

Electronic Supplementary Information

A novel design of donor-acceptor polymer semiconductors for printed electronics: application to transistors and gas sensors

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Experiments: Synthesis of 29DPP-SeTh and SiDPP-SeTh

Materials

All reactions were performed under a nitrogen atmosphere using standard Schlenk techniques. Extra dry chlorobenzene was obtained from Accros Organic and degassed with argon for 15 min prior to utilization. Other starting materials were purchased from Sigma-Aldrich, TCI or Alfa Aesar.

Measurement.

^1H NMR data were recorded using a Bruker DRX 300 MHz spectrometer and ^{13}C NMR data were measured on a Bruker DRX 500 MHz spectrometer. High resolution mass (HRMS) analysis was measured using a Jeol JMS-700. The thermal analysis measurements were performed using a TA 2050 TGA thermogravimetric analyzer under a nitrogen atmosphere. The samples were heated at 10 °C/min. Differential scanning calorimetry was conducted under nitrogen using a TA Instruments 2100 DSC. The samples were heated at 10 °C/min from 0 °C to 300 °C. Absorption spectra were measured using a PerkinElmer LAMBDA-900 UV/vis/IR spectrophotometer. Photoluminescence spectra were measured using a LS-50B luminescence spectrophotometer. Cyclic voltammograms of materials were measured on an epsilon E3 at a room temperature in a 0.10 M solution of tetrabutylammonium perchlorate (Bu_4NClO_4) in dimethylformamide at a scanning rate of 50 mV/s. A Pt wire was used as the counter electrode and an Ag/Ag^+ electrode as the reference electrode. The number-average molecular weights (M_n) were used by GPC using the Shimadzu LG solution, chloroform as the eluent with a flow rate of 1.0 mL/min.

Synthesis of 2,5-dibromoselenopheno[3,2-b]thiophene (1)

The reaction was followed by literature methods¹. ^1H -NMR (CD_2Cl_2 , 300 MHz): δ (ppm) 7.46 (s, 1H), 7.28 (s, 1H).

Synthesis of selenopheno[3,2-b]thiophene-2,5-diylbis(trimethylstannane) (2)

2,5-Dibromoselenopheno[3,2-b]thiophene (3 g, 8.69 mmol) was dissolved in ether (100 mL). $n\text{-BuLi}$ (2.5 M in hexane, 20.0 mmol, 8.0 mL) was added dropwise at -78 °C. The mixture was stirred for 3 h at -78 °C. Trimethyltin chloride (1.0 M in THF, 20.4 mmol, 20.4 mL) was added and stirred for 4 h at room temperature. The mixture was extracted with diethyl ether and dried over MgSO_4 . After the removal of the solvent, the crude product was purified

by recrystallization from methylene chloride and methanol. (3 g, 67%). ^1H NMR (300 MHz, CD_2Cl_2): δ (ppm) = 7.41(s, 1H), 7.16(s, 1H), 0.32(s, 18H) ^{13}C NMR (500 MHz, CDCl_3): δ (ppm) = 146.7, 140.6, 140.0, 129.8, 129.7, 121.6, 28.9, 27.3, 13.7, 10.9.

Synthesis of 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(7-decylnonadecyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (3)

The reaction was followed by literature methods². ^1H -NMR (300 MHz, CDCl_3 , ppm): δ 8.71 (d, 2H), 7.26 (d, 2H), 4.02-3.97 (t, 4H), 1.78-1.71 (t, 4H), 1.44-1.27(m, 98H), 0.92-0.87 (m, 12H)

Synthesis of 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(6-(didodecyl(methyl)silyl)hexyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (4)

The reaction was followed by literature methods³. ^1H NMR (CDCl_3 , 300MHz): δ (ppm) 8.79-8.77 (d, J = 6.0 Hz, 2H), 7.34-7.32 (d, J = 6.0 Hz, 2H), 4.10-4.05 (m, 4H), 1.82-1.77 (m, 4H), 1.49-1.34 (m, 94H), 0.99-0.95 (m, 12H), 0.58-0.53 (m, 12H), 0.00 (s, 6H).

