrous toluene. Subsequently, a catalyst, $Pd_2(dba)_3$ (1.5 mg, 2 mol%) and P(*o*-tolyl)$_3$ (2 mg, 8 mol%), were added to the reaction mixture, and the mixture was kept at 95 °C for 37 h under argon atmosphere. Then, the mixture was cooled down to room temperature, and the polymer precipitated in a 200 mL methanol/HCl (1 M solution) (9:1 v/v). The crude polymer was collected by filtration and then purified by Soxhlet extraction with acetone, hexane, and chloroform, successively. The resulting polymer was obtained as dark green-purple solid (127 mg, 93%). M_n = 56.8 kDa, M_w = 136.7 kDa, and PDI = 2.40. ^{1}H NMR (300MHz); δ(ppm) 0.75-1.65 (br, 108H, aliphatic-H); 8.34-9.20 (br, 8H, aromatic-H). Anal. calcd for $C_{82}H_{128}N_2O_2S_4$: C 75.63, H 9.91, N 2.15, S 9.85; found: C 75.54, H 9.87, N 2.01, S 9.72. ν_{max} (PDPPBDT film on KBr pellet/cm^{-1}) : 3003-2802 (CH stretch), 1664 (C=O), 1555, 1431 (C=C aromatic stretch).

Synthesis of PDPPDTT (4)

PDPPDTT was synthesized with the same method used for PDPPBDT using 2,5-di(2-dodecylhexadecyl)-3,6-bis-(5-bromothiophenyl)-1,4-diketopyrrolo[3,4-c]pyrrole (100 mg, 0.08 mmol) and bis(trimethyl-stannyl)DTT (50 mg, 0.1 mmol). The polymerization mixture was kept at 95 °C for 2 days. The resulting polymer was obtained (100 mg, 95%). M_n = 68.0 kDa, M_w = 180.0 kDa, and PDI = 2.65. ^{1}H NMR (300MHz); δ(ppm) 0.75-1.66 (br, 108H, aliphatic-H); 8.24-9.25 (br, 6H, aromatic-H). Anal. calcd for $C_{78}H_{120}N_2O_2S_5$: C 73.30, H 9.46, N 2.19, S 12.54; found: C 72.18, H 9.33, N 1.99, S 12.63. ν_{max} (PDPPDTT film on KBr pellet/cm^{-1}) : 2990-2807 (CH stretch), 1664 (C=O), 1551, 1431 (C=C aromatic stretch).

Synthesis of PDPPTTTT (5)

PDPPDTT was synthesized with the same method used for PDPPBDT using bis(trimethyl-stannyl)TTTT (46 mg, 0.08 mmol) and 2,5-di(2-dodecylhexadecyl)-3,6-bis-(5-bromothiophenyl)-1,4-diketopyrrolo[3,4-c]pyrrole. The polymerization mixture was kept at 95 °C for 10 h. The pure polymer was obtained as a dark green-purple solid (106 mg, 98%). M_n = 58.1 kDa, M_w = 171.7 kDa, and PDI = 2.95. ^{1}H NMR (300MHz); δ(ppm) 0.72-1.68 (br, 108H, aliphatic-H); 8.21-9.24 (br, 6H, aromatic-H). Anal. calcd for $C_{80}H_{120}N_2O_2S_6$: C 72.02, H 9.07, N 2.10, S 14.42; found: C 72.17, H 9.11, N 1.99, S 14.88. ν_{max} (PDPPTTTT film on KBr pellet/cm^{-1}) : 3002-2821 (CH stretch), 1664 (C=O), 1551, 1434 (C=C aromatic stretch).

3. FT-IR spectra of the monomers and polymers.

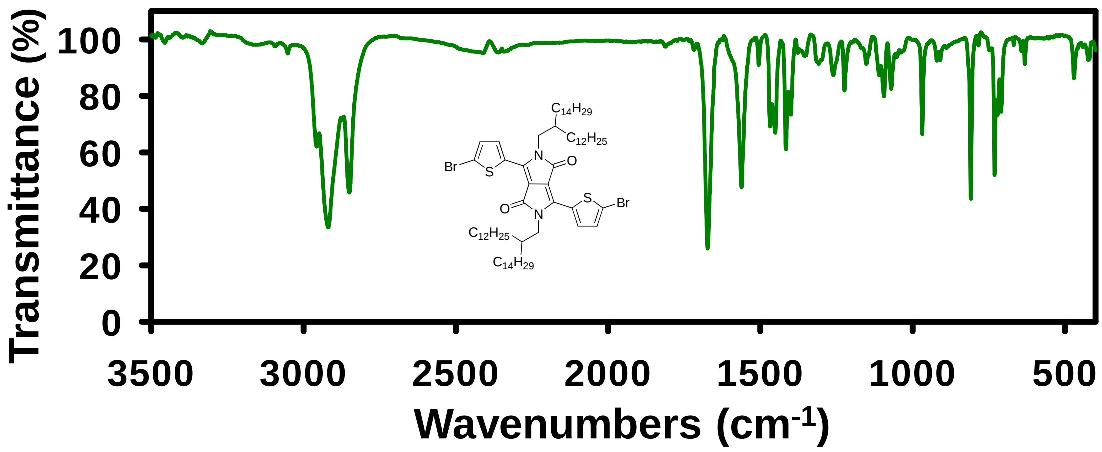


Figure S6. FT-IR spectrum of 2,5-di(2-dodecylhexadecyl)-3,6-bis-(5-bromothiophenyl)-1,4-diketopyrrolo[3,4-c]pyrrole. ν_{max} (KBr pellet/cm^{-1}) : 2998-2798 (CH stretch), 1673 (C=O), 1561, 1416 (C=C aromatic stretch).

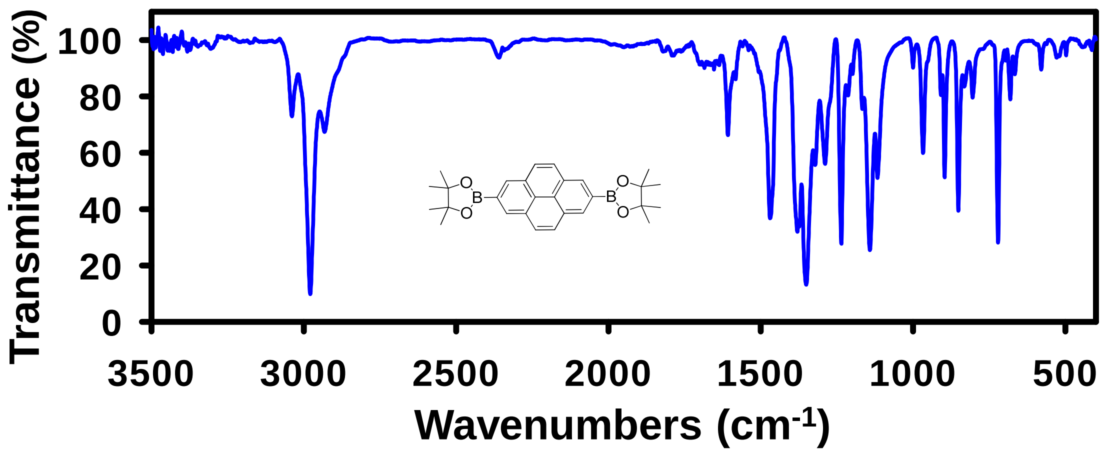


Figure S7. FT-IR spectrum of 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-pyrene,. ν_{max} (KBr pellet/cm^{-1}) : 3065-2858 (CH stretch), 1462 (C=C aromatic stretch).

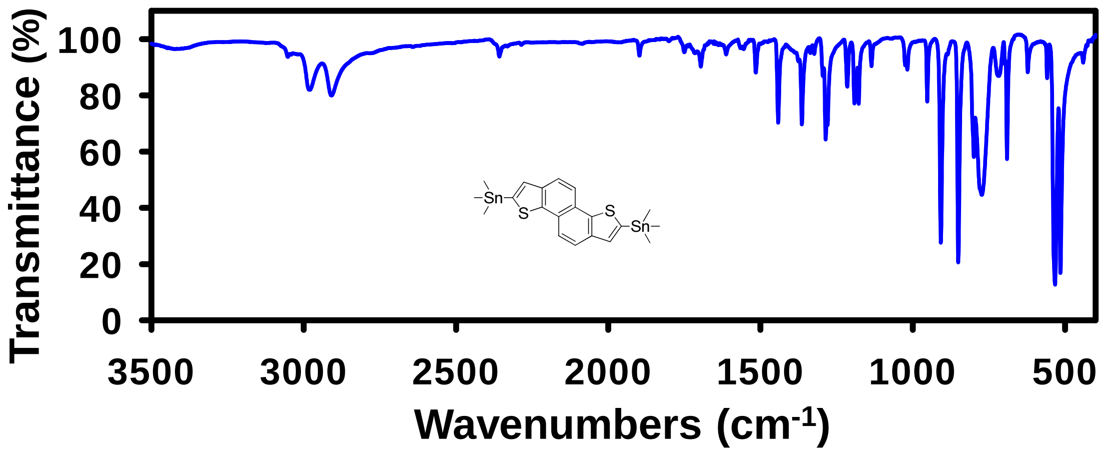


Figure S8. FT-IR spectrum of bis(trimethyl-stannyl)NDT. ν_{max} (KBr pellet/cm^{-1}) : 3009-2845 (CH stretch), 1442 (C=C aromatic stretch), 532 (Sn-C stretch).

