Supplementary information

Effect of Alkyl Spacer Length on the Electrical Performance of Diketopyrrolopyrrole-Thiophene Vinylene Thiophene Polymer Semiconductors

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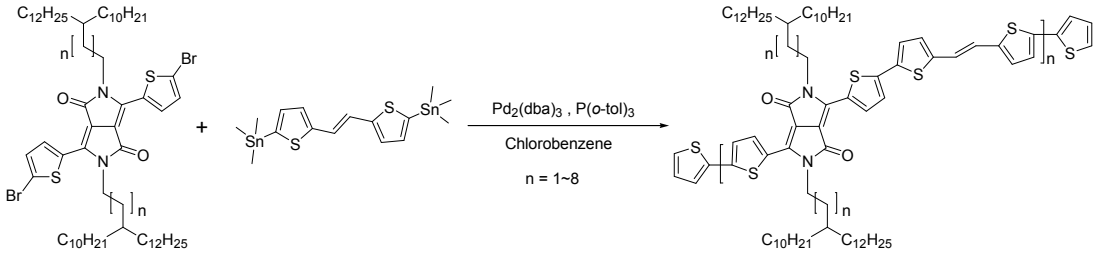
S1. Materials and Methods

All chemicals were purchased from Aldrich and Alpha : thiophene-2-carbonitrile, dimethyl succinate, 11-(bromomethyl)tricosane, DMF, THF, NBS, n-BuLi, and were used without further purification.3,6-Bis(5-bromothiophen-2-yl)-2,5-bis(2-decyltetradecyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione[S1] ,(E)-1,2-di(thiophen-2-yl)ethene[S2] , and ((2-decylpentadecyl)bromide,(2-decylhexadecyl)bromide, (2-decylheptadecyl)bromide, (2-decyloctadecyl)bromide, (2-decylnonadecyl)bromide, (2-decylicosyl)bromide, (2-decylhenicosyl)bromide, (2-decyldocosyl)bromide) were synthesized via published literature procedures.[S3]

^{1}H-NMR and ^{13}C-NMR spectra were recorded using a Bruker AM-300 and DRX-500 MHz spectrometers. Molecular weights and polydispersities of the copolymers were determined by gel permeation chromatography(GPC) analysis with polystyrene standard calibration (waters high-pressure GPC assembly Model M515 pump, u-Styragel columnsof HR4, HR4E, HR5E, with 500 and 100 Å , refractive index detectors, solvent chloroform). Thermal analysis was performed using a TA TGA 2100 thermogravimetric analyzer under a nitrogen atmosphere at a heating rate of 10°C/min. Differential scanning calorimeter (DSC) was conducted under nitrogen using a TA instrument 2100 DSC. The sample was heated at 10°C /min from 30°C to 250°C. UV–vis absorption spectra were measured using a Perkin-Elmer LAMBDA-900 UV spectrophotometer. Cyclic voltammetry (CV) was performed using an EG and G Parc model 273 Å potentiostat/galvanostat system with a three-electrode cell in a solution containing Bu_4NClO_4 (0.1 M) in acetonitrile at a scan rate of 100 mV/s. The polymer films were coated on a square carbon electrode (0.50 cm^2) by dipping the electrode into the corresponding solvents then drying in air. A Pt wire was used as the counter electrode, and an $Ag/AgNO_3$ (0.1 M) electrode was used as the reference electrode.

General Procedure for Stille Polymerization and Polymer Purification



Synthesis of P-25-DPP-TVT

The polymer was prepared using a palladium-catalyzed Stille coupling reaction. In a Schlenk flask 25-DPPBr[3] (0.5 g, 0.4 mmol) and 1,2-(E)-bis(5-(trimethylstannyl)thiophene-2-yl)ethene (0.22 g, 0.4 mmol) were dissolved in dry chlorobenzene (7.5 mL). After degassing under nitrogen for 60 min, $Pd_2(dba)_3$ (8 mg) and P(*o*Tol)$_3$ (11 mg) were added to the mixture, which was then stirred for 48 h at 110 °C. The end-capping was carried out by 2-bromothiophene and tributyl(thiophen-2-yl)stannane were injected 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, toluene, and chloroform, successively. The final product, P-25-DPP-TVTS was obtained by precipitation in methanol. Yield : 0.46g. ^{1}H-NMR (500 MHz, $CDCl_3$, ppm): δ8.98 (broad, 4H), 7.49-6.61 (broad, 6H), 4.07 (broad, 4H), 1.96-1.26 (broad, 86H), 0.88 (broad,12H).

Synthesis of P-26-DPP-TVT

The synthetic procedure is similar as described for P-25-DPP-TVT. Yield : 0.45g. ^{1}H-NMR (500 MHz, $CDCl_3$, ppm): δ9.00 (broad, 4H), 7.49-6.58 (broad, 6H), 4.08 (broad, 4H), 2.00-1.23 (broad, 90H), 0.88 (broad,12H).

Synthesis of P-27-DPP-TVT

The synthetic procedure is similar as described for P-25-DPP-TVT. Yield : 0.44g. ^{1}H-NMR (500 MHz, $CDCl_3$, ppm): δ8.96 (broad, 4H), 7.46-6.28 (broad, 6H), 4.10 (broad, 4H), 2.04-1.24 (broad, 94H), 0.86 (broad,12H).

Synthesis of P-28-DPP-TVT

The synthetic procedure is similar as described for P-25-DPP-TVT. Yield : 0.47g. ^{1}H-NMR (500 MHz, $CDCl_3$, ppm): δ8.97 (broad, 4H), 7.39-6.87 (broad, 6H), 4.1 (broad, 4H), 1.81-1.26 (broad, 98H), 0.88 (broad,12H).

Synthesis of P-29-DPP-TVT

The synthetic procedure is similar as described for P-25-DPP-TVT. Yield : 0.42g. ^{1}H-NMR (500 MHz, $CDCl_3$, ppm): δ8.86 (broad, 4H), 7.49-6.98 (broad, 6H), 4.11 (broad, 4H), 2.07-1.27 (broad, 102H), 0.91 (broad,12H).

Synthesis of P-30-DPP-TVT

The synthetic procedure is similar as described for P-25-DPP-TVT. Yield : 0.45g. ^{1}H-NMR (500 MHz, $CDCl_3$, ppm): δ8.86 (broad, 4H), 7.39-6.84 (broad, 6H), 4.04 (broad, 4H), 1.72-1.28 (broad, 106H), 0.81 (broad,12H).