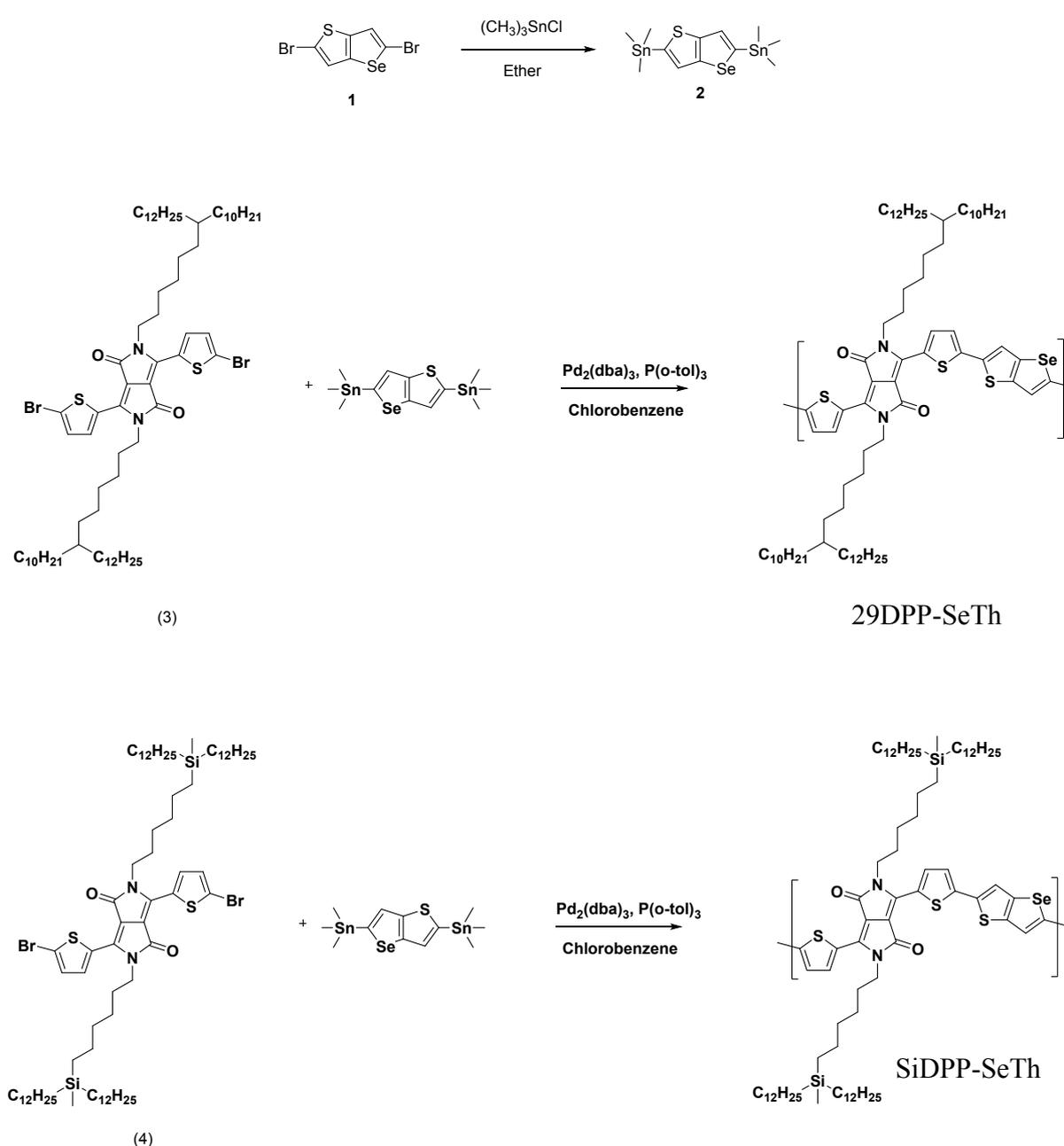
Polymerization of DPP-ThSe

The polymer was synthesized by Stille coupling reaction using a palladium-catalyzed. In a Schlenk flask, 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(7-decylnonadecyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (0.30 g, 0.235 mmol) and selenopheno[3,2-b]thiophene-2,5-diylbis(trimethylstannane) (0.12 g, 0.235 mmol) were dissolved in dry toluene (15 mL) and degassed with nitrogen for 20 min. $\text{Pd}_2(\text{dba})_3$ (1.8 mg, 0.0012 mmol) and $\text{P}(o\text{-tol})_3$ (1.4 mg, 0.0004 mmol) were added to the mixture, and stirred at 110 °C for 3 h. Afterwards, 2-(tributylstannyl)thiophene (0.1 mL) was added to the mixture for end-capping, and stirred for 3 h. The reaction mixture was precipitated into methanol (300 mL with 0.2 M HCl aq). The crude polymer was filtered and purified by soxhlet extraction with methanol, hexane, and toluene. The DPP-ThSe was obtained by precipitation of the toluene solution into methanol. (0.24 g, $M_n = 1,885,956$ Da, $M_w = 2,255,001$ Da, PDI = 1.19)

Polymerization of SiDPP-ThSe