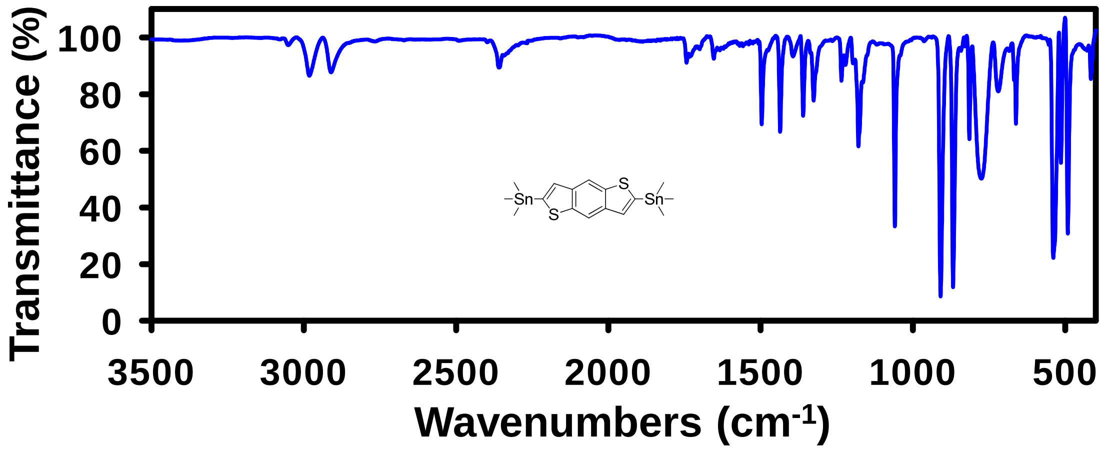


Figure S9. FT-IR spectrum of bis(trimethyl-stannyl)BDT. ν_{max} (KBr pellet/cm^{-1}) : 3018-2863 (CH stretch), 1496 (C=C aromatic stretch), 539 (Sn-C stretch).

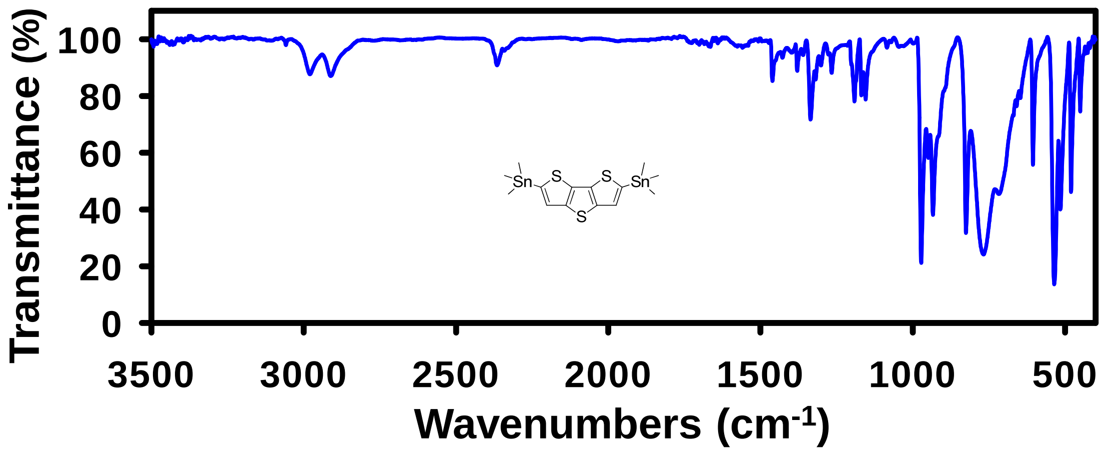


Figure S10. FT-IR spectrum of bis(trimethyl-stannyl)DTT. ν_{max} (KBr pellet/cm^{-1}) : 3023-2834 (CH stretch), 1460 (C=C aromatic stretch), 535 (Sn-C stretch).

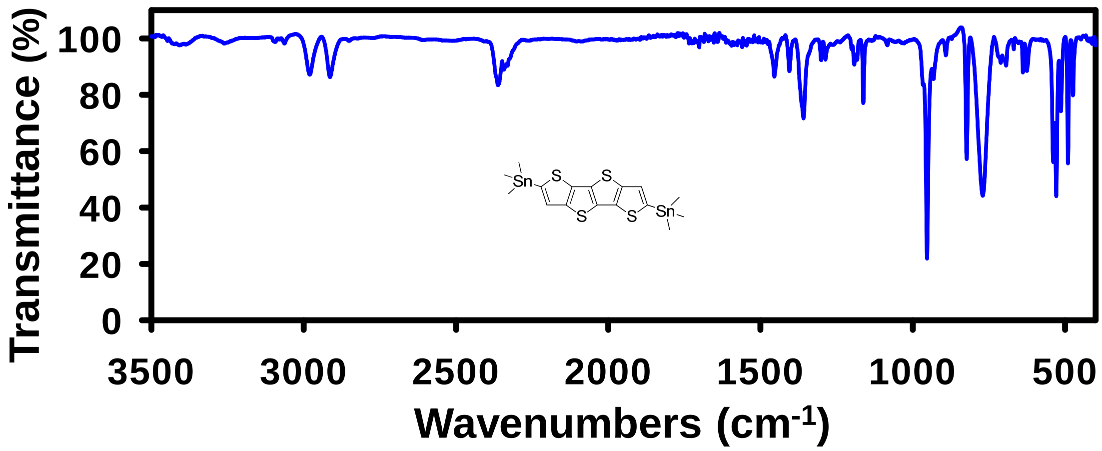


Figure S11. FT-IR spectrum of bis(trimethyl-stannyl)TTTT. ν_{max} (KBr pellet/cm^{-1}) : 3014-2879 (CH stretch), 1454 (C=C aromatic stretch), 528 (Sn-C stretch).

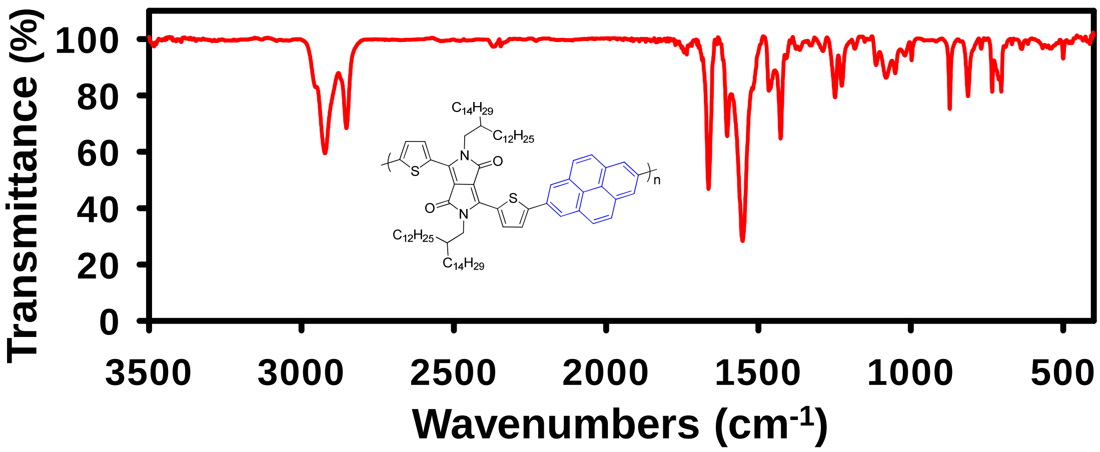


Figure S12. FT-IR spectrum of PDPPPy. ν_{max} (PDPPPy film on KBr pellet/cm^{-1}) : 2992-2809 (CH stretch), 1660 (C=O), 1552, 1427 (C=C aromatic stretch).

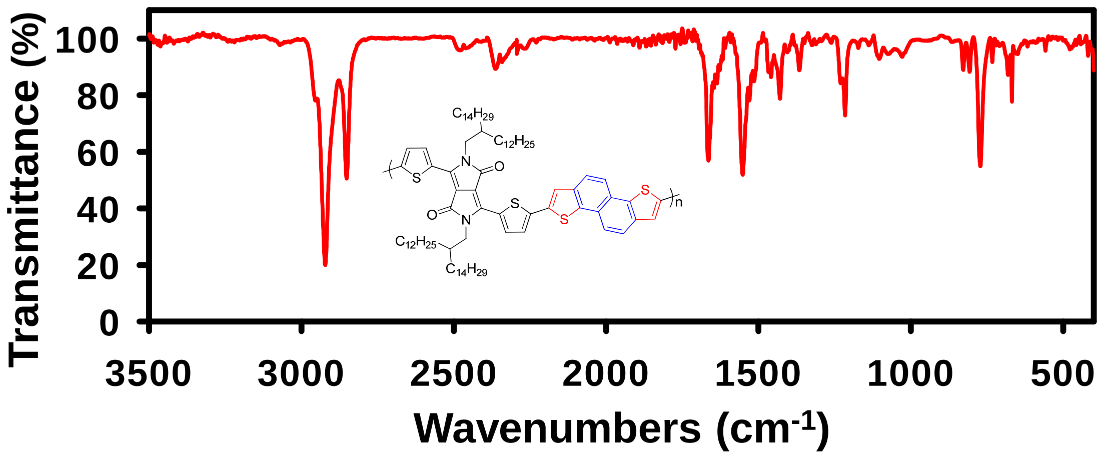


Figure S13. FT-IR spectrum of PDPPNDT. ν_{max} (PDPPNDT film on KBr pellet/cm^{-1}) : 2981-2805 (CH stretch), 1663 (C=O), 1551, 1428 (C=C aromatic stretch).