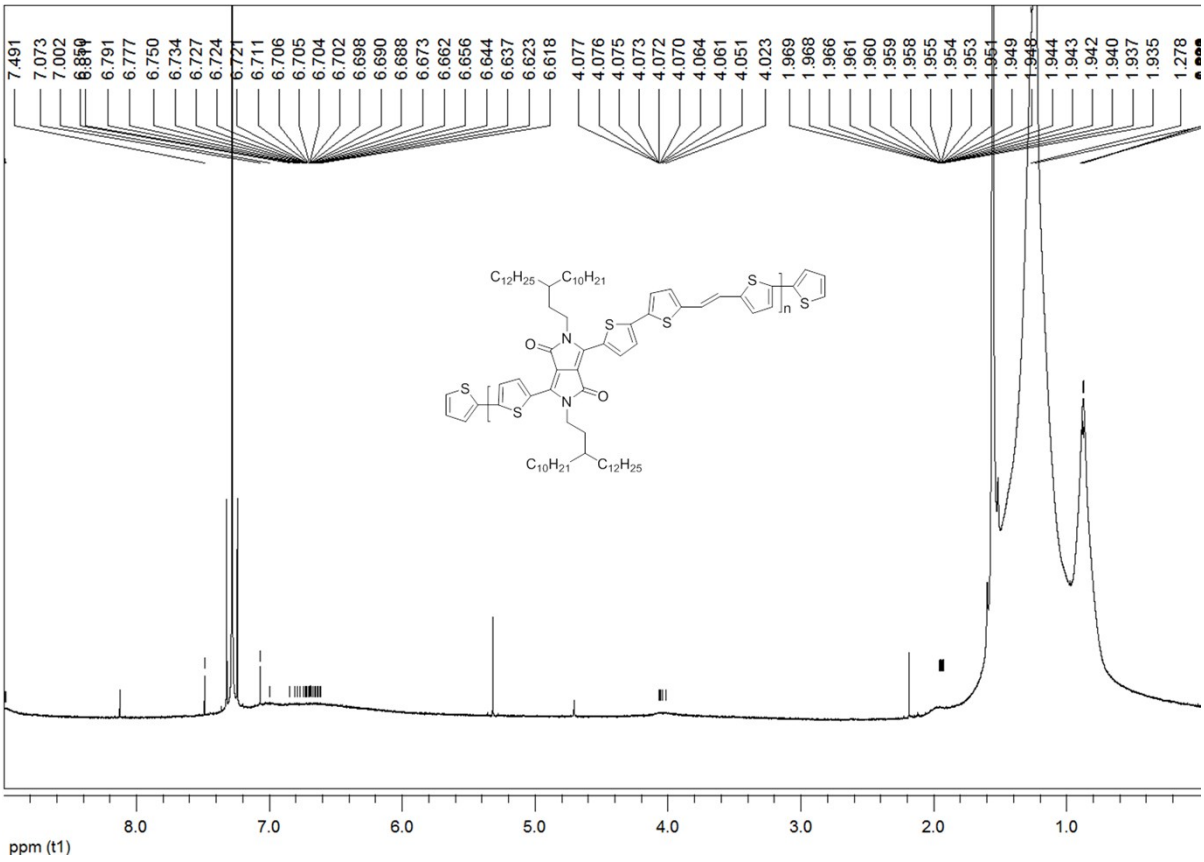
Synthesis of P-31-DPP-TVT

The synthetic procedure is similar as described for P-25-DPP-TVT. Yield : 0.43g. ^{1}H-NMR (500 MHz, $CDCl_3$, ppm): δ8.90 (broad, 4H), 7.46-6.93 (broad, 6H), 4.09 (broad, 4H), 2.04-1.24 (broad, 110H), 0.88 (broad,12H).

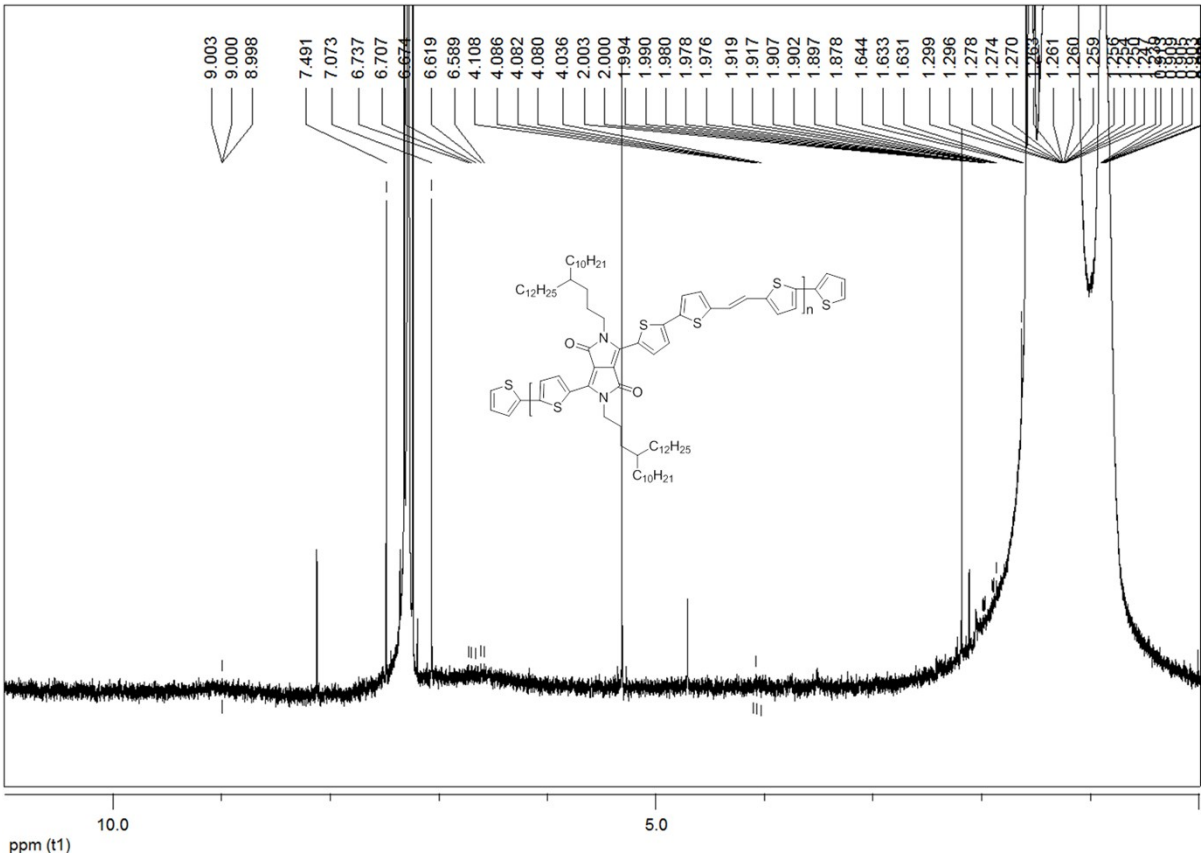
Synthesis of P-32-DPP-TVT

The synthetic procedure is similar as described for P-25-DPP-TVT. Yield: 0.41g. ^{1}H-NMR (500 MHz, $CDCl_3$, ppm): δ8.88 (broad, 4H), 7.54-6.26 (broad, 6H), 4.04 (broad, 4H), 2.03-1.31 (broad, 114H), 0.89 (broad,12H).