The polymer was synthesized by Stille coupling reaction using a palladium-catalyzed. In a Schlenk flask, 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(6-(didodecyl(methyl)silyl)hexyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (0.30 g, 0.216 mmol) and selenopheno[3,2-b]thiophene-2,5-diylbis(trimethylstannane) (0.11 g, 0.216 mmol) were dissolved in dry toluene

(15 mL) and degassed with nitrogen for 20 min. $\text{Pd}_2(\text{dba})_3$ (1.8 mg, 0.0012 mmol) and $\text{P}(o\text{-tol})_3$ (1.4 mg, 0.0004 mmol) were added to the mixture, and stirred at 110 °C for 12 h. Afterwards, 2-(tributylstannyl)thiophene (0.1 mL) was added to the mixture for end-capping, and stirred for 3 h. The reaction mixture was precipitated into methanol (300 mL with 0.2 M HCl aq). The crude polymer was filtered and purified by soxhlet extraction with methanol, hexane, and toluene. The SiDPP-ThSe was obtained by precipitation of the toluene solution into methanol. ($M_n=2,066,270$ Da, $M_w=2,339,672$ Da, PDI = 1.13)



Scheme S1. Synthetic routes and chemical structure of the polymer.

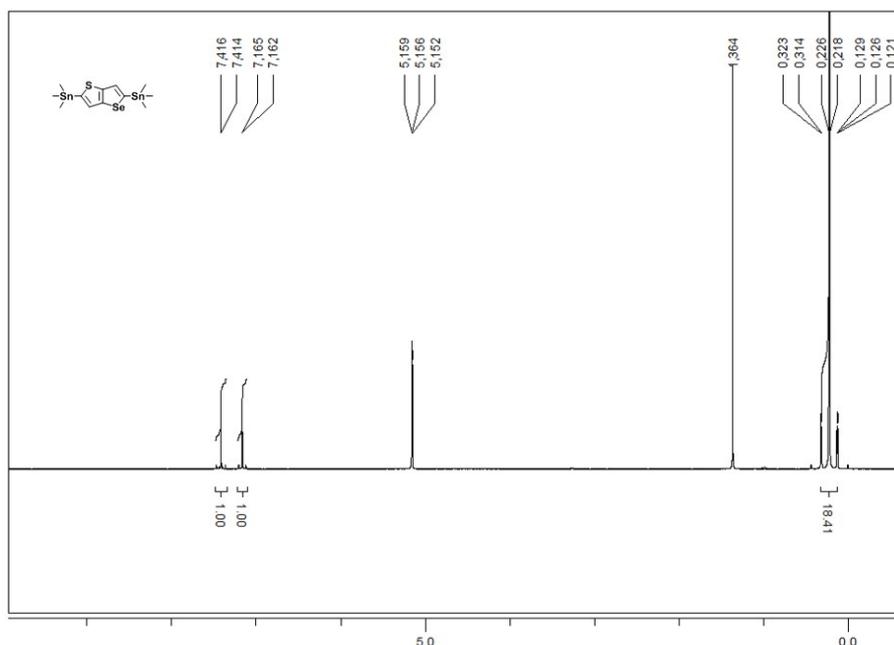


Figure S1. ^1H NMR data of selenopheno[3,2-b]thiophene-2,5-diylbis(trimethylstannane) (2)

