Electronic Supplementary Information (ESI) for:

Non-Halogenated Solution-Processed Ambipolar Plastic Transistors Based on Conjugated Polymers Prepared by Asymmetric Donor Engineering

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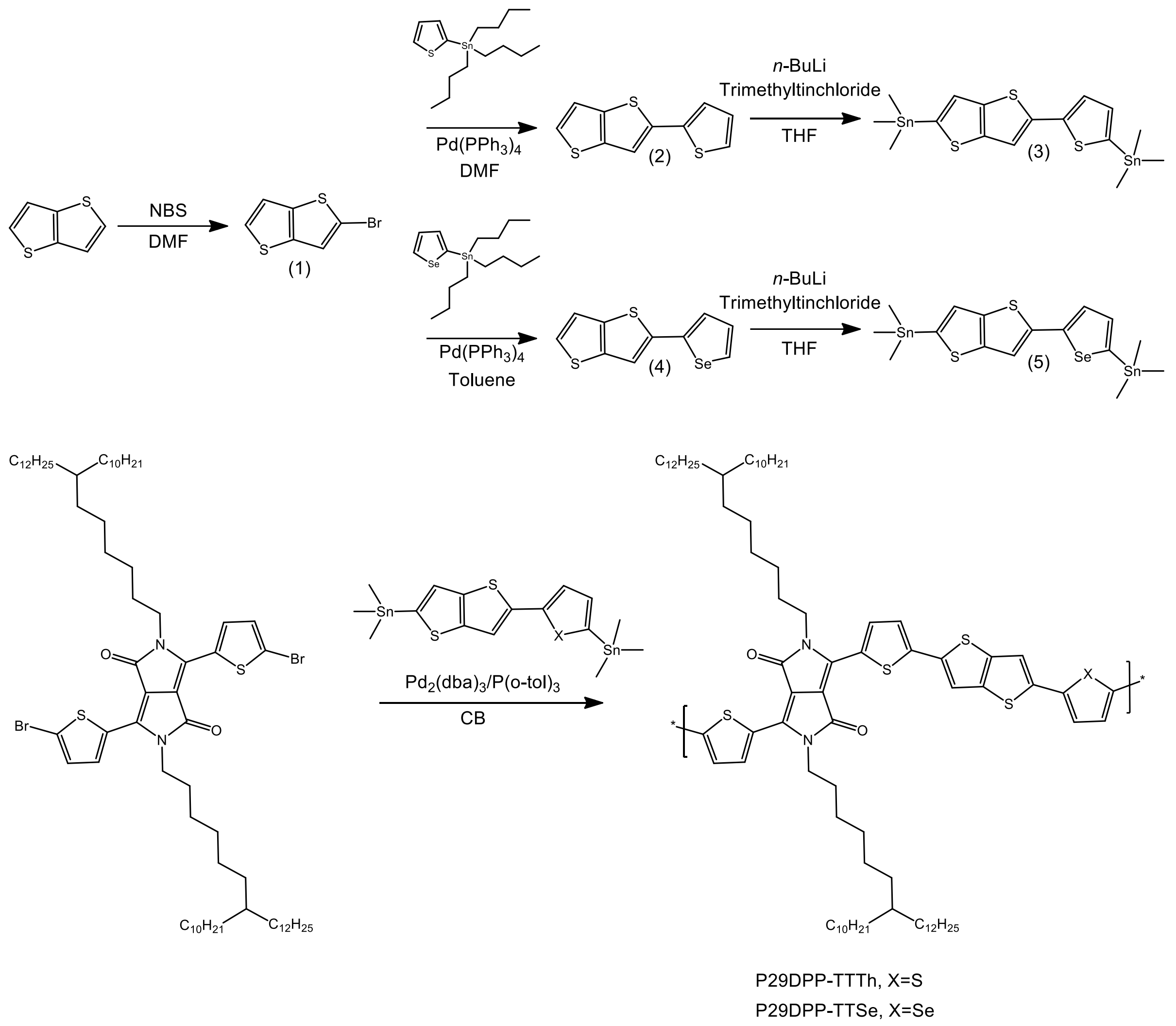
Synthesis procedure of conjugated polymers



Scheme S1. Scheme for synthesis procedure of conjugated polymers.

Synthesis of 2-bromo-thieno[3,2-b]thiophene (1)

Thieno[3,2-b]thiophene (0.50 g, 0.35 mmol) was dissolved in 5.0 mL N,N-dimethylformamide (DMF) and cooled to 0 ℃. A solution of N-bromosuccinimide (NBS) (0.65 g, 0.36 mmol) in 8.5 mL of DMF was added. After stirring for 3 h at 0 ℃, ice-water (25 mL) was added to the solution. The resulting mixture was extracted with 1,2-dichloromethane (60 mL x 3). The extracts were washed with water, dried over anhydrous magnesium sulfate ($MgSO_4$), and evaporated. The crude product was purified by silica gel chromatography with *n*-hexane, to give colorless oil (0.374 g, 47%). ^{1}H-NMR (300 MHz, CD_2Cl_2): 7.48-7.47 (d, 1H, J=5.3Hz), 7.34 (s, 1H), 7.24-7.22 (d, 1H, J=5.3Hz).

Synthesis of 2-(thiophen-2-yl)thieno[3,2-b]thiophene (2)

The mixture of compound (1) (2.0 g, 0.91 mmol), tributyl(thiophen-2-yl)stannane (4.4 g, 1.1 mmol), and tetrakis(triphenylphosphine)palladium(0) (0.52 g, 0.045 mmol) in dry DMF (40 mL) was heated under nitrogen at 90 ℃ for 3 h. After the reaction was cooled to room temperature, water (100 mL) was added to the solution. The resulting mixture was extracted with CH_2Cl_2 (180 mL x 3). The extracts were washed with water, dried over $MgSO_4$, and evaporated. The crude product was purified by silica gel chromatography with *n*-hexane, to give white solid powder (1.15 g. 56%). ^{1}H-NMR (300 MHz, DMSO): 7.68 (d, 1H, J=0.9Hz), 7.68-7.66 (d, 1H, J=3.8Hz) 7.56 (d, 1H, J=6.3Hz), 7.44 (d, 1H, J=5.9Hz), 7.36 (d, 1H, J=4.8Hz), 7.13-7.11 (q. 1H, J=3.6Hz, J=5.1Hz). ^{13}C-NMR (DMSO, ppm): 139.9, 138.5, 137.9, 137.2, 128.9, 128.8, 126.3, 124.7, 120.4, 116.8. HRMS (EI$^+$): Calcd. for $C_{10}H_6S_3$: 221.9632. Found : (M^+) 221.9636.

Synthesis of trimethyl(5-(5-(trimethylstannyl)thieno[3,2-b]thiophen-2-yl)thiophen-2-yl)stannane (3)

Compound (2) (1.0 g, 0.44 mmol) was dissolved in anhydrous THF (30 mL) under nitrogen, and was cooled to -78°C. After n-butyl lithium (3.95 mL, 0.98 mmol, 2.5 M in hexane) was slowly added to the solution, trimethyltin chloride (9.89 mL, 0.98 mmol, 1.0 M in hexane) was then added, and the solution was stirred for 12 h at room temperature. The solution was poured into ice-water, and extracted with diethyl ether (100 mL x 3). The extracts were washed with water, dried over $MgSO_4$, and evaporated. The crude product, which was then purified by recrystallization from diethyl ether, and ethanol (12 mL, 3 mL) to give blue solids (0.65 g, 26%), ^{1}H-NMR (300 MHz, CD_2Cl_2): 7.17 (d, 1H, J=0.5Hz). 7.15 (d, 1H, J=3.4Hz), 7.08 (d, 1H, J=0.7Hz), 6.95-6.94 (d, 1H, J=3.4Hz), 0.23-0.21 (d, 18H, 4.7Hz).