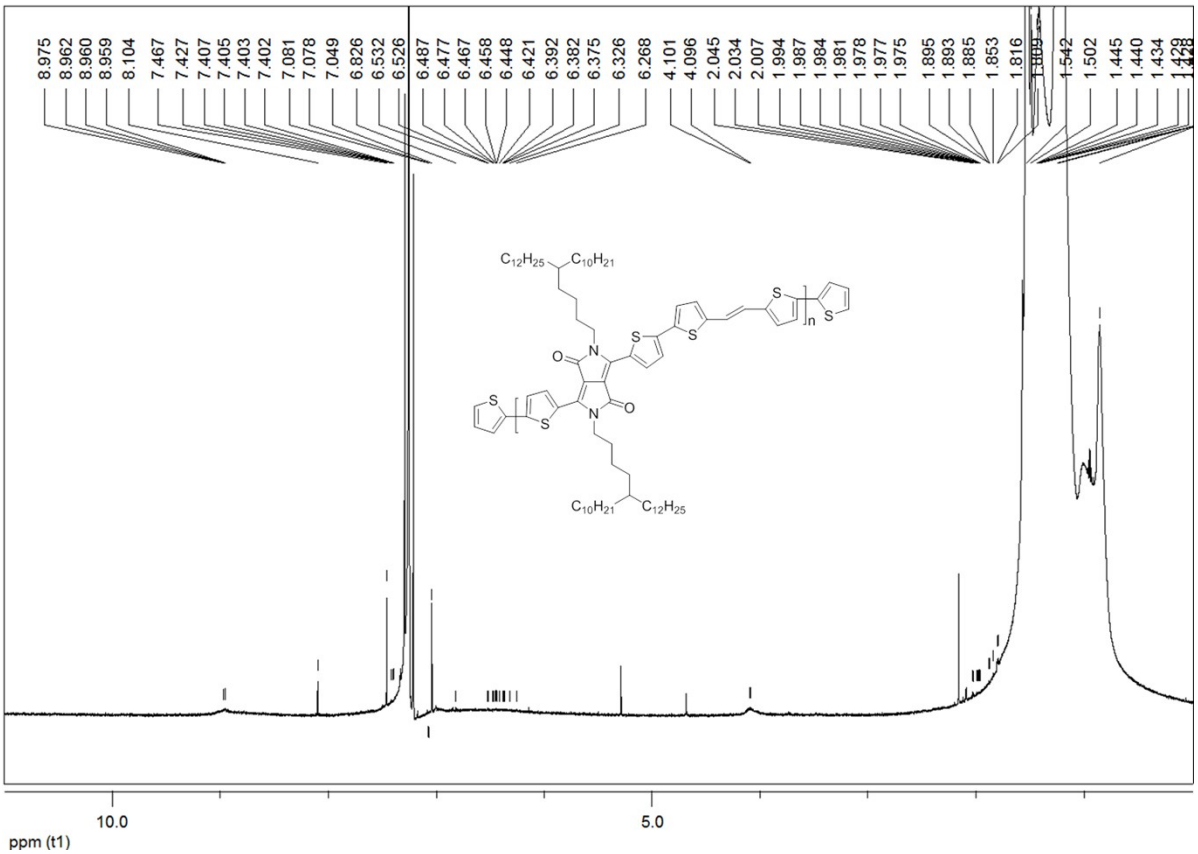
25-DPP-TVT



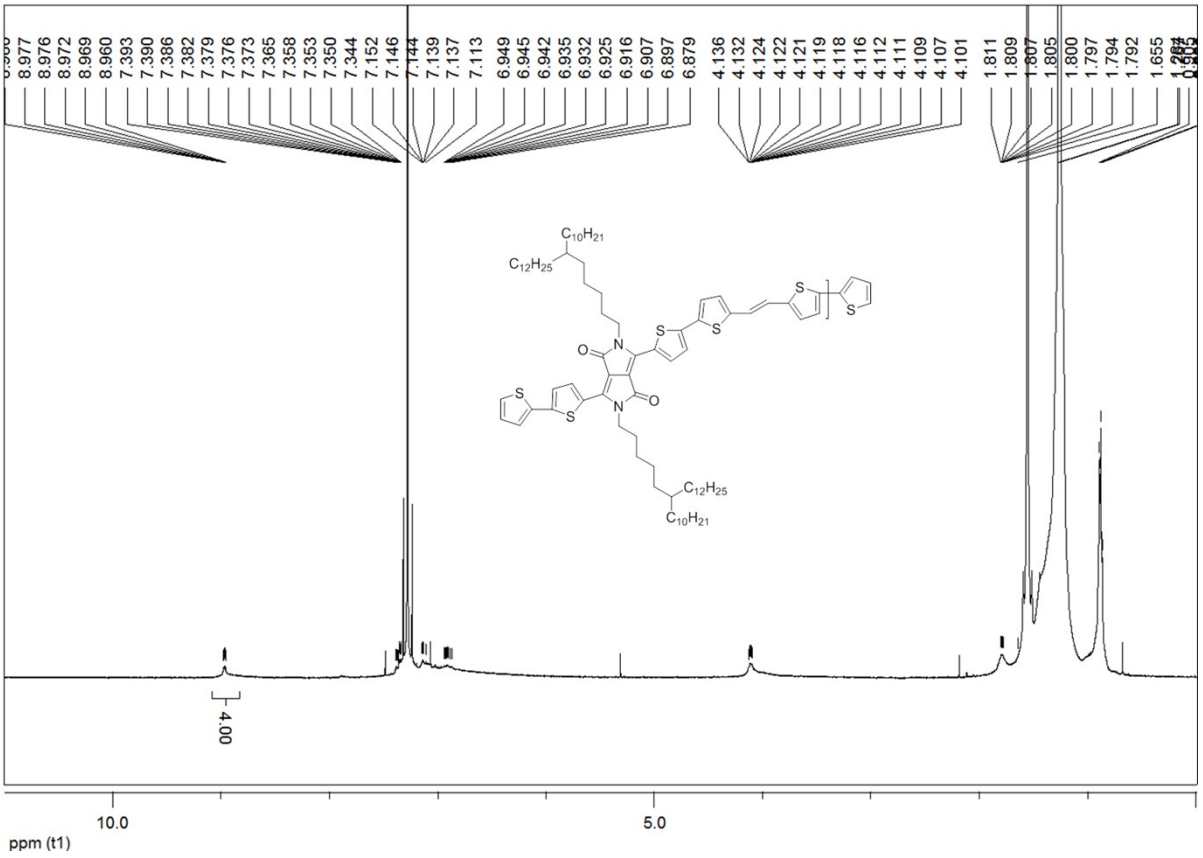
26-DPP-TVT



27-DPP-TVT



28-DPP-TVT