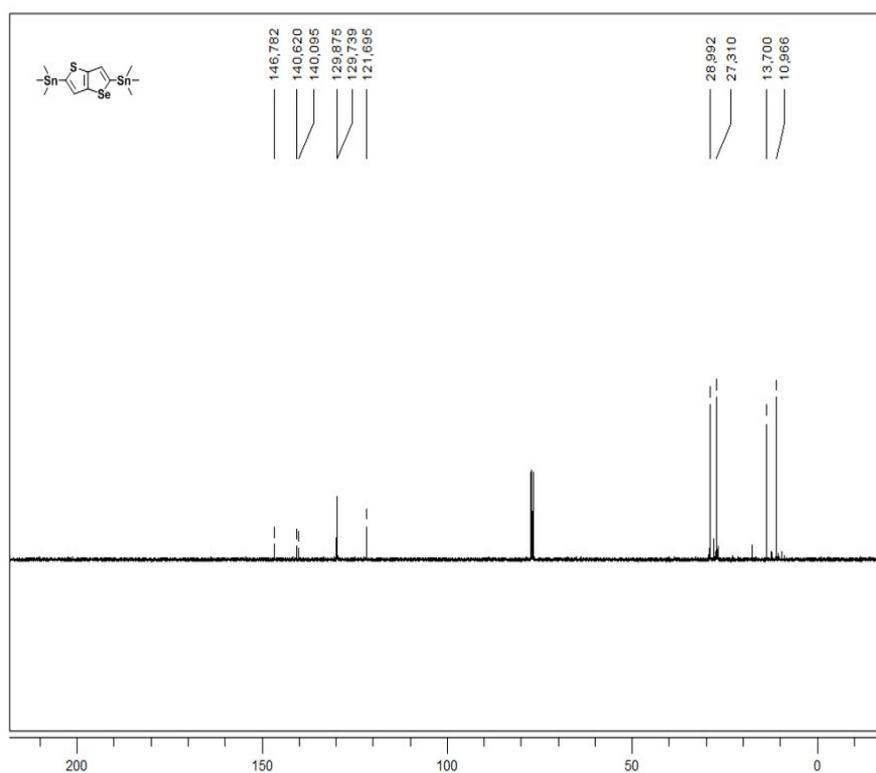


Figure S2. ^{13}C NMR data of selenopheno[3,2-b]thiophene-2,5-diylbis(trimethylstannane) (2)