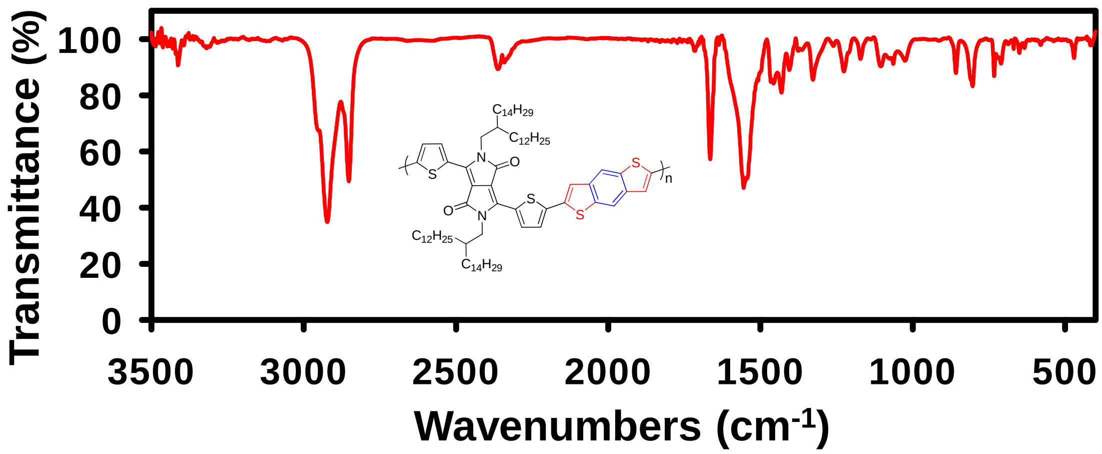


Figure S14. FT-IR spectrum of PDPPBDT. ν_{max} (PDPPBDT film on KBr pellet/cm^{-1}) : 3003-2802 (CH stretch), 1664 (C=O), 1555, 1431 (C=C aromatic stretch).

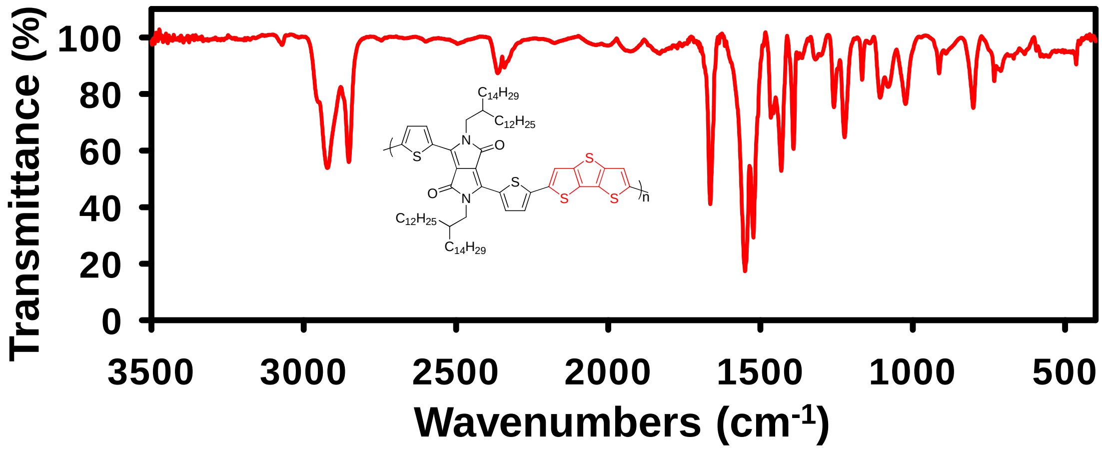


Figure S15. FT-IR spectrum of PDPPDTT. ν_{max} (PDPPDTT film on KBr pellet/cm^{-1}) : 2990-2807 (CH stretch), 1664 (C=O), 1551, 1431 (C=C aromatic stretch).

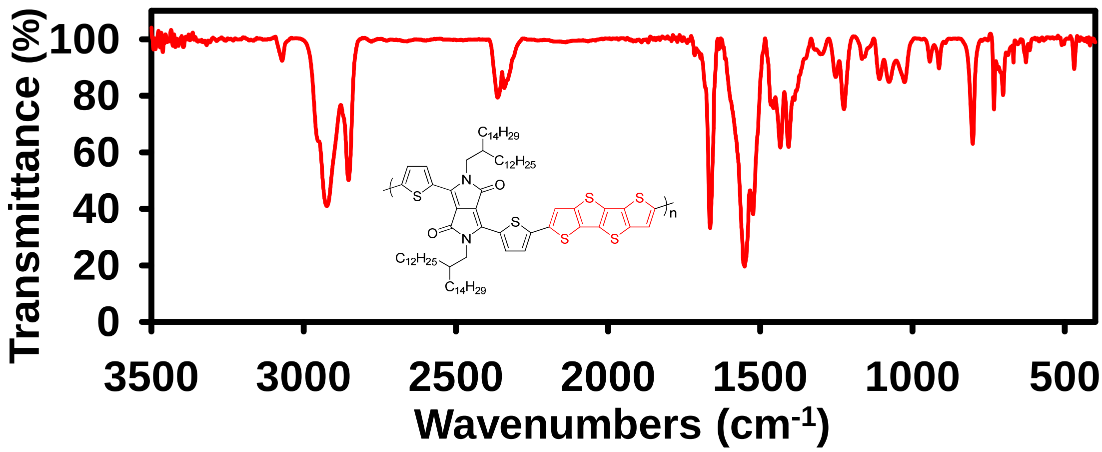


Figure S16. FT-IR spectrum of PDPPTTTT. ν_{max} (PDPPTTTT film on KBr pellet/cm^{-1}) : 3002-2821 (CH stretch), 1664 (C=O), 1551, 1434 (C=C aromatic stretch).

4. NMR spectra of acene-containing conjugated polymers

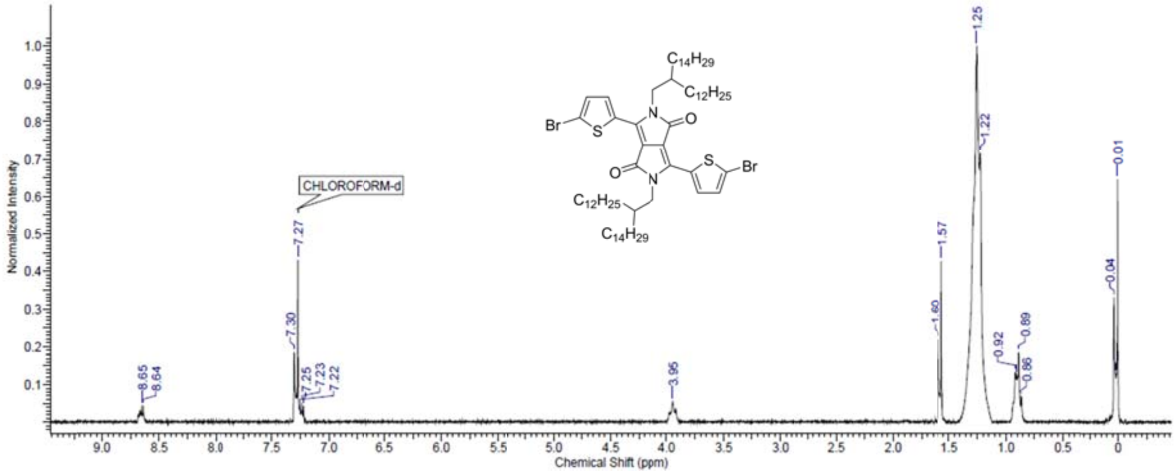


Figure S17. [1]H NMR of 2,5-di(2-dodecylhexadecyl)-3,6-bis-(5-bromothiophenyl)-1,4-diketopyrrolo[3,4-c]pyrrole in $CDCl_3$.

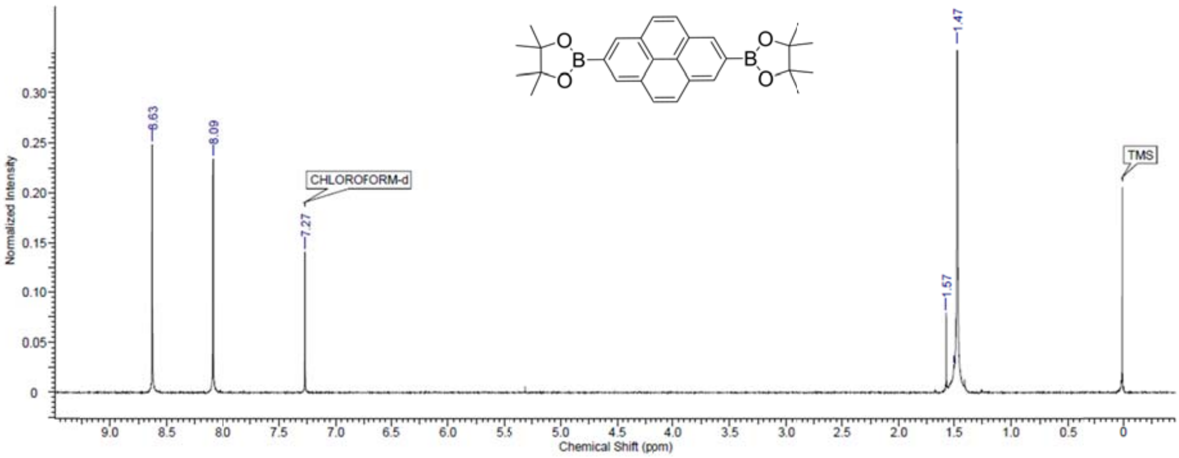


Figure S18. [1]H NMR of 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-pyrene in $CDCl_3$.