Synthesis of 2-(selenophen-2-yl)thieno[3,2-b]thiophene (4)

The solution of compound (1) (2.0 g, 0.912 mmol) and tributyl(selenophene-2-yl)stannane (4.98 g, 1.18 mmol), and tetrakis(triphenylphosphine)palladium(0) (0.52 g, 0.045 mmol) in dry toluene (35 mL) was heated under nitrogen at 110°C for 12 h. After the reaction was cooled to room temperature, water (100 mL) was added to the solution. The resulting mixture was extracted with CH_2Cl_2 (180 mL x 3). After the extracts were washed with water, dried over $MgSO_4$, and evaporated. The crude product was purified by silica gel chromatography with n-hexane, to give white solid powder (1.6 g. 65%). ^{1}H-NMR (300 MHz, DMSO): 8.15 (d, 1H, J=6.7Hz), 7.68-7.65 (t, 2H, J=6.5Hz), 7.46 (d, 1H, J=4.9Hz), 7.42 (d, 1H, J=5.9Hz), 7.32-7.29 (q, 1H, J=3.8Hz, J=5.6 Hz). ^{13}C-NMR (DMSO, ppm): 142.48, 141.04, 139.96, 138.02, 132.13, 130.95, 128.94, 126.63, 120.51, 117.42. HRMS (EI$^+$): Calcd. for $C_{10}H_6S_2Se$: 269.9076. Found : (M$^+$) 269.9075.

Synthesis of trimethyl(5-(5-(trimethylstannyl)selenophen-2-yl)thieno[3,2-b]thiophen-2-yl)stannane (5)

Compound (4) (1.8 g, 0.81 mmol) and TMEDA (2.67 mL, 1.78 mmol) were dissolved in anhydrous THF (60 mL) under nitrogen and was cooled to 0°C. n-Butyl lithium (7.76 mL, 1.94 mmol, 2.5 M in hexane) was slowly added. The reaction mixture was heated to reflux for 1 h. After the reaction was cooled to 0°C, trimethyltin chloride (17.81 mL, 1.78 mmol, 1.0 M in hexane) was added, and the solution was stirred for 12 h at room temperature. The solution was poured into ice-water, and extracted with diethyl ether (180 mL x 3). The extracts were washed with water, dried over $MgSO_4$, and evaporated. The crude product was then purified by recrystallization diethyl ether, and ethanol (20 mL, 5 mL) to give brown solids (2.0 g, 50%). ^{1}H-NMR (300 MHz, CD_2Cl_2): 7.29-7.28 (d, 1H, J=3.6Hz), 7.25-7.24 (d, 1H, J=3.6Hz), 7.13 (s, 1H), 7.08 (d, 1H, J=0.7Hz), 0.24-0.21 (d, 18H, J=7.2Hz).

Synthesis of P29DPP-TTTh

The polymer was prepared using a palladium-catalyzed Stille coupling reaction. In a Schlenk flask 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(7-decylnonadecyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (0.50 g 0.0004 mol) and compound (3) (0.172 g 0.0004 mmol) were dissolved in dry chlorobenzene (6.0 mL). After degassing under nitrogen for 60 min, $Pd_2(dba)_3$ (0.007 mg, 2 mol%) and $P(o\text{-}Tol)_3$ (0.095 g/ 8 mol%) were added to the mixture, which was then stirred for 48 h at 110°C. 2-Bromothiophen and tributyl(thiophen-2-yl)stannane 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, hexane, and toluene, successively. The final product, poly[2,5-bis(7-decylnonadecyl)-3-(5-(5-(thiophen-2-yl)thieno[3,2-b]thiophen-2-yl)thiophen-2-yl)-6-(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione] (P-29-TT-Th) was obtained by precipitation in methanol. Yield : 0.305 g

(56.9%). (M_n =40.59 KDa, M_w =55.57 KDa, PDI =1.36). ^{1}H NMR (500 MHz), δ(ppm) : 8.9 (br , 4H), 7.3-6.8 (br, 8H), 4.5-4.0 (br, 4H), 3.2--0.5 (br, 114H)

Synthesis of P29DPP-TTSe

The polymer was prepared using a palladium-catalyzed Stille coupling reaction. In a Schlenk flask 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(7-decylnonadecyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (0.50 g 0.0004 mol) and compound (5) (0.187 g 0.0004 mmol) were dissolved in dry chlorobenzene (6.0 mL). After degassing under nitrogen for 60 min, $Pd_2(dba)_3$ (0.007 mg, 2 mol%) and $P(o\text{-}Tol)_3$ (0.095 g/ 8 mol%) were added to the mixture, which was then stirred for 48 h at 110°C. 2-Bromothiophen and tributyl(thiophen-2-yl)stannane 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, hexane, and toluene, successively. The final product, poly[2,5-bis(7-decylnonadecyl)-3-(5-(5-(selenophen-2-yl)thieno[3,2-b]thiophen-2-yl)thiophen-2-yl)-6-(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione] (P-29-TT-Se) was obtained by precipitation in methanol. Yield : 0.255 g (45. 9%). (M_n =33.90 KDa, M_w = 44.32 KDa, PDI =1.31). ^{1}H NMR (500 MHz), δ(ppm) : 8.9 (br , 4H), 7.3-6.8 (br, 8H), 4.5-4.0 (br, 4H), 3.2--0.5 (br, 114H)

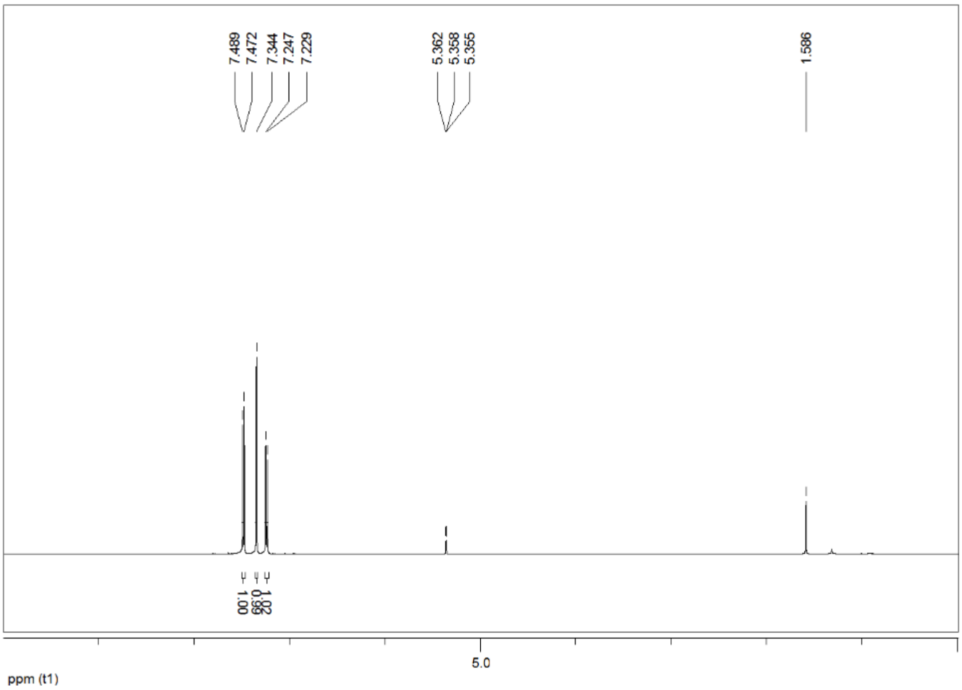


Fig. S1 ^{1}H-NMR of 2-bromo-thieno[3,2-b]thiophene (1).