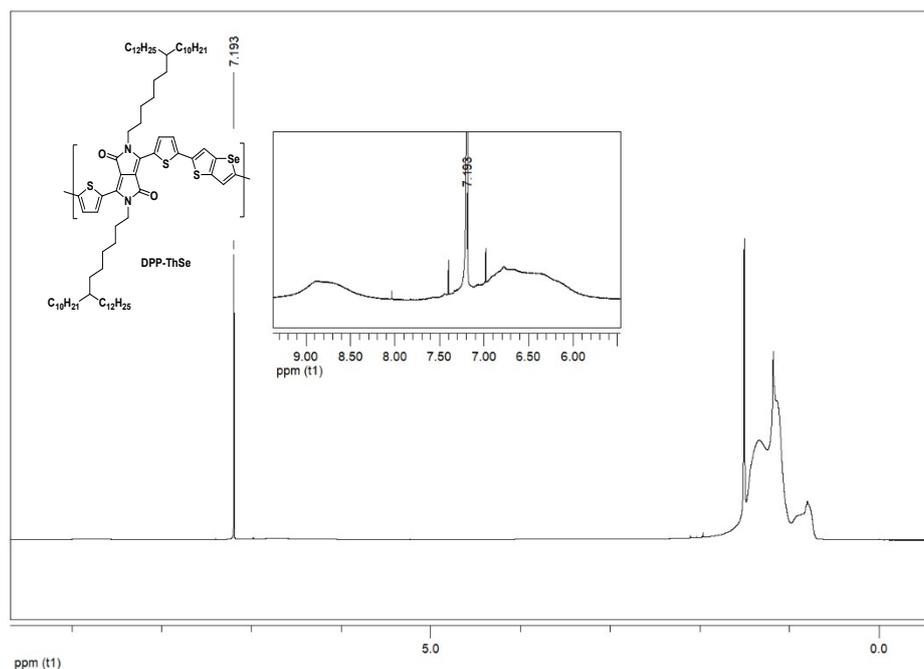


Figure S3. 1H NMR data of 29DPP-SeTh

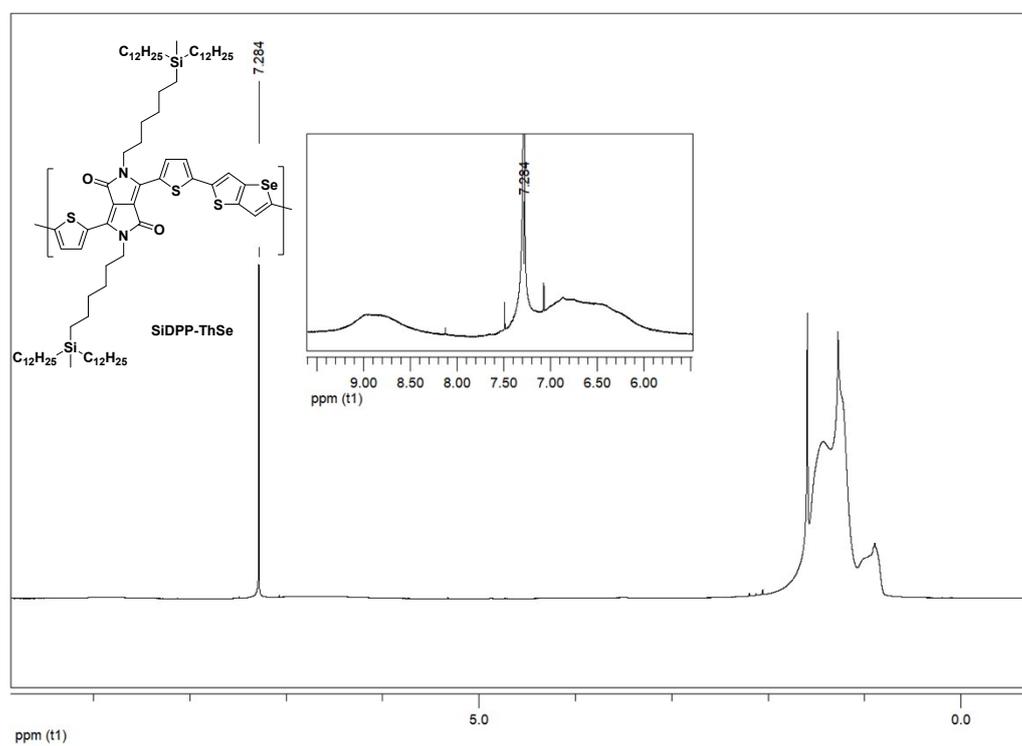
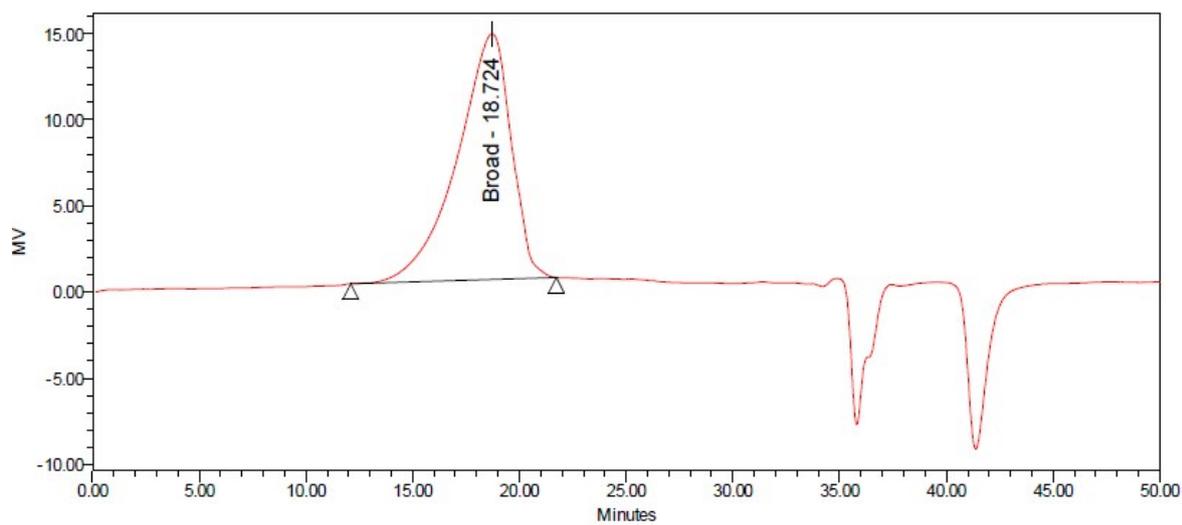