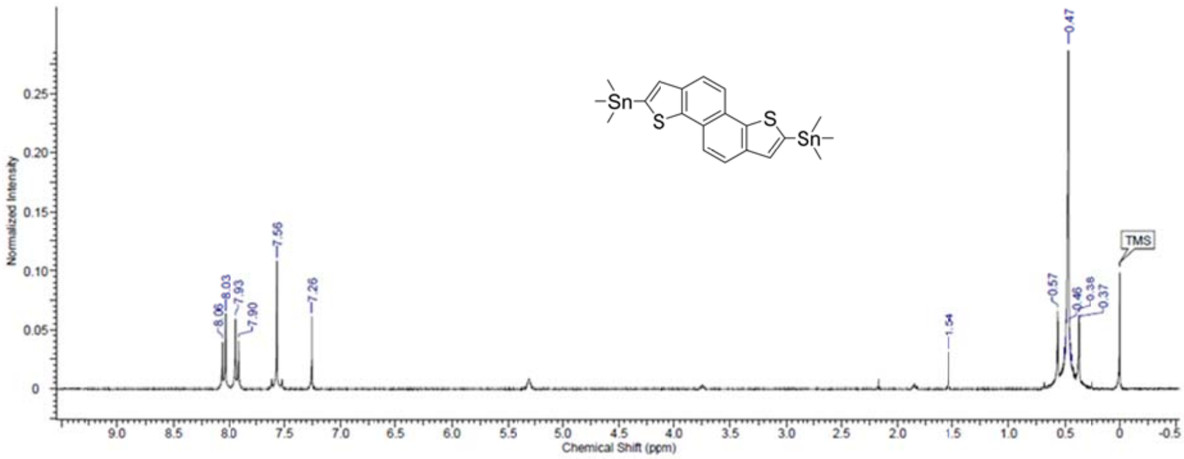


Figure S19. ^{1}H NMR of bis(trimethyl-stannyl)NDT in $CDCl_3$.

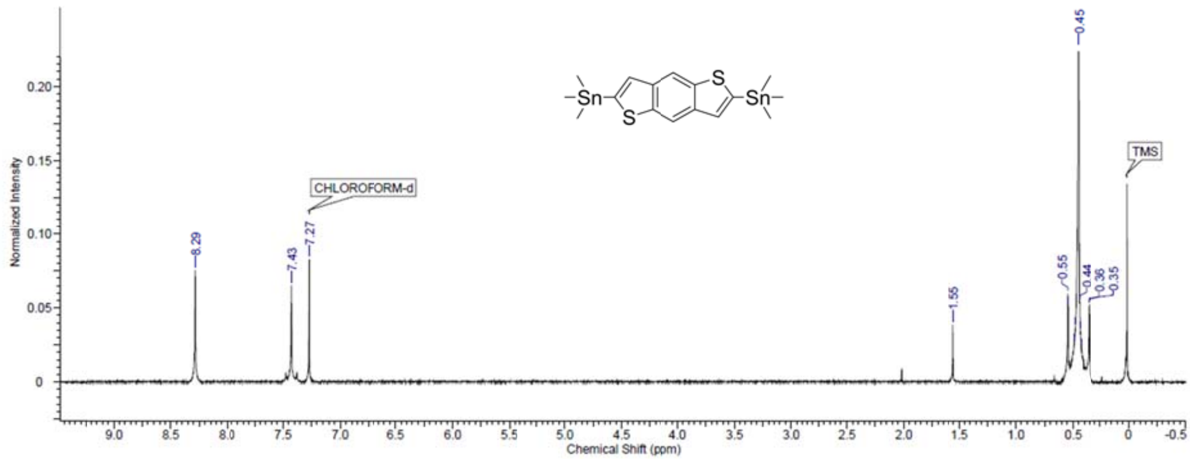


Figure S20. ^{1}H NMR of bis(trimethyl-stannyl)BDT in $CDCl_3$.

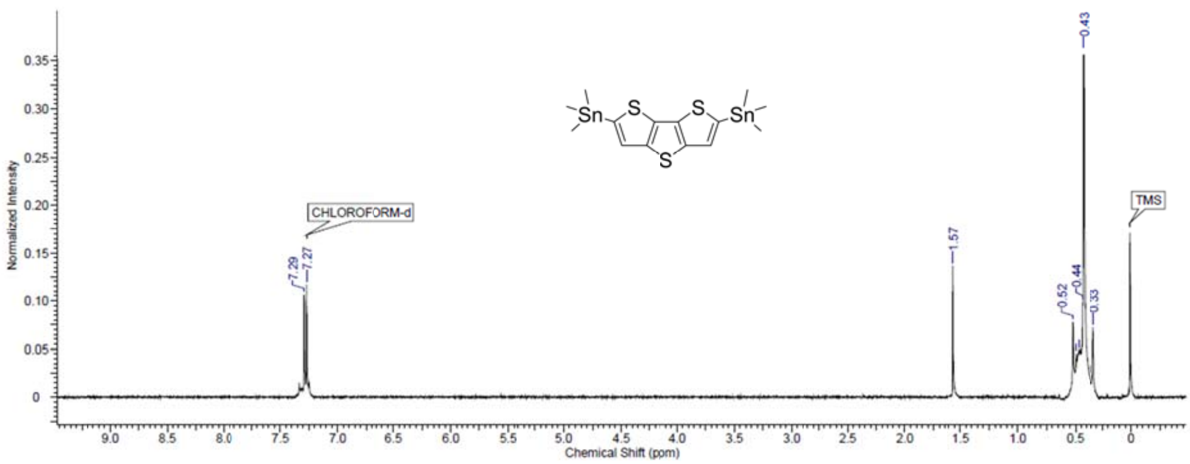


Figure S21. ^{1}H NMR of bis(trimethyl-stannyl)DTT in $CDCl_3$.

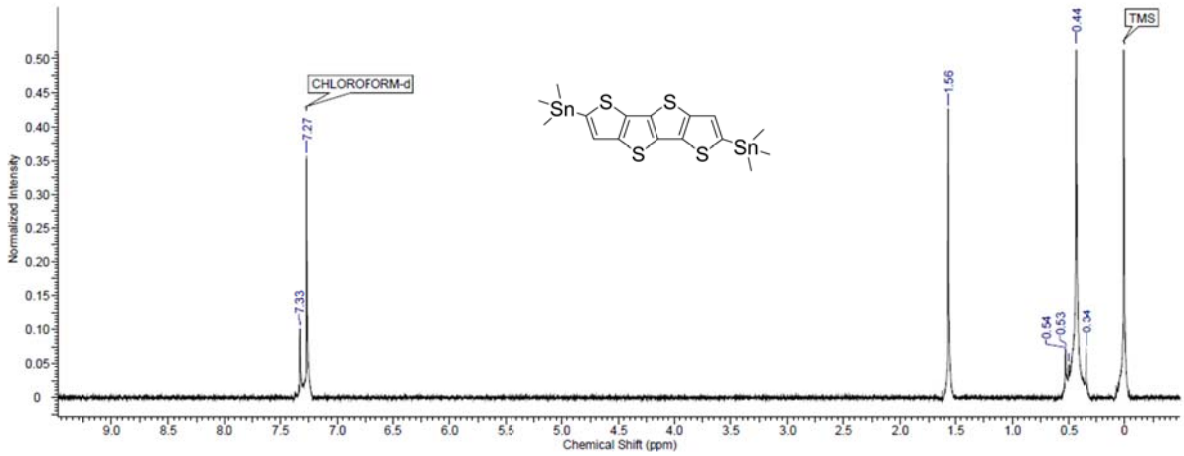


Figure S22. ^{1}H NMR of bis(trimethyl-stannyl)TTTT in $CDCl_3$.