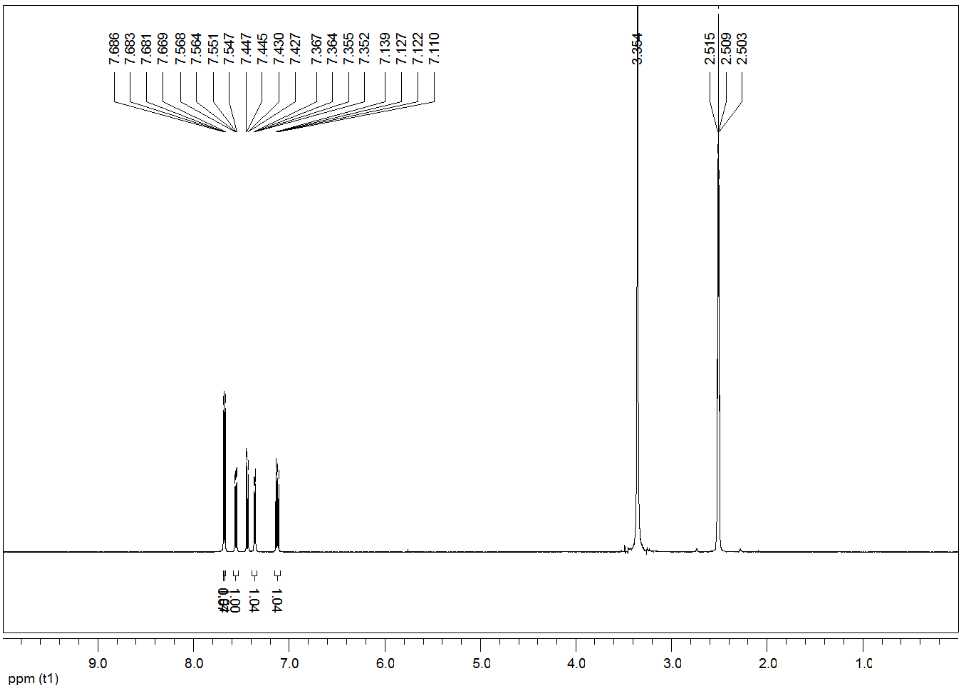


Fig. S2 ^{1}H-NMR of 2-(thiophen-2-yl)thieno[3,2-b]thiophene (2).

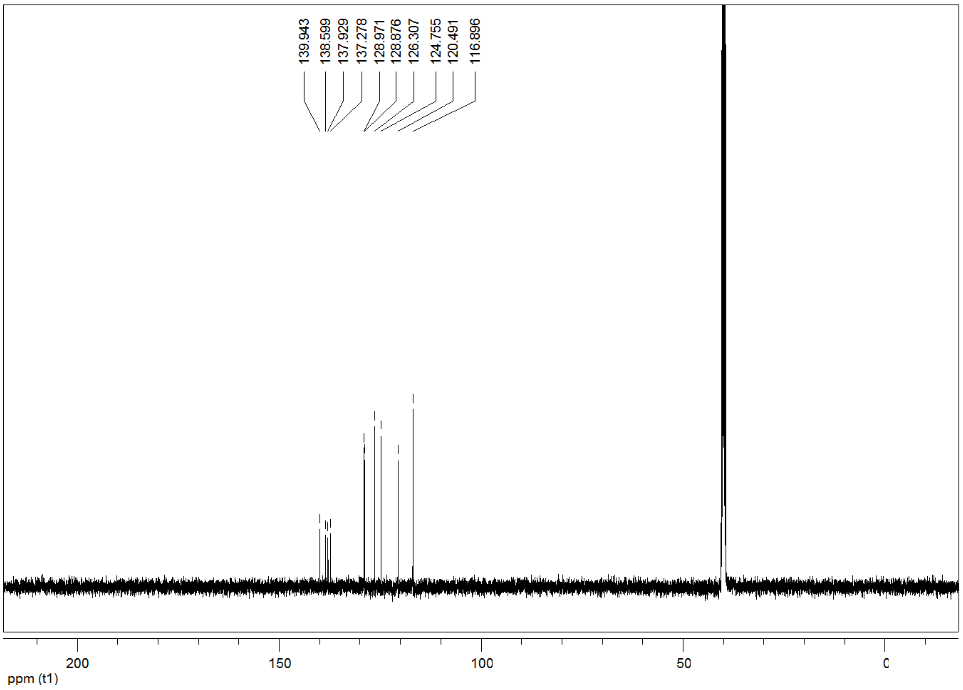
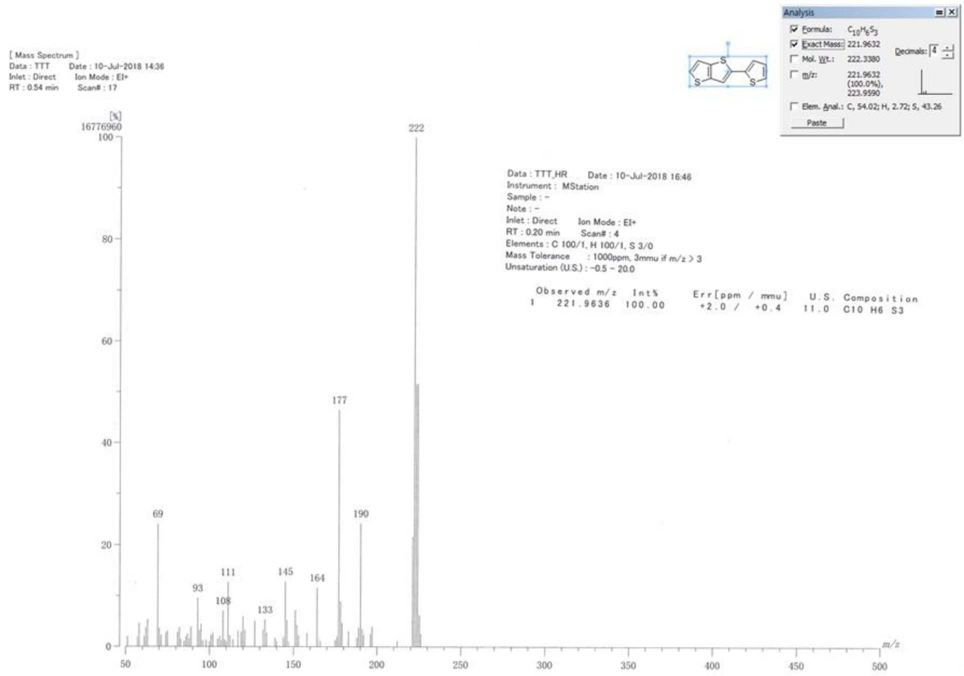


Fig. S3 ^{13}C-NMR of 2-(thiophen-2-yl)thieno[3,2-b]thiophene (2).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RT : 0.54 min       Scan# : 17
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Analysis
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☑ Exact Mass:     221.9632        Decimals: 4
☐ Mol. Wt.:       222.3380
☐ m/z:            221.9632
                  (100.0%),
                  223.9590
☐ Elem. Anal.: C, 54.02; H, 2.72; S, 43.26
Paste
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Sample : -
Note : -
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RT : 0.20 min       Scan# : 4
Elements : C 100/1, H 100/1, S 3/0
Mass Tolerance      : 1000ppm, 3mmu if m/z > 3
Unsaturation (U.S.) : -0.5 - 20.0

   Observed m/z  Int%     Err[ppm / mmu]   U.S.  Composition
 1   221.9636  100.00     +2.0 /  +0.4     11.0  C10 H6 S3
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Fig. S4 Mass spectrum of 2-(thiophen-2-yl)thieno[3,2-b]thiophene (2).