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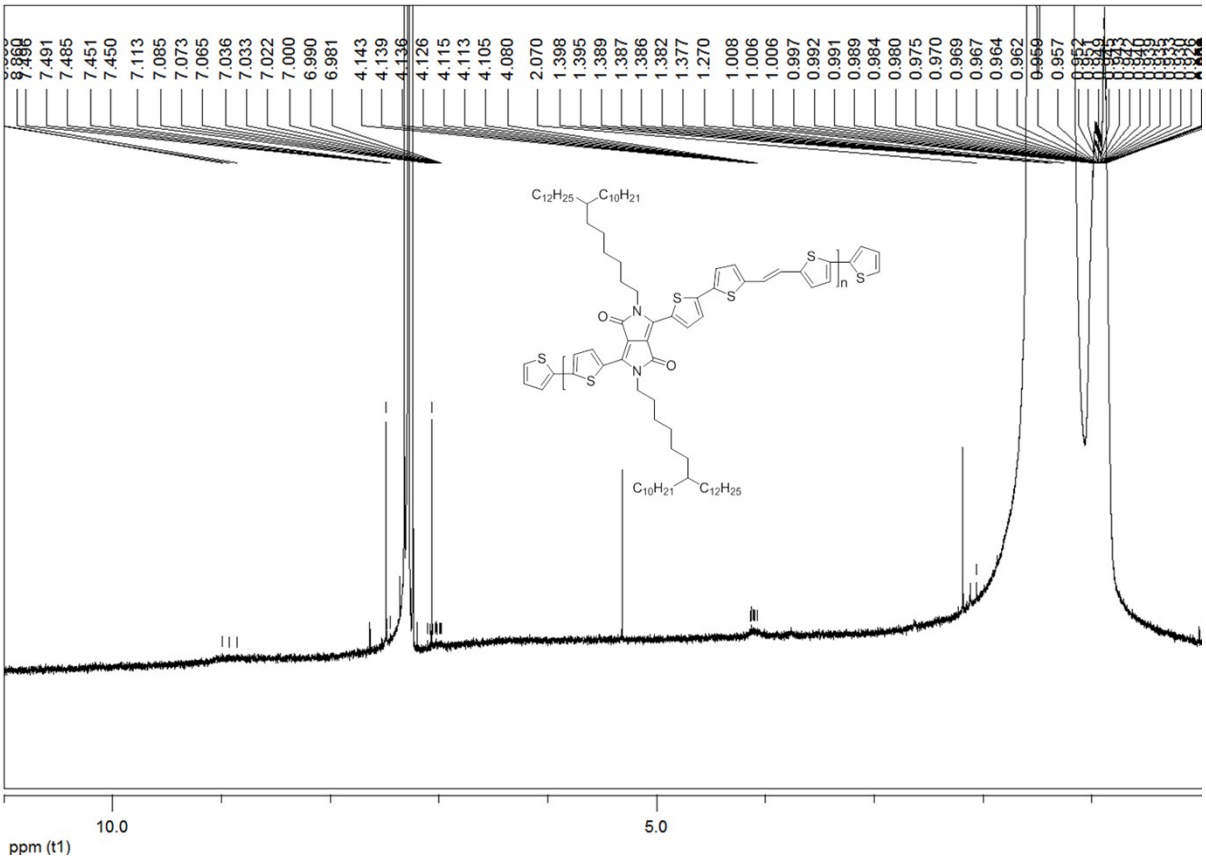
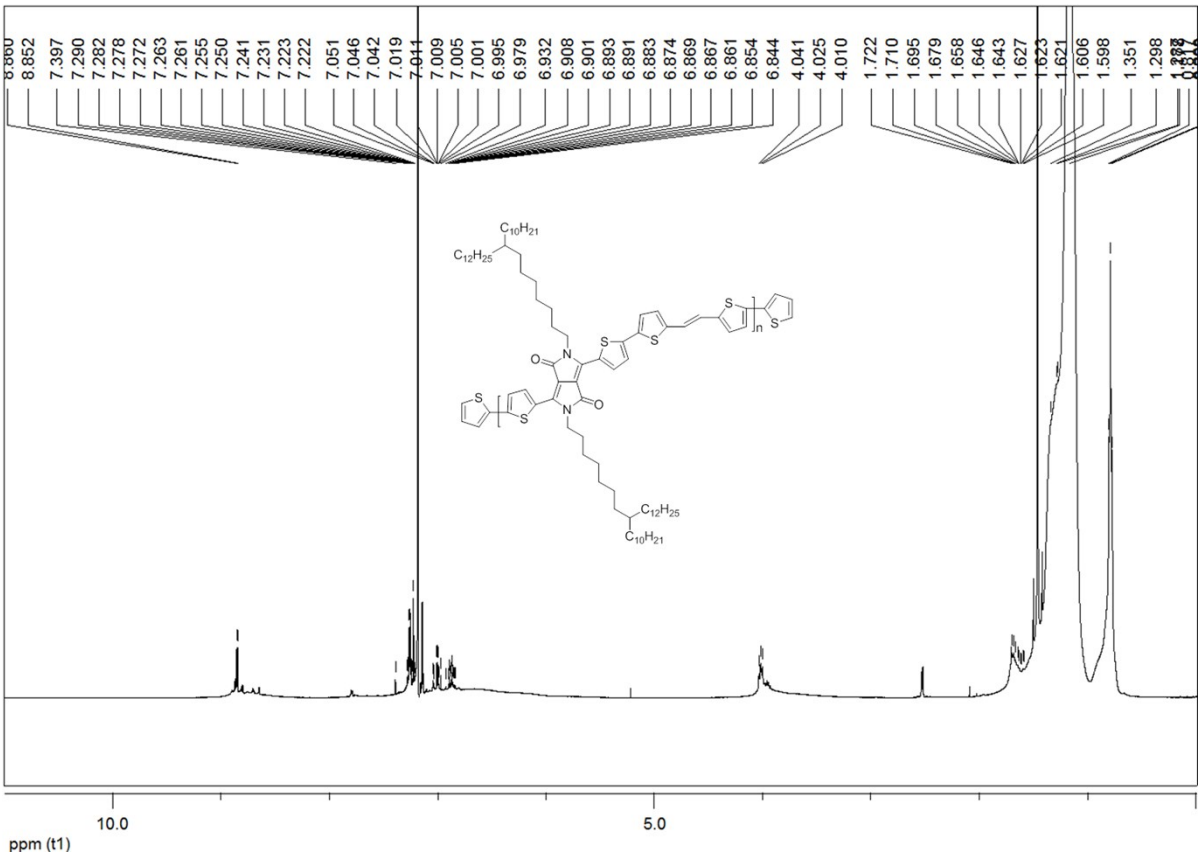
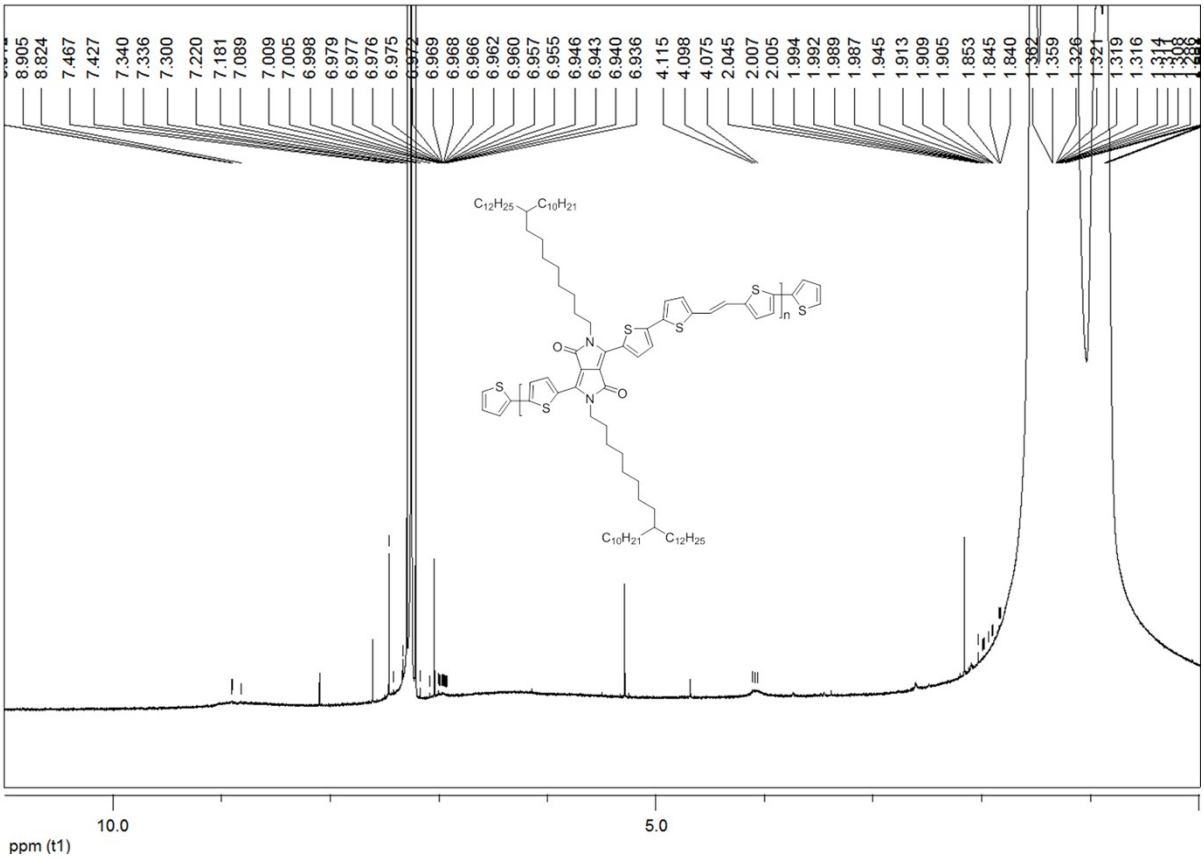