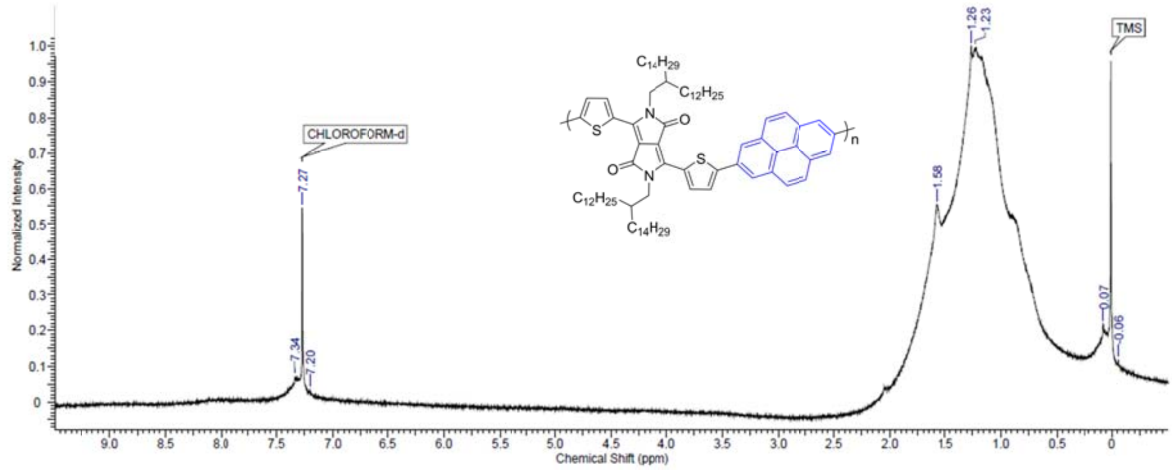


Figure S23. ^{1}H NMR of PDPPPy in $CDCl_3$.

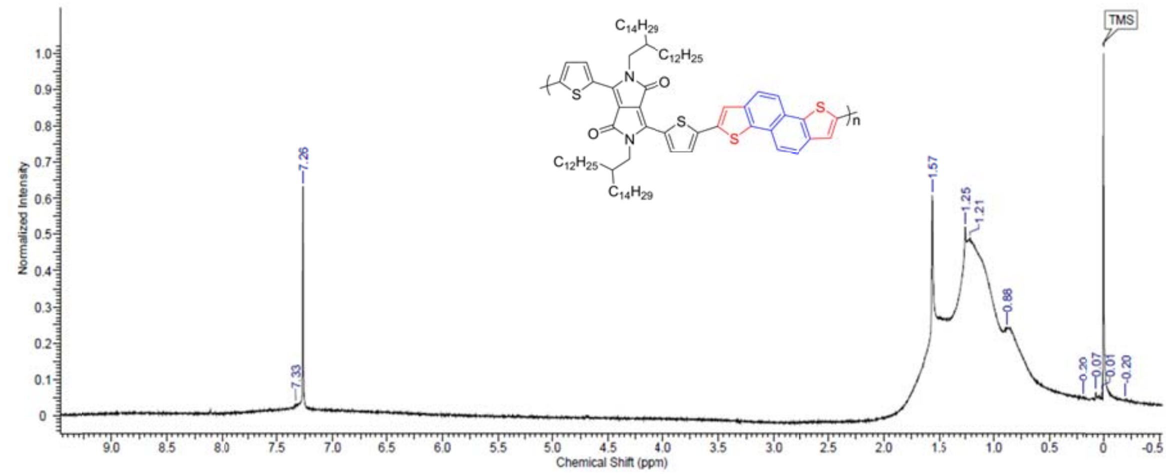


Figure S24. ^{1}H NMR of PDPPNDT in $CDCl_3$.

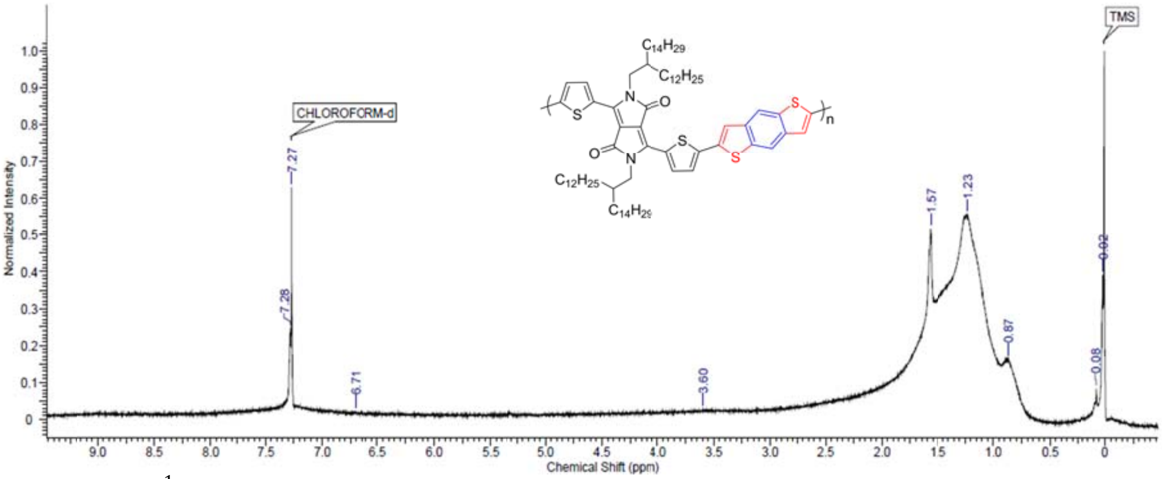


Figure S25. ^{1}H NMR of PDPPBDT in $CDCl_3$.

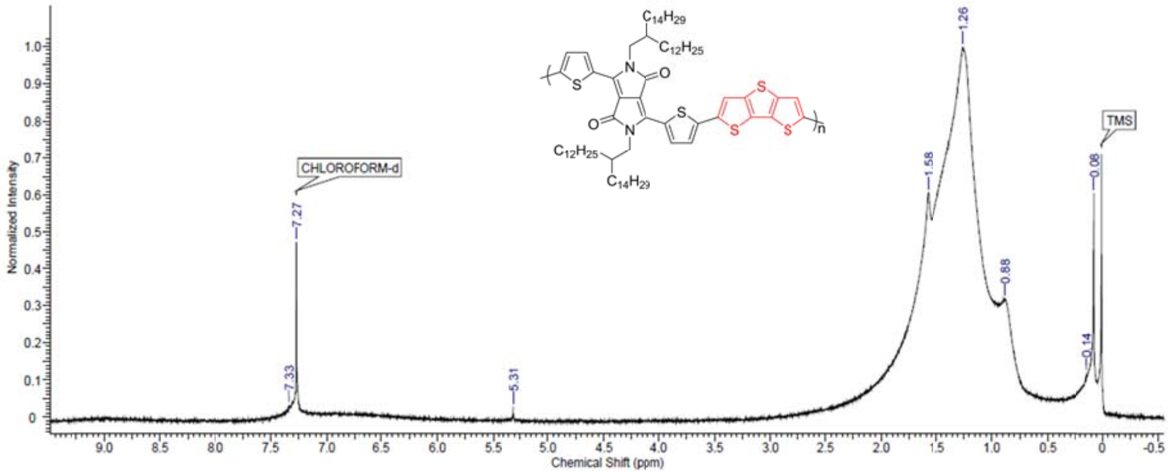


Figure S26. ^{1}H NMR of PDPPDTT in $CDCl_3$.

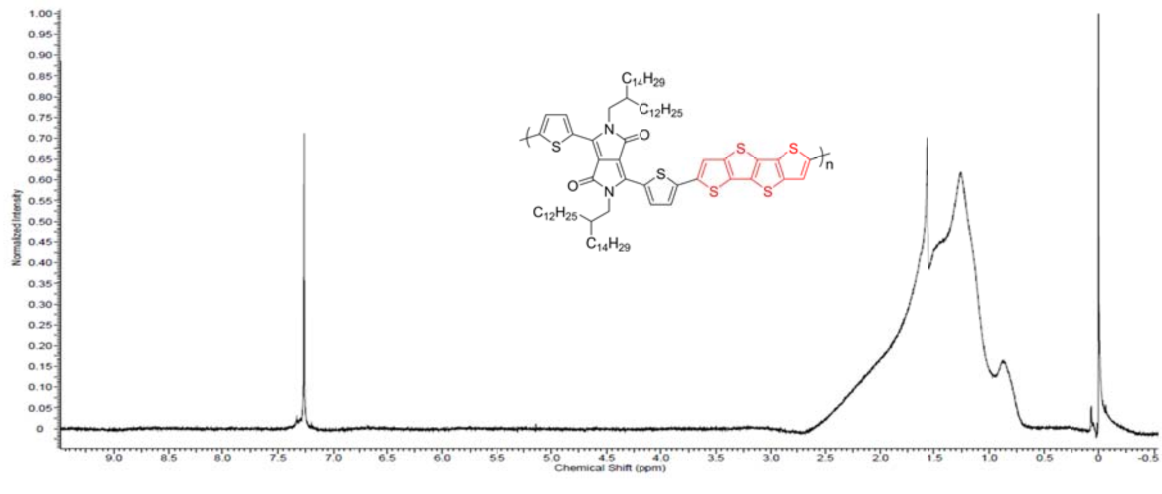


Figure S27. ^{1}H NMR of PDPPTTTT in $CDCl_3$.