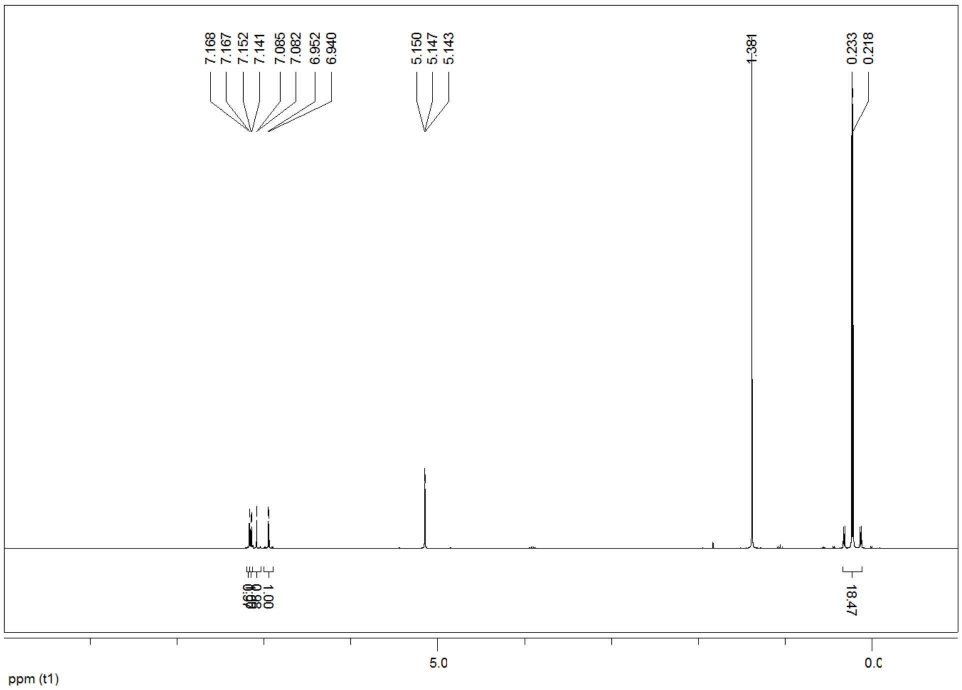


Fig. S5 ^{1}H-NMR of trimethyl(5-(5-(trimethylstannyl)thieno[3,2-b]thiophen-2-yl)thiophen-2-yl)stannane (3).

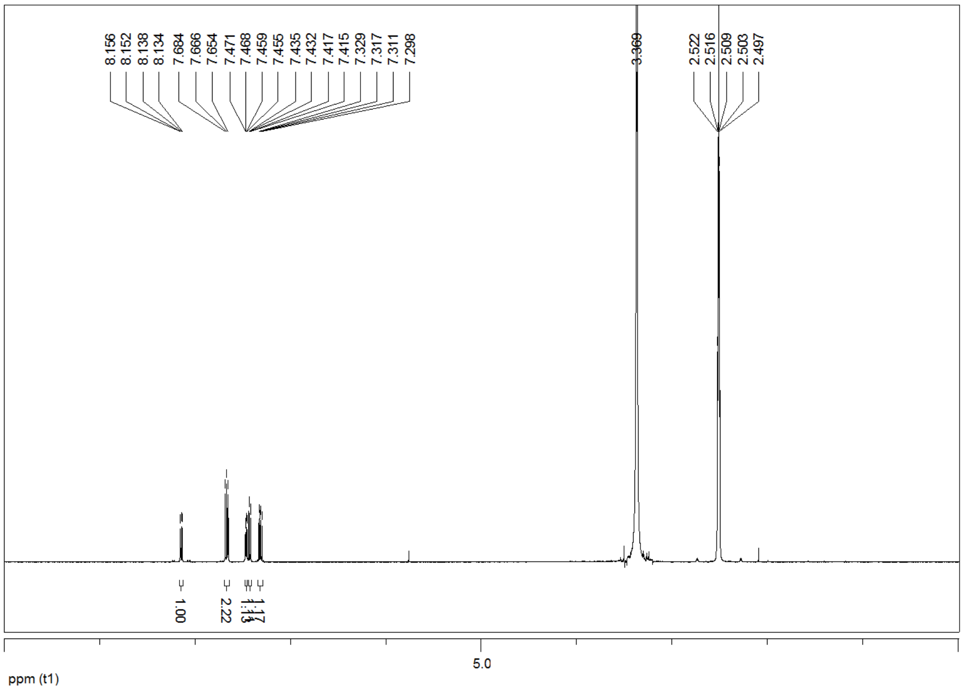


Fig. S6 ^{1}H-NMR of 2-(selenophen-2-yl)thieno[3,2-b]thiophene (4).

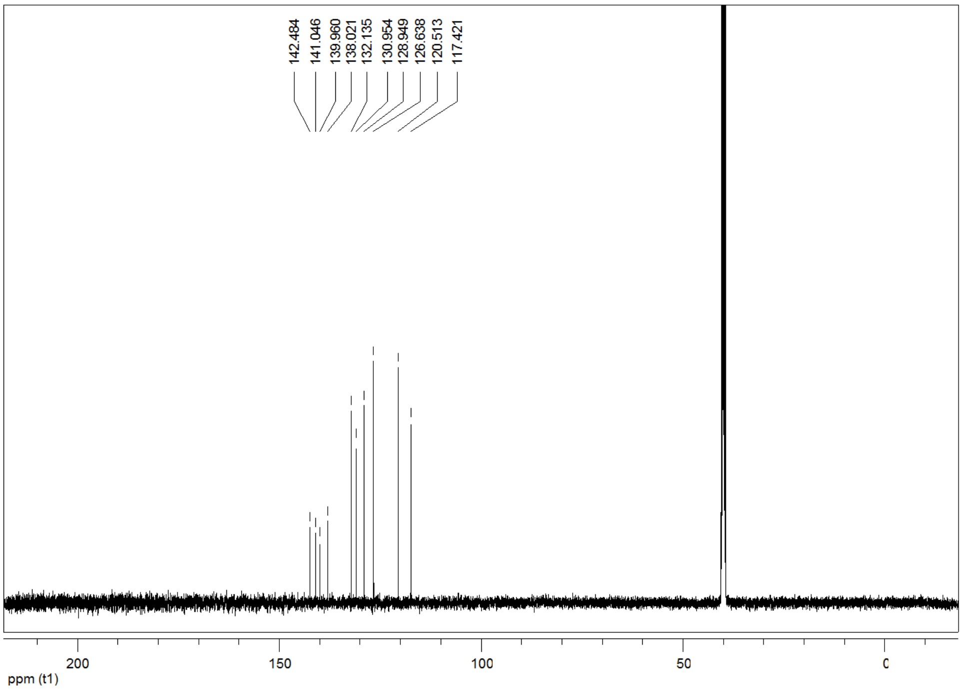
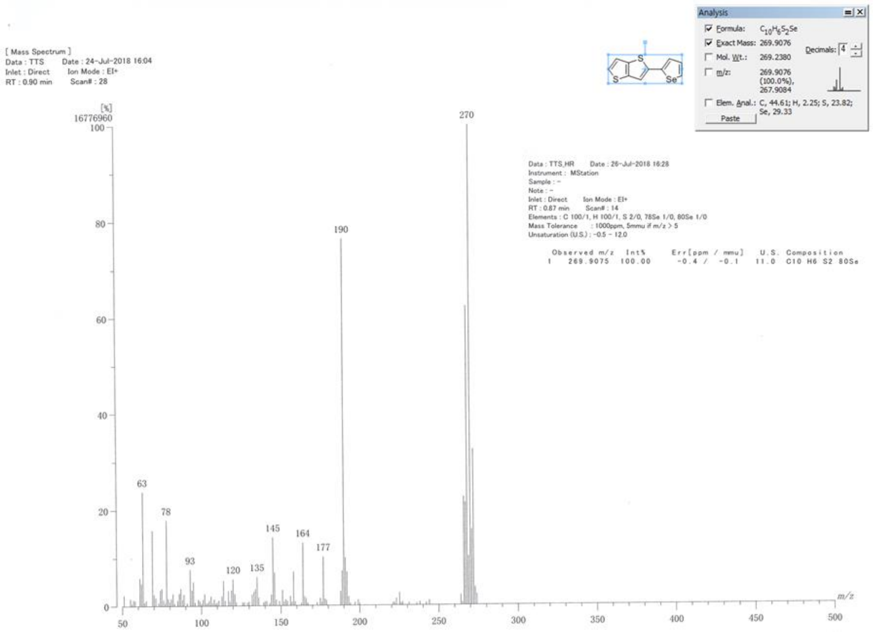


Fig. S7 ^{13}C-NMR of 2-(selenophen-2-yl)thieno[3,2-b]thiophene (4).