30-DPP-TVT



31-DPP-TVT



32-DPP-TVT

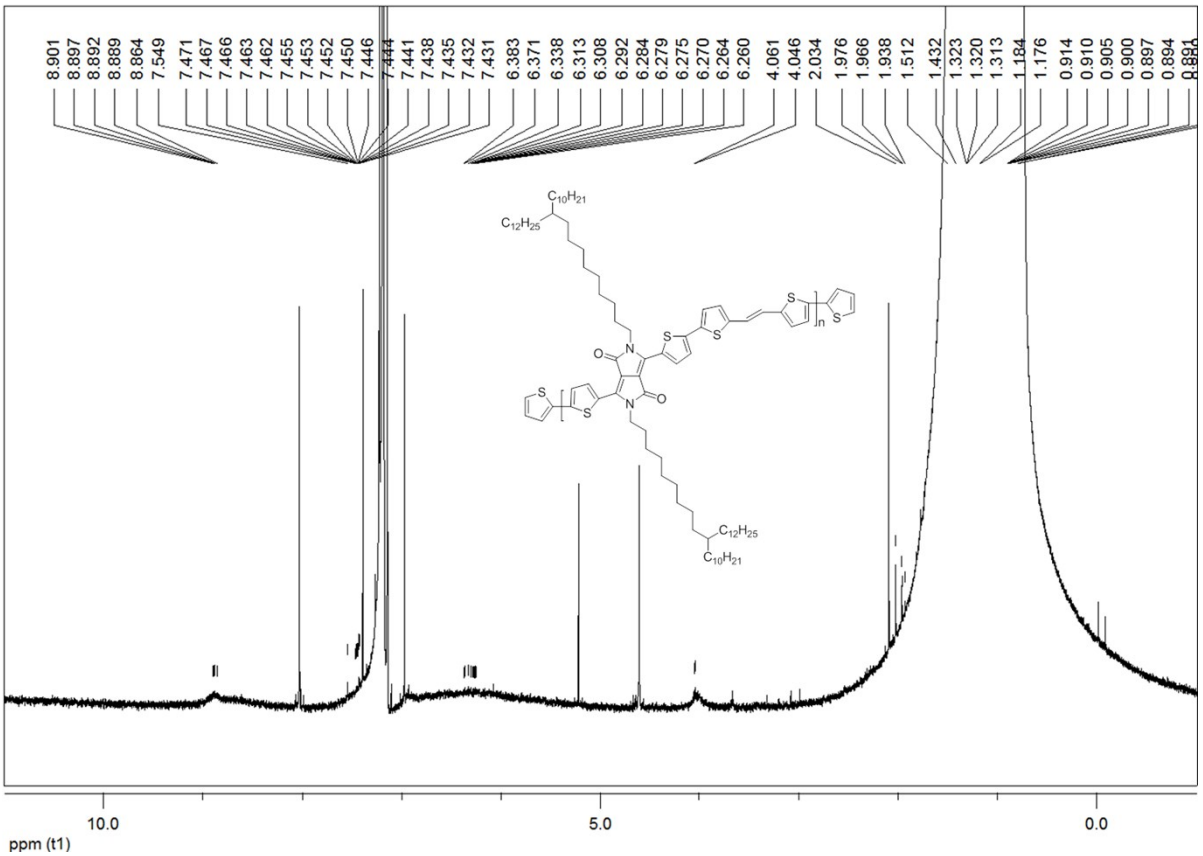


Figure S1. ^{1}H-NMR of DPP-TVT polymers

25DPPTVT

Element Anal. $C_{74}H_{112}N_2O_2S_4$ Cal: C, 74.75; H, 9.43; N, 2.36; S, 10.77; Found: C, 72.11; H, 9.28; N, 2.23; S, 10.69.

26DPPTVT

Element Anal. $C_{76}H_{116}N_2O_2S_4$ Cal: C, 75.00; H, 9.54; N, 2.30; S, 10.53; Found: C, 74.5; H, 9.46; N, 2.41; S, 11.29.

27DPPTVT

Element Anal. $C_{78}H_{120}N_2O_2S_4$ Cal: C, 75.24; H, 9.65; N, 2.25; S, 10.29; Found: C, 70.44; H, 9.23; N, 2.13; S, 9.13.

28DPPTVT

Element Anal. $C_{80}H_{124}N_2O_2S_4$ Cal: C, 75.47; H, 9.75; N, 2.20; S, 10.06; Found: C, 75.08; H, 9.98; N, 2.16; S, 9.62.

29DPPTVT

Element Anal. $C_{82}H_{128}N_2O_2S_4$ Cal: C, 75.69; H, 9.85; N, 2.15; S, 9.85; Found: C, 74.16; H, 10.30; N, 1.89; S, 8.73.

30DPPTVT

Element Anal. $C_{84}H_{132}N_2O_2S_4$ Cal: C, 75.90; H, 9.94; N, 2.11; S, 9.64; Found: C, 70.14; H, 9.67; N, 1.92; S, 8.53.

31DPPTVT

Element Anal. $C_{86}H_{136}N_2O_2S_4$ Cal: C, 76.11; H, 10.03; N, 2.06; S, 9.44; Found: C, 74.05; H, 10.41; N, 1.92; S, 8.34.

32DPPTVT

Element Anal. $C_{88}H_{140}N_2O_2S_4$ Cal: C, 76.30; H, 10.12; N, 2.02; S, 9.25; Found: C, 72.28; H, 9.93; N, 1.97; S, 8.89.