5. Thermal analysis data of acene-containing conjugated polymers

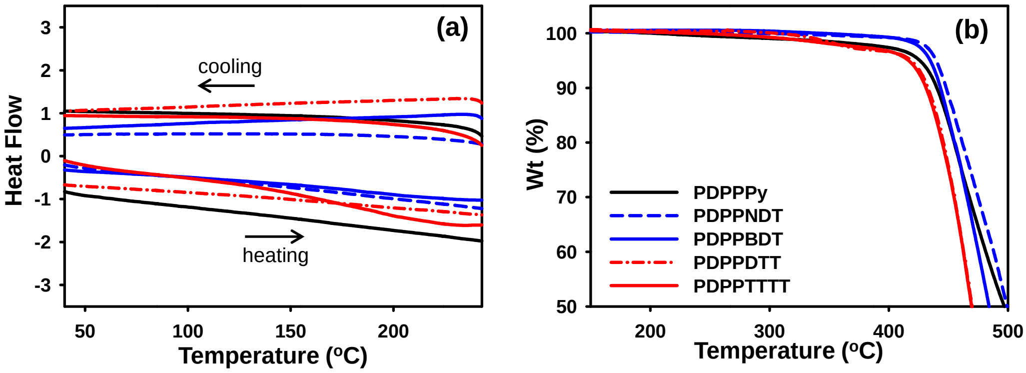


Figure S28. (a) DSC and (b) TGA thermograms of PDPPPy (black), PDPPNDT (blue dashed line), PDPPBDT (blue solid line), PDPPDTT (red dashed-dot line), and PDPPTTTT (red solid line). T_d = 432 °C, 436 °C, 439 °C, 432 °C, and 433 °C for PDPPPy, PDPPNDT, PDPPBDT, PDPPDTT, and PDPPTTTT, respectively.

6. GI-XRD data of the unannealed films of acene-containing conjugated polymers

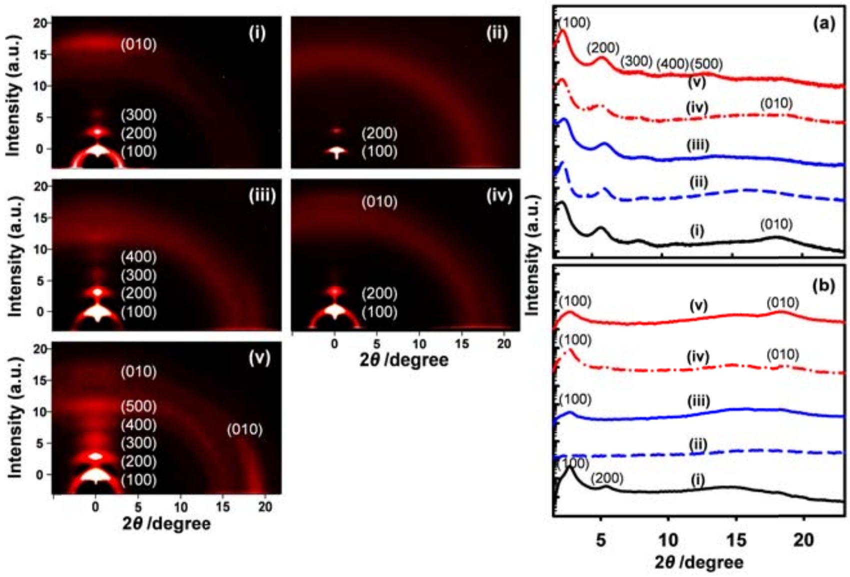


Figure S29. 2-D GI-XRD patterns, (a) out-of-plane and (b) in-plane XRD patterns of unannealed films. (i) PDPPPy (black solid line), (ii) PDPPNDT (blue dashed line), (iii) PDPPBDT (blue solid line), (iv) PDPPDTT (red dash-dot-dashed line), and (v) PDPPTTTT (red solid line).

Table S1. Peak assignments for the out-of-plane and in-plane XRD patterns of thin films annealed at 200 °C.

		Out-of-plane					In-plane		
		(100)	(200)	(300)	(400)	(500)	(100)	(200)	(010)
PDPPPy	2θ (deg)	2.91	5.68	8.40	11.20		2.67	5.40	
	d-spacing (Å)	22.94	11.76	7.95	5.97		25	12.37	
PDPPNDT	2θ (deg)	3.08	6.07	8.97	11.64	13.67			18.16
	d-spacing (Å)	21.68	11	7.45	5.75	4.90			3.69
PDPPBDT	2θ (deg)	3	5.91	8.70	11.18	13.77			17.93
	d-spacing (Å)	22.26	11.3	7.68	5.98	4.86			3.74
PDPPDTT	2θ (deg)	2.88	5.78	8.54	11.36	13.67	2.65		18.93
	d-spacing (Å)	23.15	11.56	7.82	5.89	4.90	25.19		3.54
PDPPTTTT	2θ (deg)	2.98	5.89	8.70	11.40	13.71			18.6
	d-spacing (Å)	22.4	11.34	7.68	5.87	4.88			3.60

7. AFM height images of the polymer films

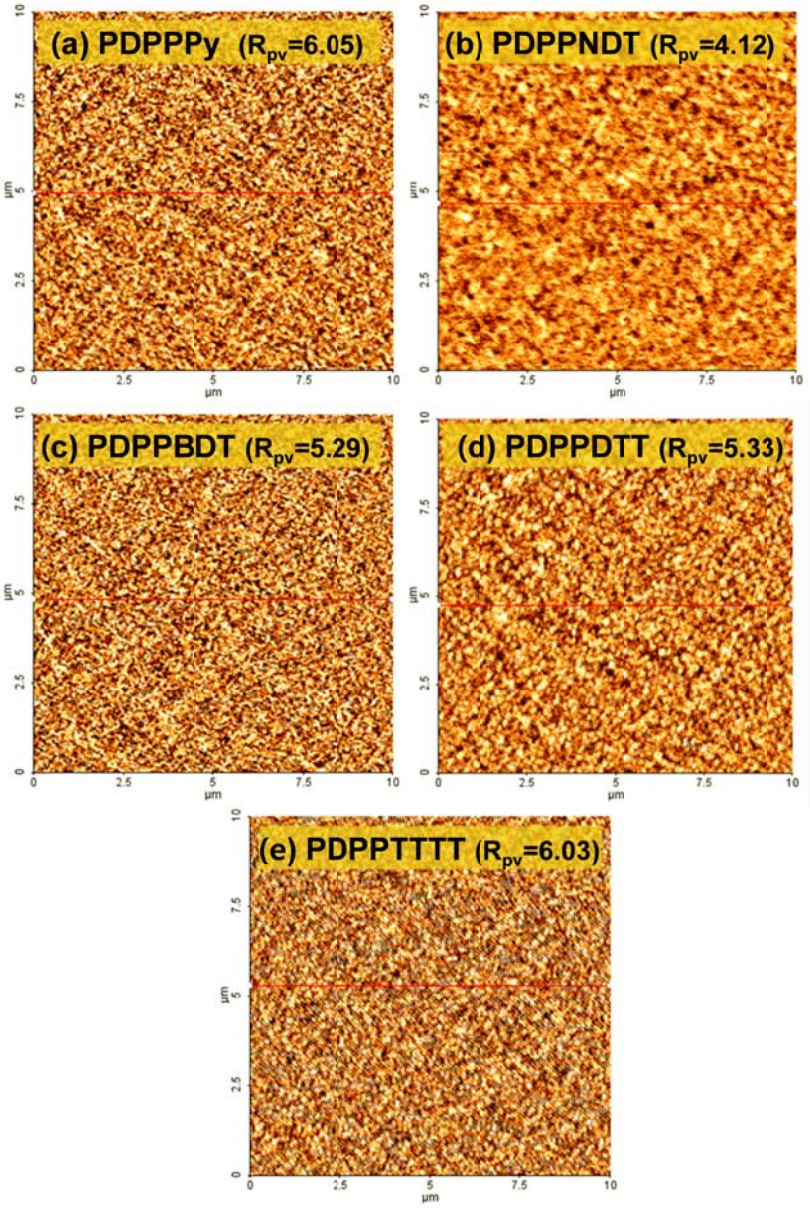


Figure S30. AFM height images of (a) PDPPPy, (b) PDPPNDT, (c) PDPPBDT, (d) PDPPDTT, and (e) PDPPTTTT thin films annealed thermally at 200 °C.

8. Transfer and output curves of TFTs made of the polymers

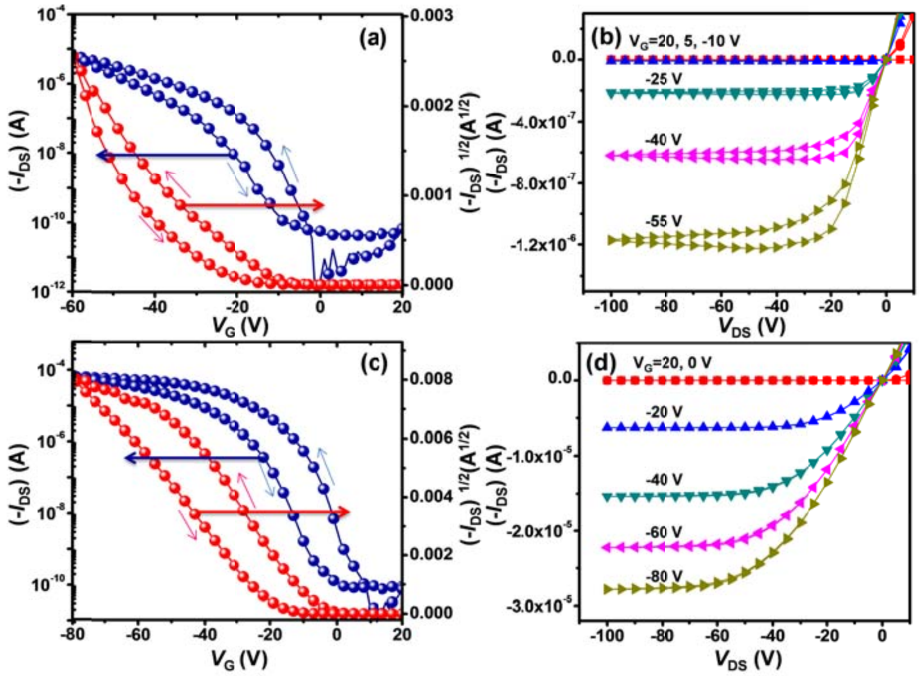


Figure S31. (a), (c) Transfer and (b), (d) output curves of TFTs made of PDPPPy. V_{DS} = -100 V (a), (b) unannealed films and (c), (d) films annealed at 200 °C.