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Analysis
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☑ Exact Mass:    269.9076        Decimals: 4
☐ Mol. Wt.:      269.2380
☐ m/z:           269.9076
                 (100.0%),
                 267.9084
☐ Elem. Anal.:   C, 44.61; H, 2.25; S, 23.82;
                 Se, 29.33
Paste
```

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Data : TTS_HR      Date : 26-Jul-2018 16:28
Instrument :  MStation
Sample : -
Note : -
Inlet : Direct      Ion Mode : EI+
RT : 0.87 min       Scan# : 14
Elements : C 100/1, H 100/1, S 2/0, 78Se 1/0, 80Se 1/0
Mass Tolerance      : 1000ppm, 5mmu if m/z > 5
Unsaturation (U.S.) : -0.5 - 12.0

    Observed m/z  Int%      Err[ppm / mmu]   U.S.  Composition
 1    269.9075   100.00      -0.4 /  -0.1    11.0  C10 H6 S2 80Se
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Fig. S8 Mass spectrum of 2-(selenophen-2-yl)thieno[3,2-b]thiophene (4).

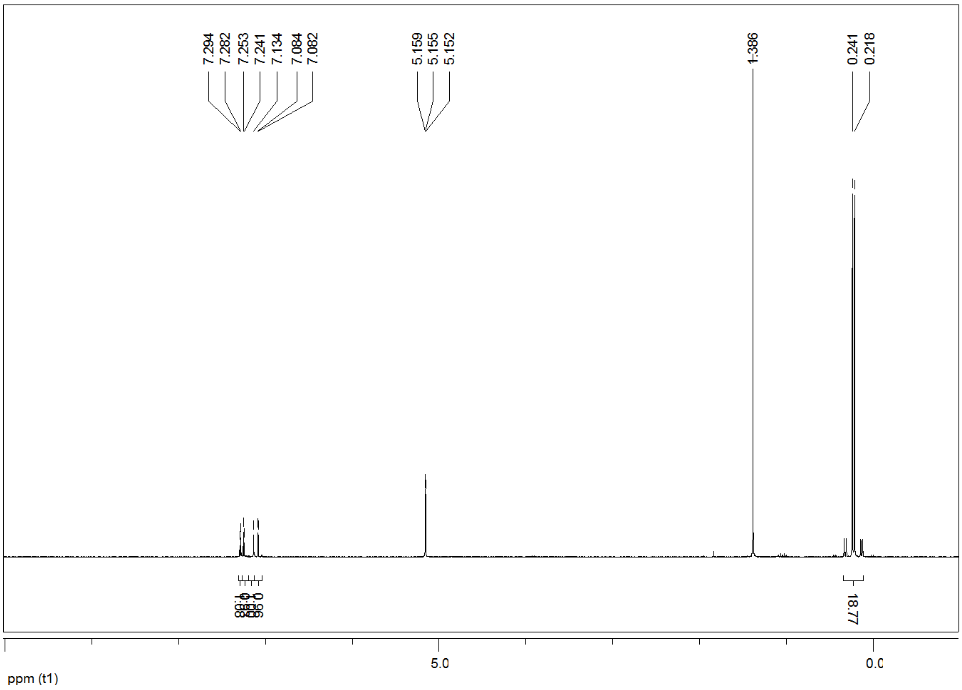


Fig. S9 ^{1}H-NMR of trimethyl(5-(5-(trimethylstannyl)selenophen-2-yl)thieno[3,2-b]thiophen-2-yl)stannane (5).

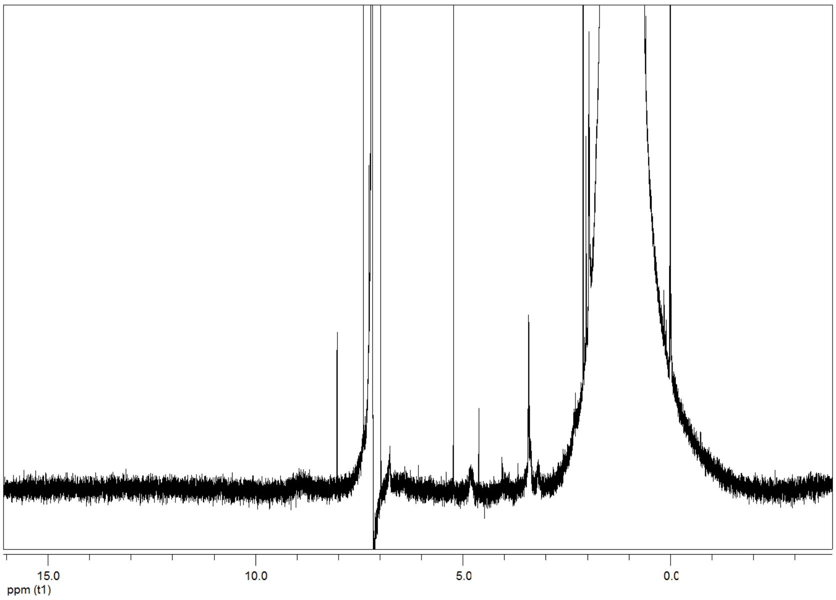


Fig. S10 ^{1}H-NMR of **P29DPP-TTTh**.

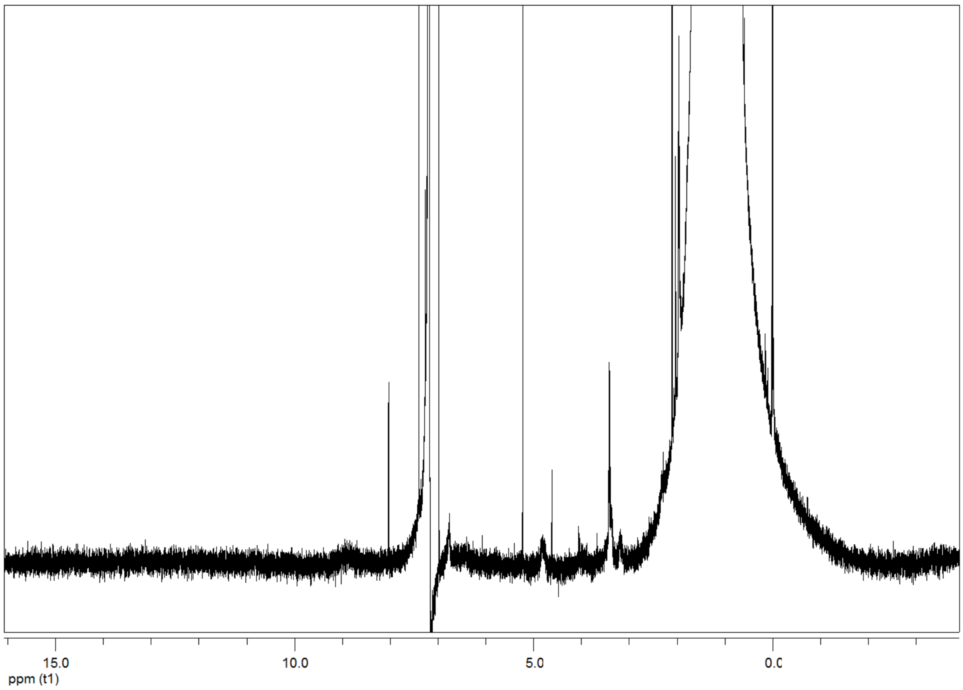
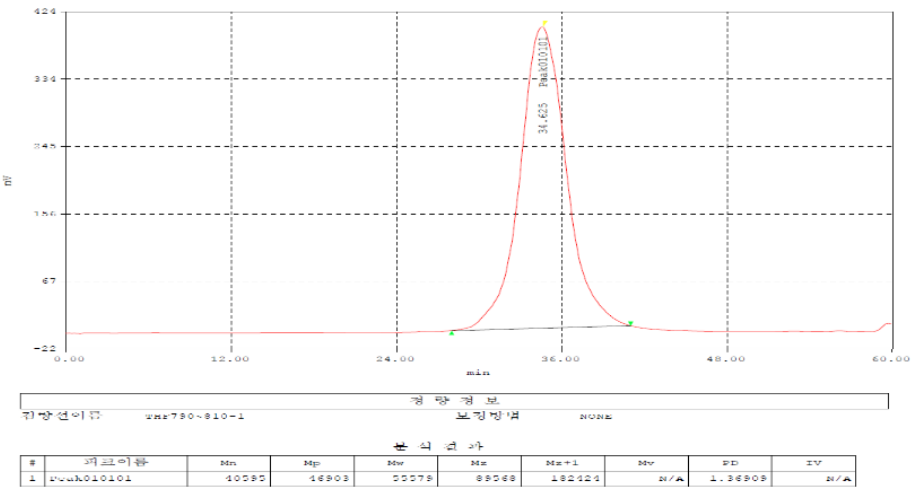


Fig. S11 ^{1}H-NMR of **P29DPP-TTSe**.



검 량 정 보

검량선이름 THF790~810-1 보정방법 NONE

분 석 결 과

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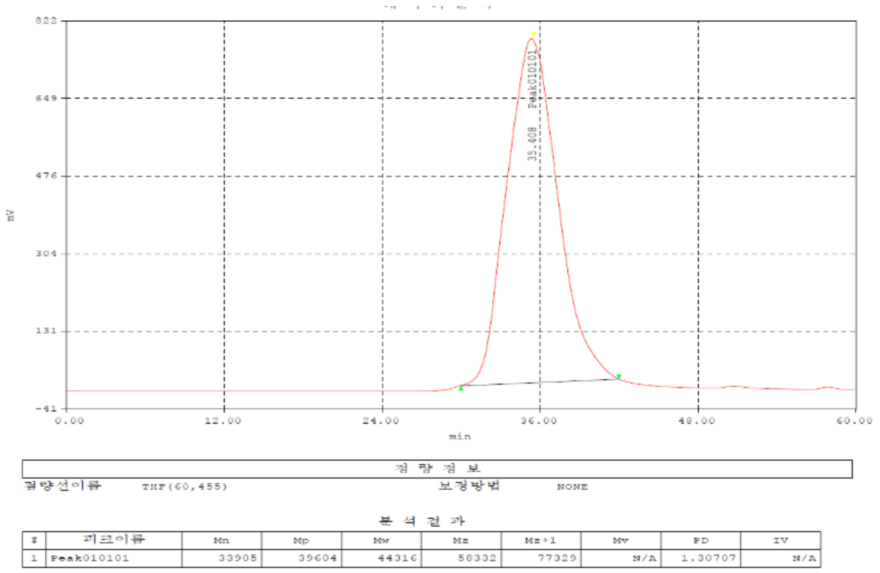
1	Peak010101	40595	46903	55579	89568	182424	N/A	1.36909	N/A

Fig. S12 GPC data of **P29DPP-TTTh**. The molecular weight and polydispersity index of the copolymers were determined with a polystyrene standard calibration (Waters high-pressure GPC assembly model M515 pump, *u*-Styragel columns of HR4, HR4E, HR5E with 500 and 100 Å refractive index detectors, and THF solvent).



검 량 정 보

검량선이름 THF(60,455) 보정방법 NONE

분 석 결 과

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1	Peak010101	33905	39604	44316	58332	77329	N/A	1.30707	N/A