Figure S2. Quantitative elemental analysis of DPP-TVT polymers

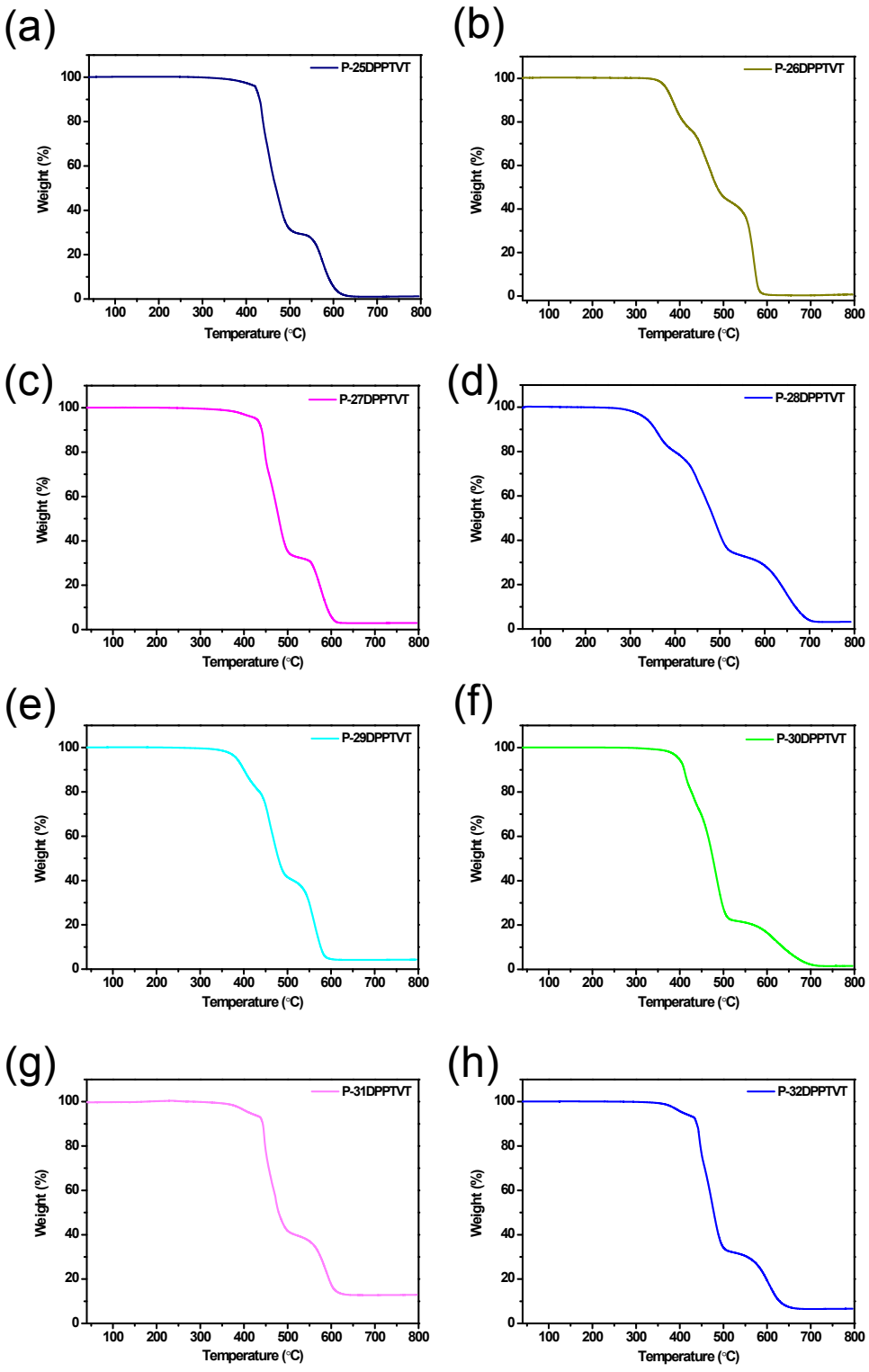


Figure S3. TGA thermograms of DPP-TVT polymers

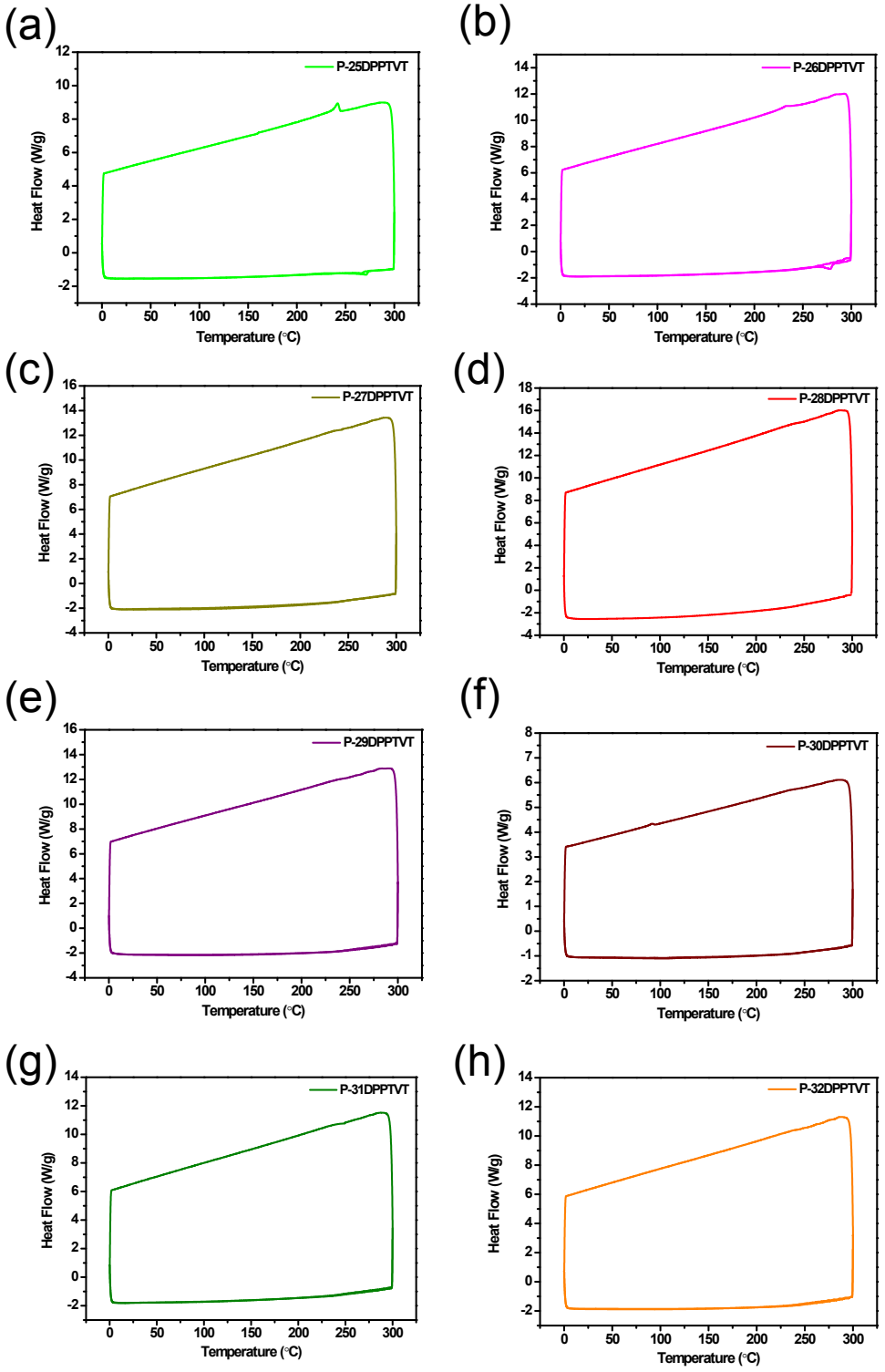


Figure S4. DSC thermograms of DPP-TVT polymers

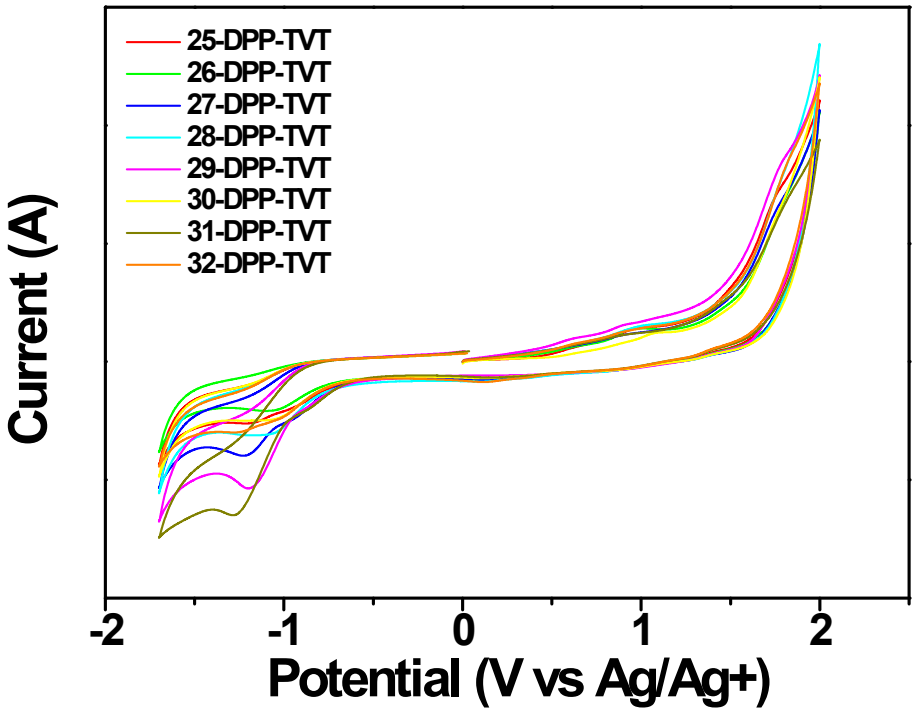


Figure S5. Cyclovoltammetry plots of DPP-TVT polymers in acetonitrile solution.

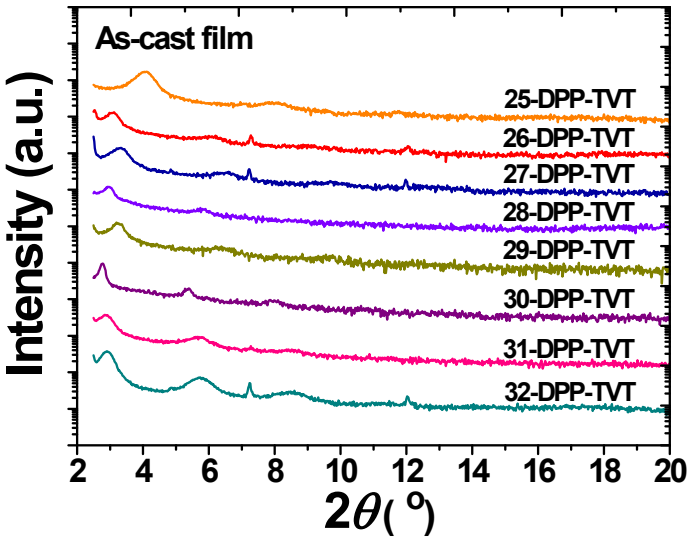


Figure S6. Out-of-plane X-ray diffraction (XRD) diffractogram profiles of the as-cast DPP-TVT polymer films.