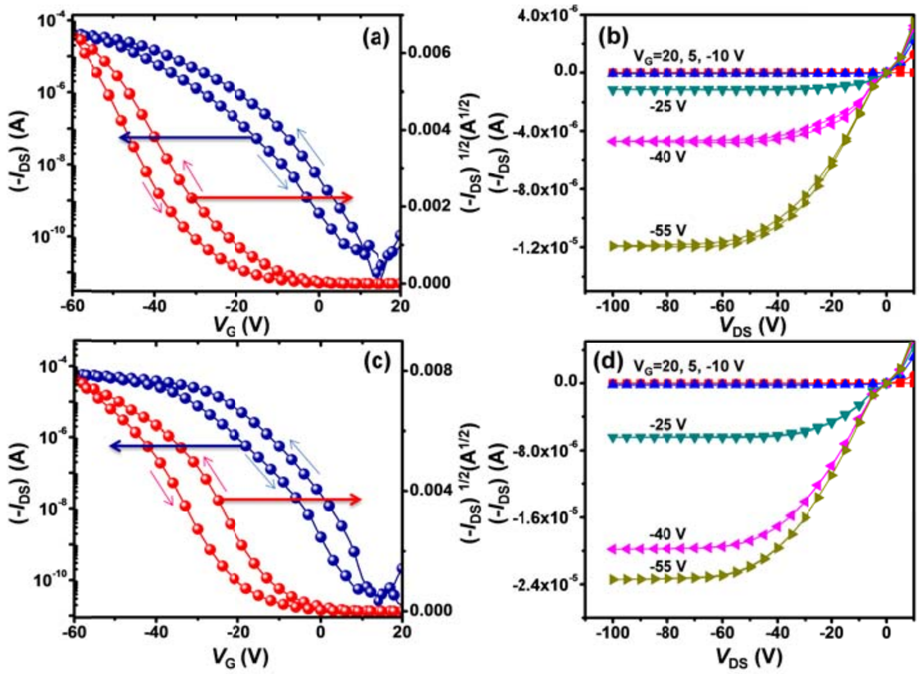


Figure S32. (a), (c) Transfer and (b), (d) output curves of TFTs made of PDPPNDT. V_{DS} = -100 V (a), (b) unannealed films and (c), (d) films annealed at 200 °C.

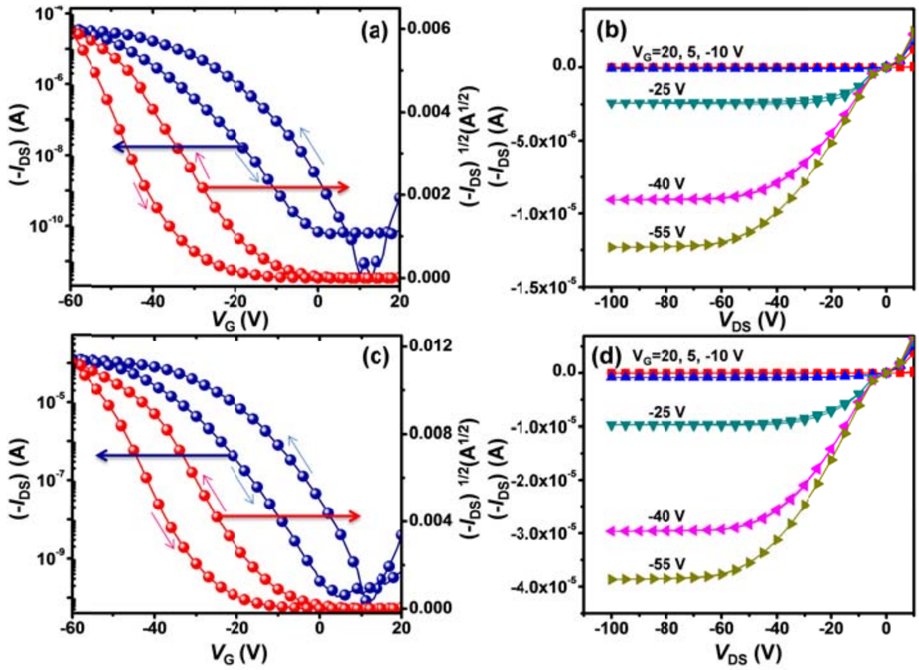


Figure S33. (a), (c) Transfer and (b), (d) output curves of TFTs made of PDPPBDT. V_{DS} = -100 V (a), (b) unannealed films and (c), (d) films annealed at 200 °C.

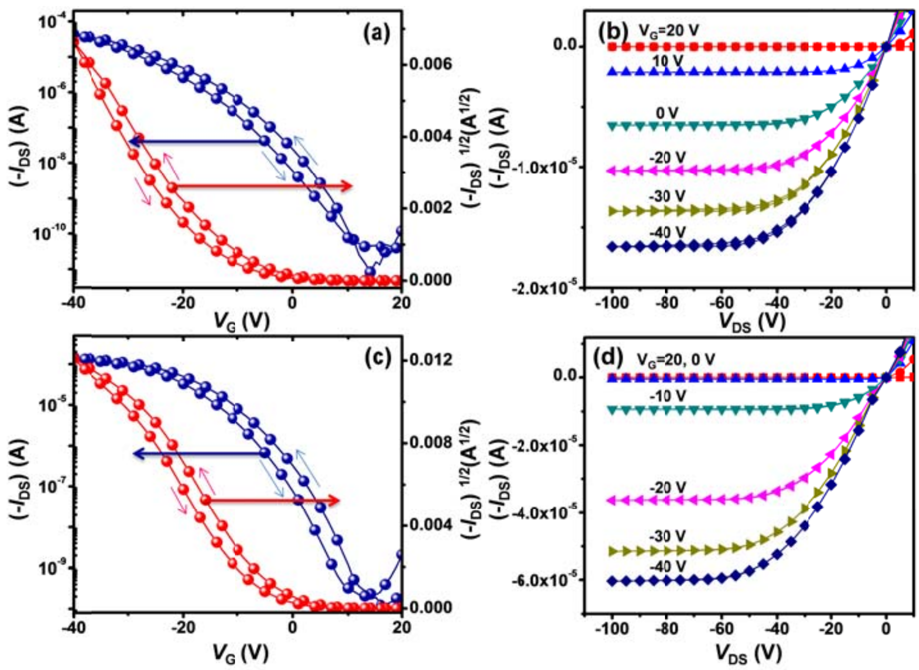


Figure S34. (a), (c) Transfer and (b), (d) output curves of TFTs made of PDPPDTT. V_{DS} = -100 V (a), (b) unannealed films and (c), (d) films annealed at 200 °C.

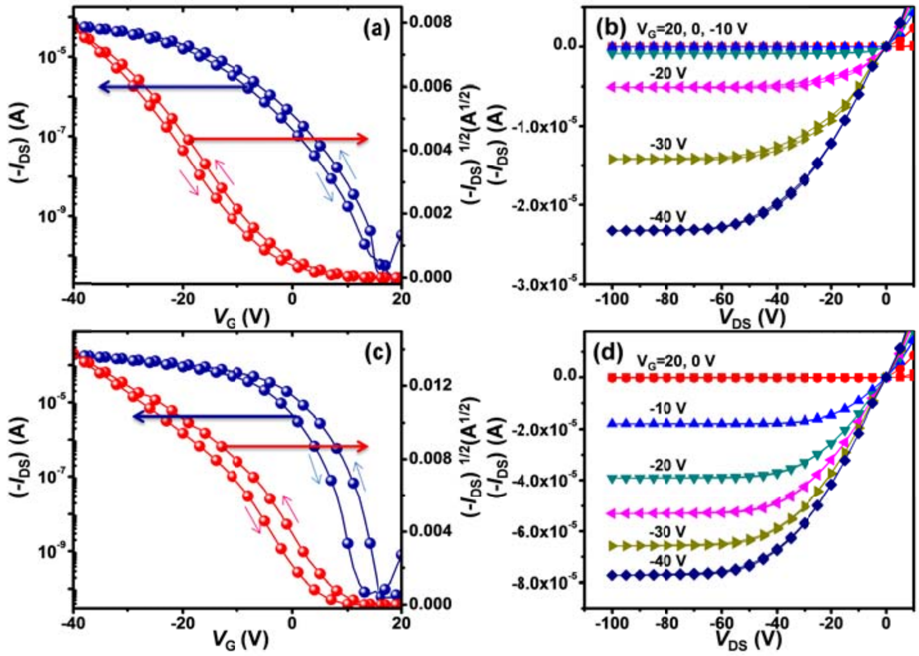


Figure S35. (a), (c) Transfer and (b), (d) output curves of TFTs made of PDPPTTTT. V_{DS} = -100 V (a), (b) unannealed films and (c), (d) films annealed at 200 °C.