Figure S4. 1H NMR data of SiDPP-SeTh

SAMPLE INFORMATION			
Sample Name:	29DPP-ThSe	Acquired By:	System
Sample Type:	Broad Unknown	Sample Set Name:	190905
Vial:	9	Acq. Method Set:	Test
Injection #:	1	Injection Volume:	50.00 ul
Run Time:	50.0 Minutes	Date Acquired:	9/6/2019 4:27:24 PM KST

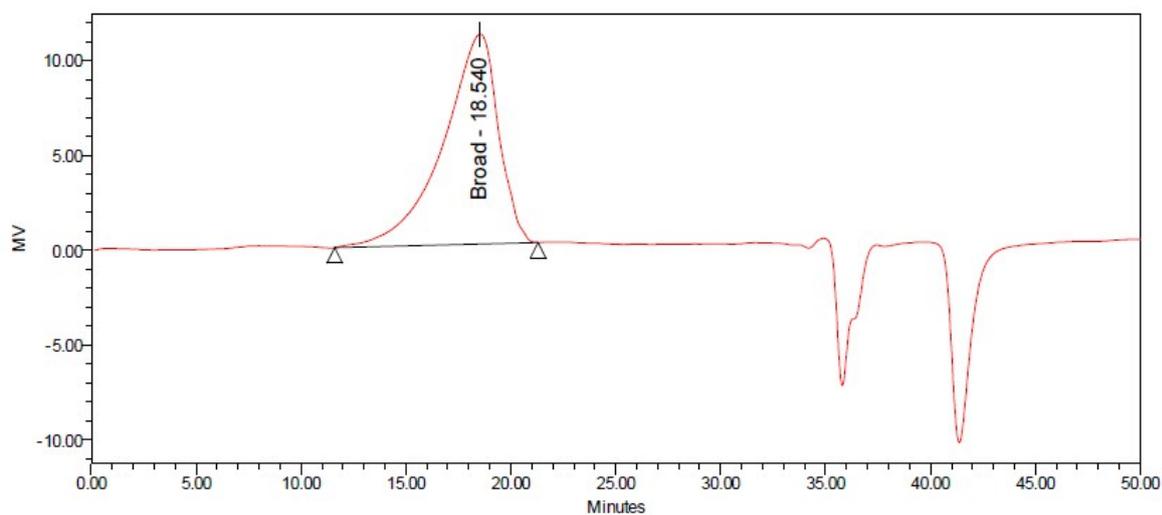


GPC Results

	Dist Name	Retention Time (min)	% Area	% Height	Mn	Mw	MP	Polydispersity
1		18.724	100.00	100.00	1885956	2255001		1.195681