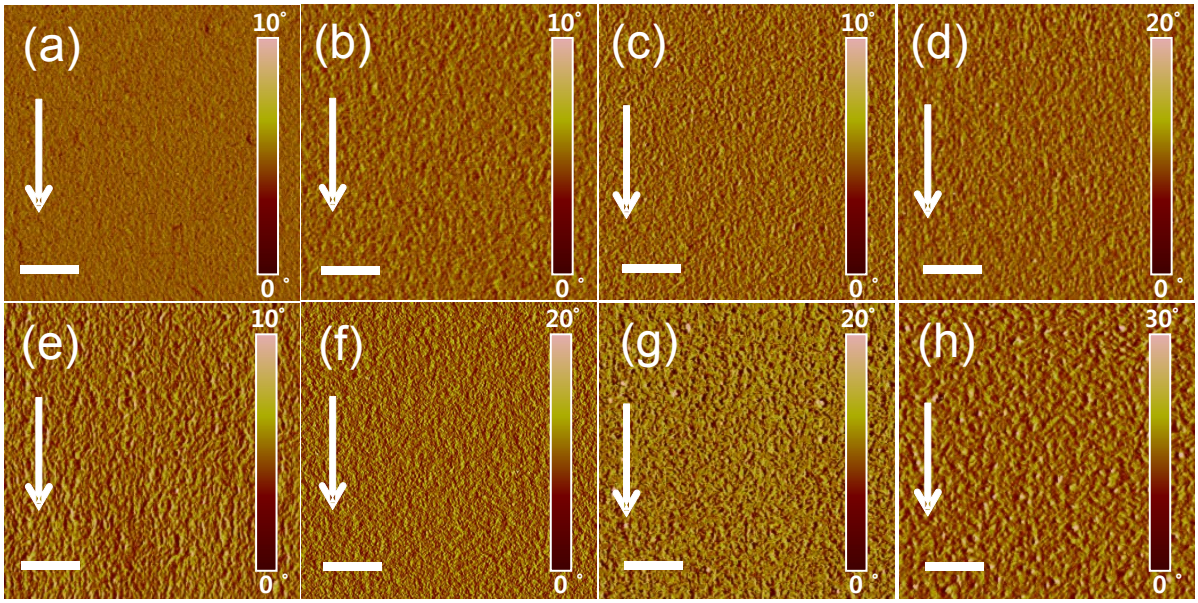


Figure S7. AFM phase image of DPP-TVT polymer films annealed at 200 °C. Solution-sheared film of (a) 25-DPP-TVT, (b) 26-DPP-TVT, (c) 27-DPP-TVT, (d) 28-DPP-TVT, (e) 29-DPP-TVT, (f) 30-DPP-TVT, (g) 31-DPP-TVT, and (h) 32-DPP-TVT. The shearing direction (top to bottom) is vertical to the scanning direction (left to right). The arrow indicates the direction of shearing. The scale bars represent 1 μm.