Fig. S13 GPC data of **P29DPP-TTSe**. The molecular weight and polydispersity index of the copolymers were determined with a polystyrene standard calibration (Waters high-pressure GPC assembly model M515 pump, *u*-Styragel columns of HR4, HR4E, HR5E with 500 and 100 Å refractive index detectors, and THF solvent).

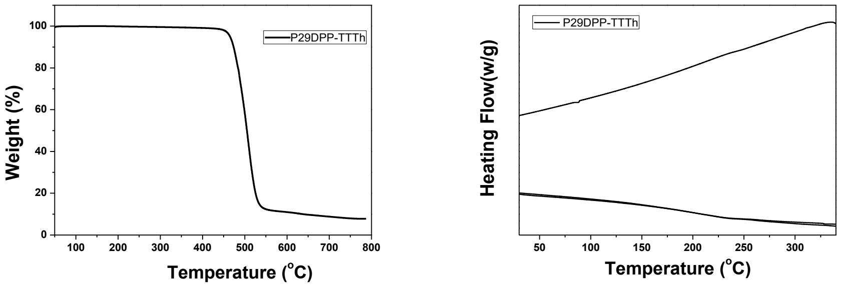

Fig. S14 TGA and DSC thermograms of **P29DPP-TTTh**. TGA analysis was performed in a nitrogen atmosphere at a rate of 10°C min^{-1}. DSC analysis was conducted in nitrogen at a rate of 10°C min^{-1} from 30°C to 320°C.

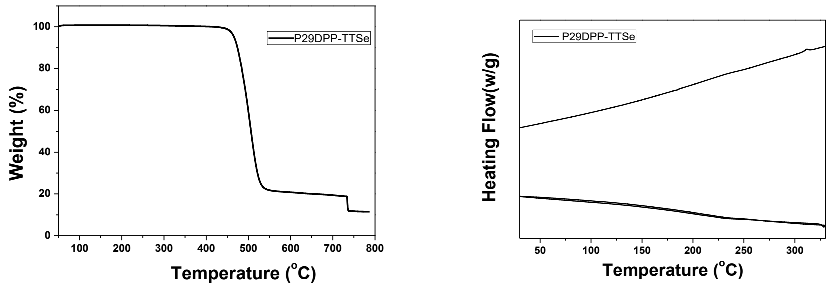

Fig. S15 TGA and DSC thermograms of **P29DPP-TTSe**. TGA analysis was performed in a nitrogen atmosphere at a rate of 10°C min^{-1}. DSC analysis was conducted in nitrogen at a rate of 10°C min^{-1} from 30°C to 320°C.

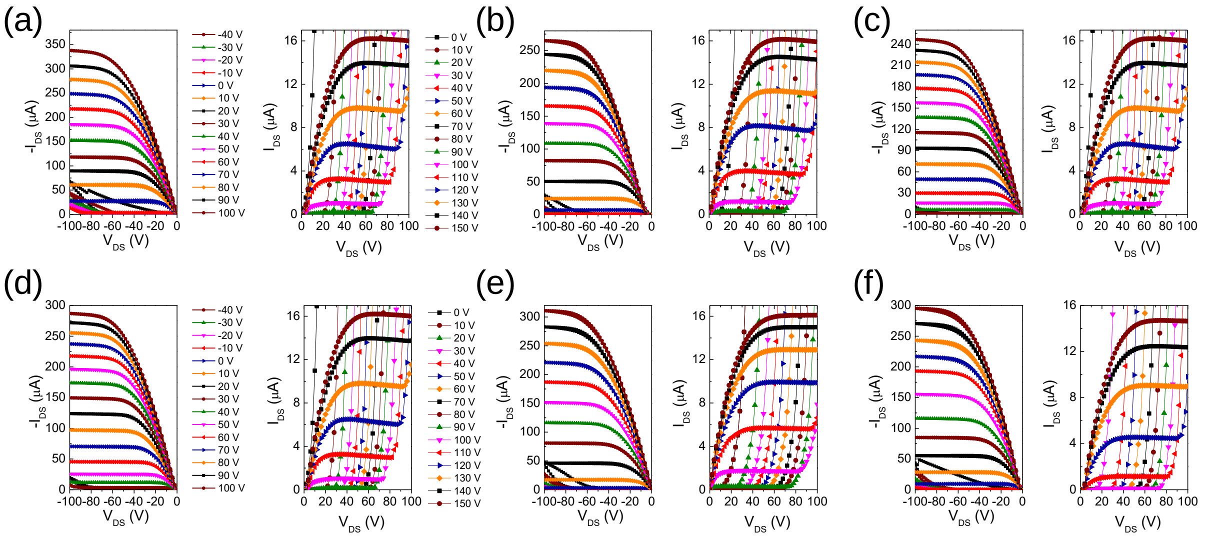

Fig. S16 (a–c) Output characteristics of OFET based on **P29DPP-TTTh** polymer films using (a) chlorobenzene, (b) toluene, and (c) *o*-xylene solution after optimal thermal annealing at 250°C. (d–f) Output characteristics of OFET based on **P29DPP-TTSe** polymer films using (d) chlorobenzene, (e) toluene, and (f) *o*-xylene solution after optimal thermal annealing at 250°C. The interval of the gate voltage was 10 V.

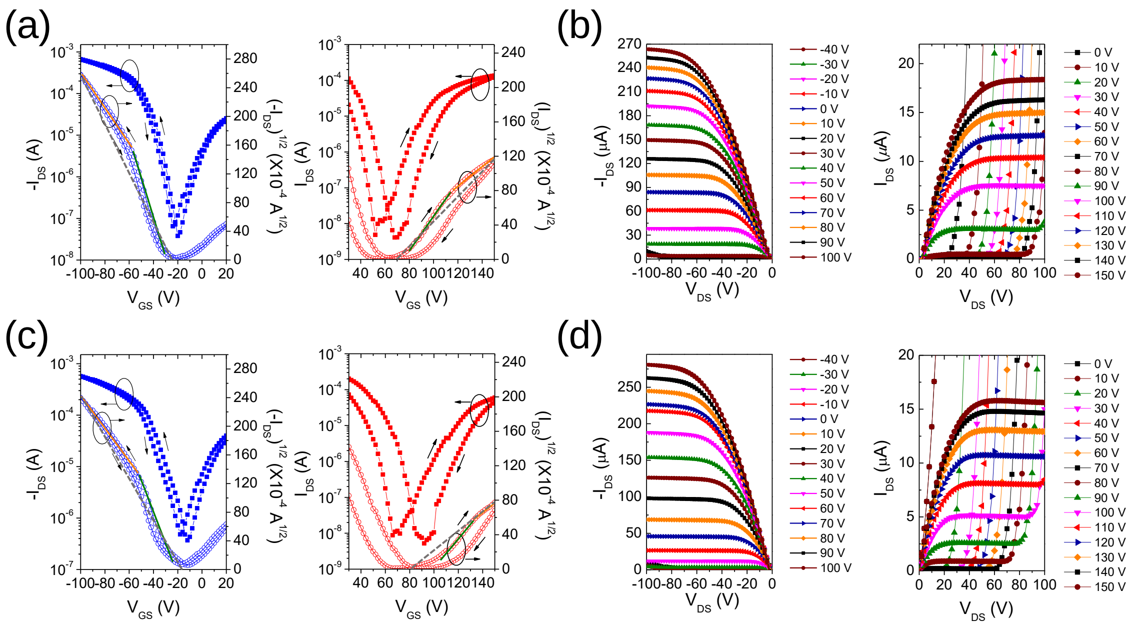

Fig. S17 (a) Transfer characteristics and (b) output characteristics of OFET based on **P29DPP-TTTh** polymer films using toluene and DMSO additive after optimal thermal annealing at 250°C. (c) Transfer characteristics and (d) output characteristics of OFET based on **P29DPP-TTTh** polymer films using *o*-xylene and DMSO additive after optimal thermal annealing at 250°C. In transfer curves, the left and right panels indicate the results of hole- and electron-enhancement operations with $V_{DS} = -100$ and +150 V, respectively. Solid green, orange, and dotted grey fitting lines indicate the region for maximum mobility estimation, mobility at kinks and considering the reliability factor (r), respectively. In the output curves, the interval of the gate voltage was 10 V.

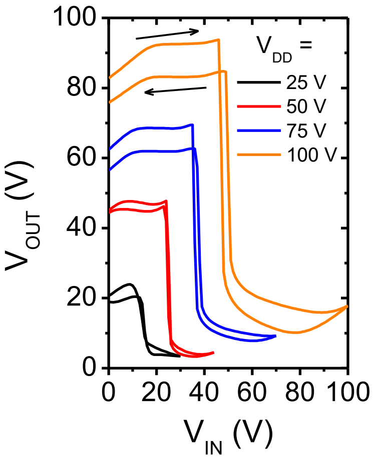