Figure S5. GPC data of 29DPP-SeTh

SAMPLE INFORMATION			
Sample Name:	29DPpSi-ThSe	Acquired By:	System
Sample Type:	Broad Unknown	Sample Set Name	190905
Vial:	8	Acq. Method Set:	Test
Injection #:	1	Injection Volume:	50.00 ul
Run Time:	50.0 Minutes	Date Acquired:	9/6/2019 3:36:29 PM KST



GPC Results

Dist Name	Retention Time (min)	% Area	% Height	Mn	Mw	MP	Polydispersity
1	18.540	100.00	100.00	2066270	2339672		1.132316

Figure S6. GPC data of SiDPP-SeTh

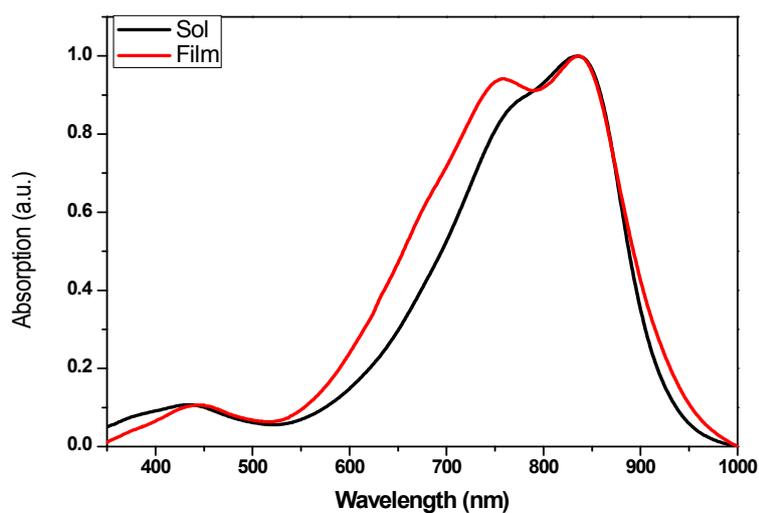


Figure S7. UV-vis absorption spectra of 29DPP-SeTh solution and 29DPP-SeTh thin film.

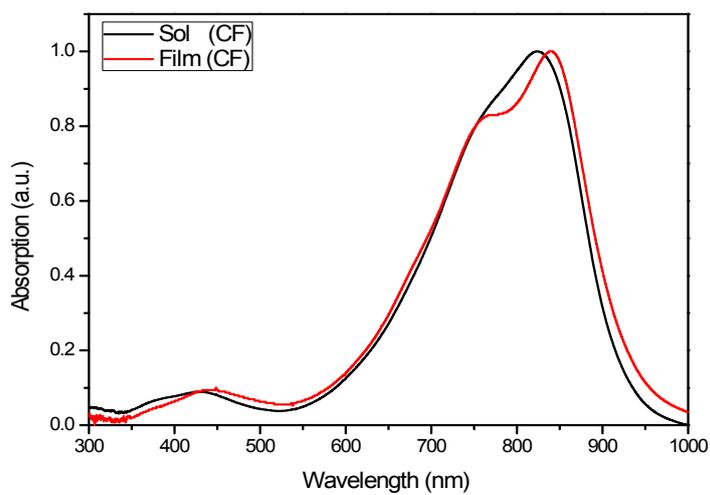


Figure S8. UV-vis absorption spectra of SiDPP-SeTh solution and SiDPP-SeTh thin film.