9. Properties of resistor-loaded inverters

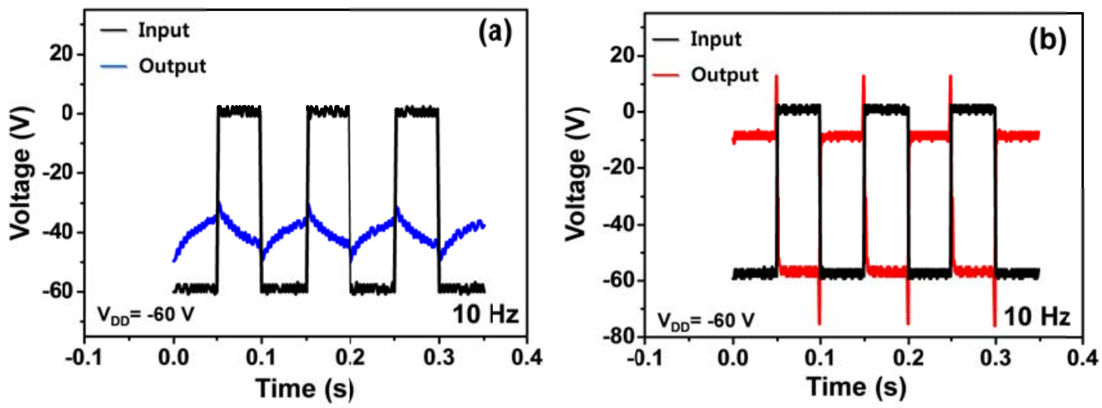


Figure S36. Resistor loaded inverters. (a) poly(3-hexylthiophene) (P3HT)-based RL-inverter at 10 Hz. (hole mobility of 5 x 10^{-3} cm^2 V^{-1} s^{-1}). (b) PDPPTTTT-based RL-inverter at 10 Hz exhibiting a hole mobility of 3.2 cm^2 V^{-1} s^{-1} at V_{DS} = -100 V.

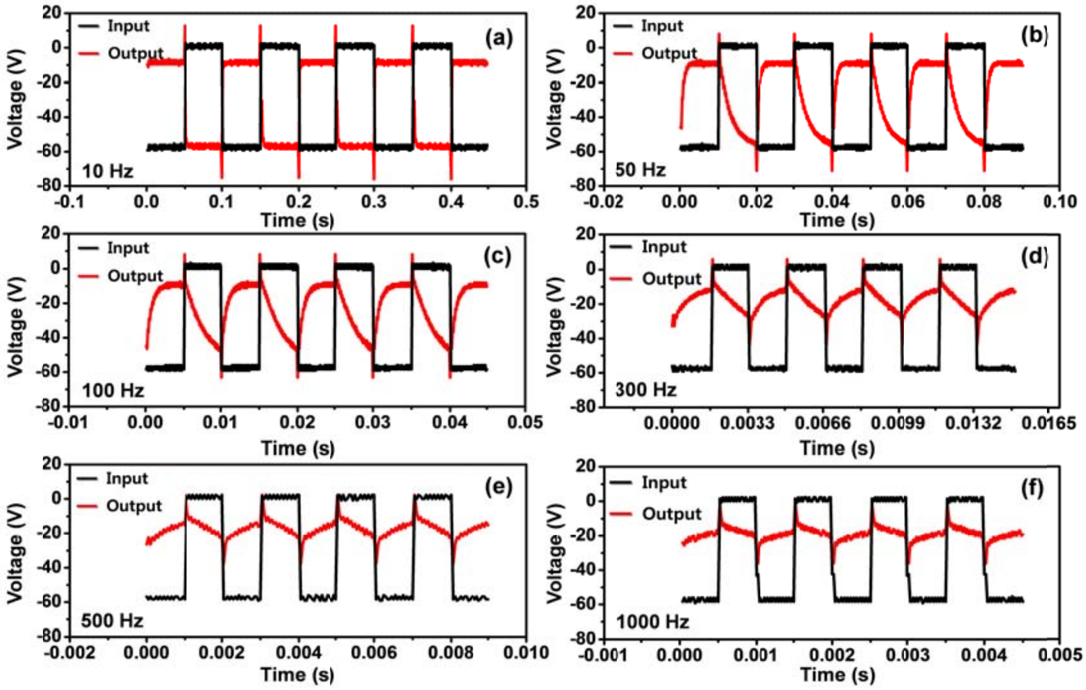


Figure S37. Dynamic output voltage response of PDPPTTTT polymer-based RL-inverter. Output responses when the input voltage was switched from 10 Hz to 1 kHz.

Figure S37 shows the drain current output (V_{OUT}) of PDPPTTTT-based inverter in response to 10 Hz and 1kHz square-wave gate voltage input (V_{IN}) signals when the drain voltage (V_{DD}) was fixed at -60 V. It is clearly observed that the output voltage (V_{OUT}) of the inverter tracks the trace of the input square wave gate voltage signal ($V_G = V_{IN}$) even at 1 kHz.

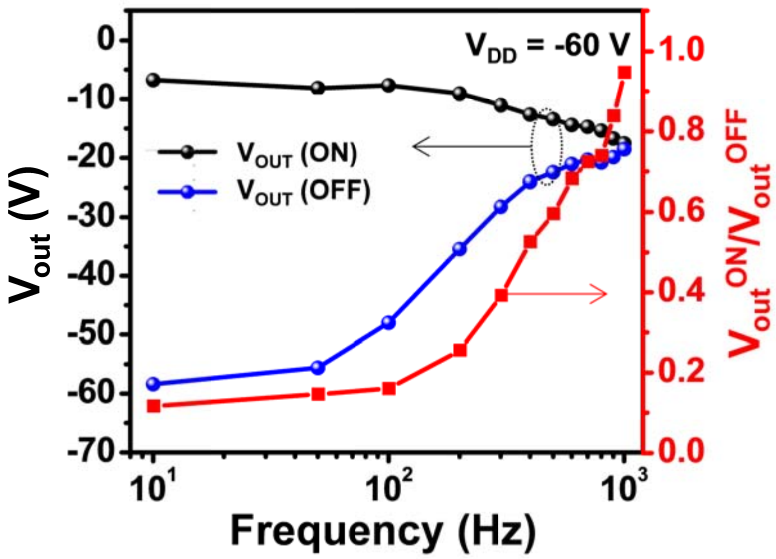


Figure S38. Output voltages at "ON" and "OFF" states of PDPPTTTT-based resistor-loaded inverter as a function of switching frequency. *Square: V_{out}^{ON} / V_{out}^{OFF}

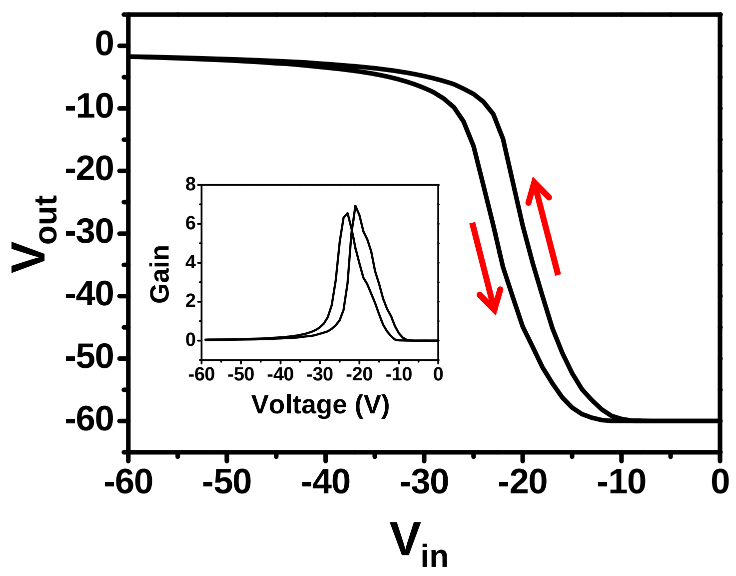


Figure S39. Input-output voltage characteristics of the PDPPTTTT RL-inverter measured with increasing and decreasing input voltage, V_{IN}. (V_{DD}=-60 V). Inset: voltage gain in the inverter as a function of V_{IN}.

The voltage transfer characteristics (V_{IN}-V_{OUT}) and corresponding gain of the RL inverter based on DPPPTTTT for forward (i.e., from 0 V to -60 V) and reverse (i.e., from -60 V to 0 V) scans at V_{DD} = -60 V are shown in **Figure S39**. It is clear that the output voltage switched between logic from "1" state (–60 V) to the "0" state (~ -2.0 V) when the input signal was swept from -60 V to 0 V. The RL inverter shows a clear switching response with moderate hysteresis (ΔV = 3 V) between 0 V and -60 V with a voltage gain (i.e., dV_{OUT}/dV_{IN}) of almost 7.

Reference

1. Lee, T. W.; Lee, D. H.; Shin, J.; Cho, M. J.; Choi, D. H. *J. Polym. Sci. Part A: Polym. Chem.* **2013**, *51*, 5280.