Fig. S18 Voltage transfer characteristics of CMOS-like inverter characteristics of **P29DPP-TTSe** inverters processed in toluene and DMSO additive solution at different V_{DD} ranging from 100 V down to 25 V.

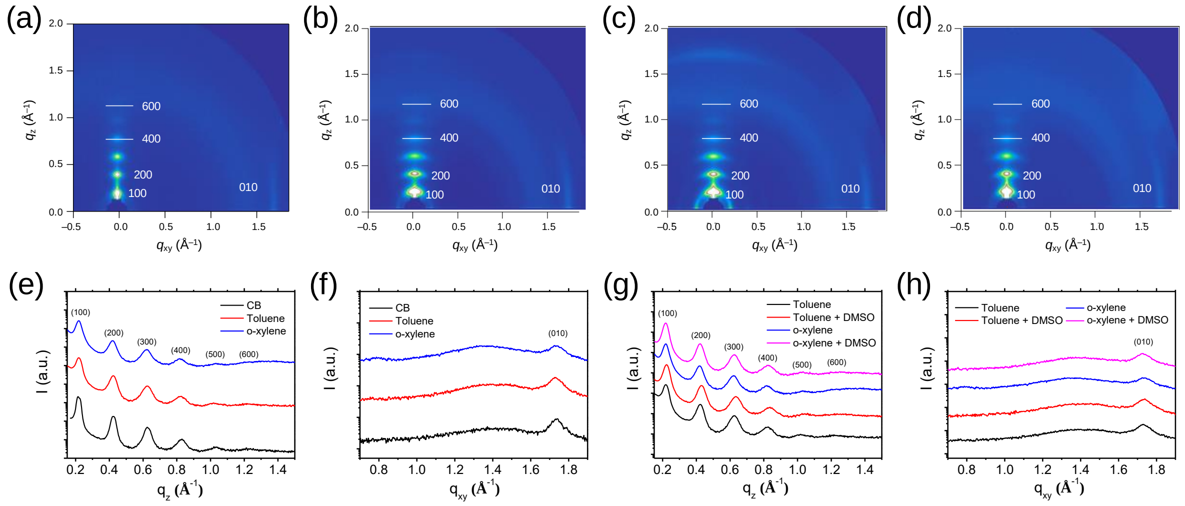

Fig. S19 2D-GIXD images of **P29DPP-TTTh** polymer films using (a) chlorobenzene, (b) toluene, (c) *o*-xylene, and (d) toluene with DMSO additive after optimal thermal annealing at 250°C. (e, f) The corresponding 1D-GIXD profiles of (e) out-of-plane and (f) in-plane GIXD patterns of **P29DPP-TTTh** polymer films in different processing solvent. (g, h) The corresponding 1D-GIXD profiles of (g) out-of-plane and (h) in-plane GIXD patterns of **P29DPP-TTTh** polymer films with the DMSO additive treatment.

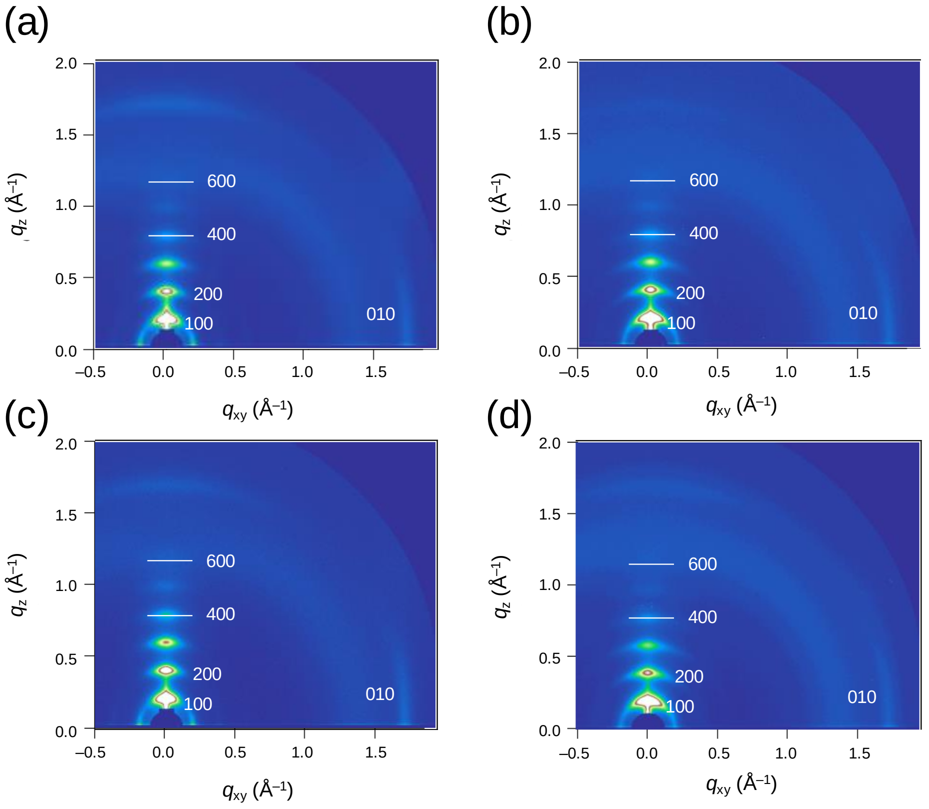

Fig. S20 2D-GIXD images of **P29DPP-TTTh** polymer films using (a) *o*-xylene and (b) *o*-xylene with DMSO additive after optimal thermal annealing at 250°C. 2D-GIXD images of **P29DPP-TTSe** polymer films using (c) *o*-xylene and (d) *o*-xylene with DMSO additive after optimal thermal annealing at 250°C.

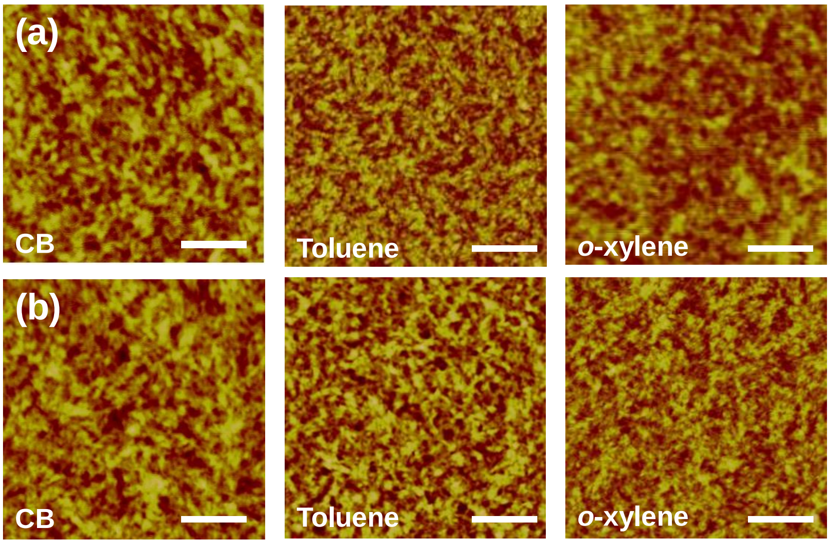

Fig. S21 AFM topography images of (a) **P29DPP-TTTh** and (b) **P29DPP-TTSe** polymer films using different processing solvents after optimal thermal annealing at 250°C (Scale bar = 500 nm).

Table S1. Solubility test results for **P29DPP-TTTh** and **P29DPP-TTSe** polymers. The solubility was tested by checking the solution with a concentration of 0.5 wt% mL^{-1}.

Material	Acetone	MeOH	THF	Toluene	Xylene	Tetralin	$CHCl_3$	CB	DCB
P29DPP-TTTh	×	×	○	○	○	○	○	○	○
P29DPP-TTSe	×	×	○	○	○	○	○	○	○

Table S2. Summary of optical and electrical characterization for **P29DPP-TTTh** and **P29DPP-TTSe** polymers.

Material	UV_{max}-S[a] (nm)	UV_{max}-F[b] (nm)	UV_{max}-ann[c] (nm)	UV-edge (nm)	Bandgap (eV)	HOMO (eV)	LUMO (optical) (eV)	LUMO (electrochemical)) (eV)
P29DPP-TTTh	788 448	793 712 448	716, 790	910	1.36	-5.38	-4.02	-3.64
P29DPP-TTSe	802 448	803 723 448	724, 703	928	1.33	-5.37	-4.04	-3.63

[a] in dilute toluene solution
[b] solid thin-film states on a quartz plate before thermal annealing
[c] solid thin-film states on a quartz plate after thermal annealing at 200°C