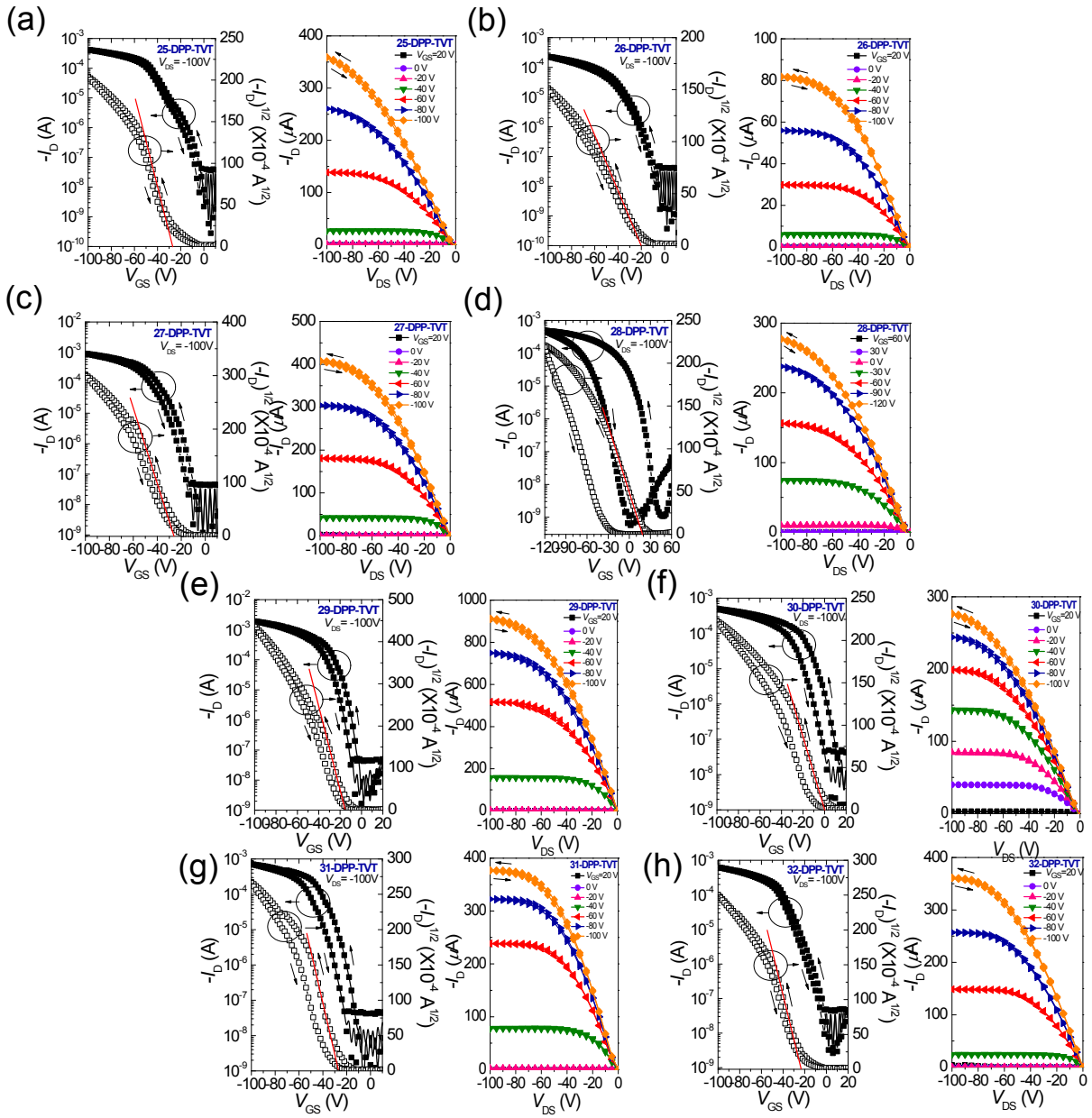


Figure S8. Transfer and output curves of DPP-TVT FETs obtained from solution-shearing: (a) 25-DPP-TVT, (b) 26-DPP-TVT, (c) 27-DPP-TVT, (d) 28-DPP-TVT, (e) 29-DPP-TVT, (f) 30-DPP-TVT, (g) 31-DPP-TVT, and (h) 32-DPP-TVT. The hole mobilities were calculated from the *I-V* data set obtained using the range of 10 V in the gate voltage sweep.

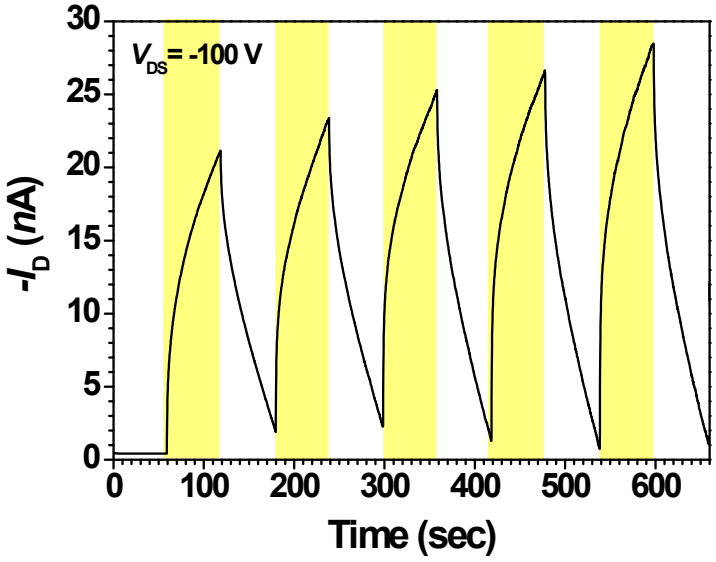


Figure S9. Photo-response test of the 29-DPP-TVT FETs upon on-and-off switching of polychromatic light (λ = 450 – 650 nm, λ_{max} = 640 nm, P_{max} = 36 mWcm^{-2}) at the transistor off-state (V_{GS} = 0 V and V_{DS} = –100 V).

Table S1. TGA and DSC data of DPP-TVT polymers

Polymer	TGA [a] T_d	DSC T_g	DSC T_m	DSC T_c
25-DPP-TVT	422.6	-	270.9	241.6
26-DPP-TVT	370.7	-	278.7	232.0
27-DPP-TVT	428.0	-	-	-
28-DPP-TVT	334.7	-	-	-
29-DPP-TVT	383.9	-	-	-
30-DPP-TVT	397.9	-	-	-
31-DPP-TVT	412.8	-	-	-
32-DPP-TVT	407.6	-	-	-

[a] The temperature of 5% weight-loss under nitrogen.

Table S2. Peak assignments for the out-of-plane XRD diffractogram profiles obtained from the as-cast DPP-TVT polymer films.

Polymer	(n00)	2θ (˚)	*d(100)*-spacing (Å)
25-DPP-TVT	(100)	4.04	21.85
	(200)	8.04	-
	(300)	11.82	-
	(400)	-	-
26-DPP-TVT	(100)	3.12	28.28
	(200)	6.10	-
	(300)	-	-
	(400)	-	-
27-DPP-TVT	(100)	3.34	26.42
	(200)	6.50	-
	(300)	9.94	-
	(400)	-	-
28-DPP-TVT	(100)	2.98	29.62
	(200)	5.78	-
	(300)	-	-
	(400)	-	-
29-DPP-TVT	(100)	3.20	27.58
	(200)	6.38	-
	(300)	9.72	-
	(400)	-	-
30-DPP-TVT	(100)	2.87	30.81
	(200)	5.40	-
	(300)	7.98	-
	(400)	-	-
31-DPP-TVT	(100)	2.83	31.18
	(200)	5.70	-
	(300)	8.52	-
	(400)	-	-
32-DPP-TVT	(100)	2.90	30.43
	(200)	5.74	-
	(300)	8.60	-
	(400)	-	-

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