Table S3. Literature table for comparison of charge transport mobility in OFETs using nonchlorinated solvent processing.

Reference	Solvent	Material	$\mu_{h,gca}$	$\mu_{e,gca}$
(This work)	Toluene/DMSO	P29DPP-TTTh	4.29	0.57
	Toluene/DMSO	P29DPP-TTSe	6.36	0.71
Adv. Funct. Mater. **2014**, *24*, 3524–3534	THN/*p*-xylene	PTDPPTFT4	3.94	-
Adv. Mater. **2015**, *27*, 3626–3631	THF	PDPP-TVS-C24	3.0	-
	Tetralin	PDPP-TVS-C29	8.2	-
ACS Appl. Mater. Interfaces **2017**, *9*, 15652–15661	Toluene	PTDPPTT-Si	1.54	-
	Toluene	PFDPPTT-Si	1.55	-
ACS Appl. Mater. Interfaces. **2016**, *8*, 24325–24330	Hexane	PDPPF-DFT	0.26	0.12
Adv. Mater. **2014**, *26*, 6612–6616	Tetralin	P-DPP-BTT(1)-SVS(9)	3.7	0.62
	Tetralin	P-DPP-BTT(3)-SVS(7)	3.1	0.49
Adv. Funct. Mater. **2015**, *25*, 4844–4850	Ethanol	P-DPP-TT(7)-SVS(3)	1.03	-
ACS Nano **2015**, *9*, 5264–5274	THF	DPPBTSPE	1.53	-
ACS Appl. Mater. Interfaces **2017**, *9*, 28817–28827	TMB	PDPP2DT-F2T2	1.28	0.39
Chem. Mater. **2013**, *25*, 782–789	*p*-xylene	PTDPPTFT4	2.1	-
Macromolecules **2014**, *47*, 8602–8610	TMB/1-methylnaphthalene	pDTTG-DTBT	0.26	-
Macromol. Rapid Commun. **2018**, *39*, 1800225	Toluene	PTTFDPP-TT	0.12	-
Org. Electron. **2015**, *23*, 193–198	*d*-limonene	FBT-Th_4	1.06	-
Adv. Mater. **2016**, *28*, 943–950	TMB/DPE	PDPPTT-2T	6.21	-
	TMB/DPE	PDPPMT-2T	10.89	-

Table S4. Crystallographic parameters of **P29DPP-TTTh** and **P29DPP-TTSe** polymer films after optimal thermal annealing at 250°C.

Materials	Solvent	Additive	$q_{z,(100)}$ [Å^{-1}]	$d_{z,(100)}$ [Å]	FWHM$_{xy,(100)}$	$L_{c,z(h00)}$ [Å]	$q_{xy,(010)}$ [Å^{-1}]	$d_{xy,(010)}$ [Å]
P29DPP-TTTh	CB	-	0.210	28.89	0.0255	221.4	1.720	3.65
	Toluene	-	0.219	28.67	0.0296	190.8	1.731	3.63
		additive	0.223	28.19	0.0331	170.9	1.737	3.62
	o-xylene	-	0.218	28.77	0.0304	185.9	1.737	3.62
		additive	0.218	28.87	0.0314	180.0	1.730	3.63
P29DPP-TTSe	CB	-	0.208	28.88	0.0299	228.5	1.716	3.66
	Toluene	-	0.224	27.96	0.0264	214.6	1.720	3.65
		additive	0.222	29.24	0.0286	197.8	1.727	3.64
	o-xylene	-	0.223	28.12	0.0272	208.2	1.721	3.65
		additive	0.217	28.89	0.0310	182.7	1.731	3.63