In Figure S7 and S8, there can observe clear red-shift from solution to film in the UV-Vis absorption spectra, which may result from extension of their conjugation length by self-assembly when cast into the thin films. In addition, the 29DPP-SeTh might have better face-to-face chain packing that caused the growth of a blue-shifted absorption shoulder peaks, like previously reported DPP-based semiconductors.^{S4-S6} On the other hand, the Si-DPP-SeTh did not show blue shift but have weak absorption shoulder peaks because of weak chain packing. This different behavior might be attributed to the structural order resulted from the bulkiness of side chains. In the case of Si-DPP-SeTh, Si atom in its side chain was bonded with four carbon atoms. These side chains were bulkier than that of 29DPP-SeTh having carbon atom bonded with three carbon and one hydrogen. As a result, Si-DPP-SeTh had more steric hindrances that interrupted the chain packing (packing with the formation of H-aggregates).

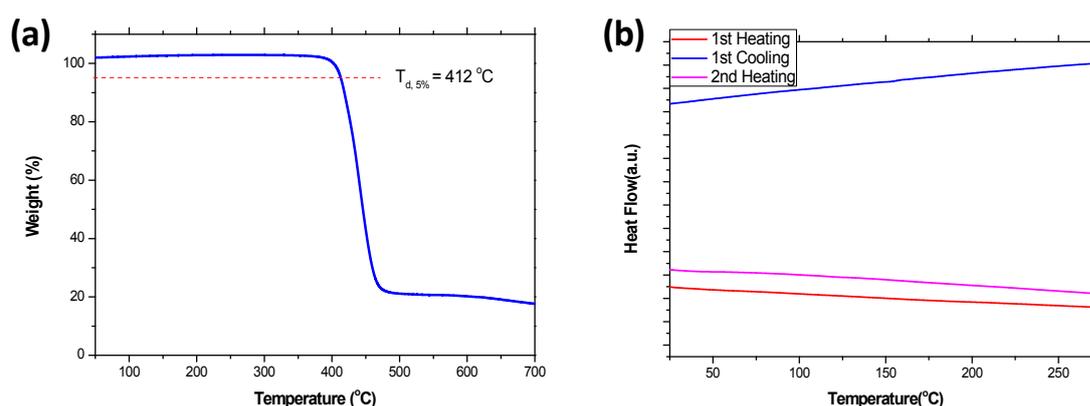


Figure S9. (a) TGA and (b) DSC of 29DPP-SeTh

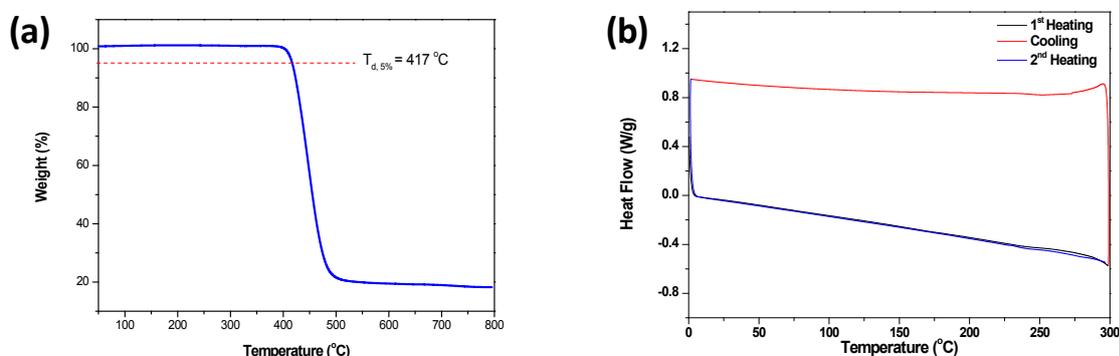


Figure S10. (a) TGA and (b) DSC of SiDPP-SeTh

Table S1. Physical properties of 29DPP-SeTh and SiDPP-SeTh.

	UV-Sol. CHCl₃ max. (nm)	UV-Film rt. max. (nm)	λ_{edge} (nm) rt Film	E_g (optical) (eV)	T_d (5%) (°C)
29DPP-SeTh	835,783	835,757	947	1.31	412
SiDPP-SeTh	824, 773	840767	929	1.34	417

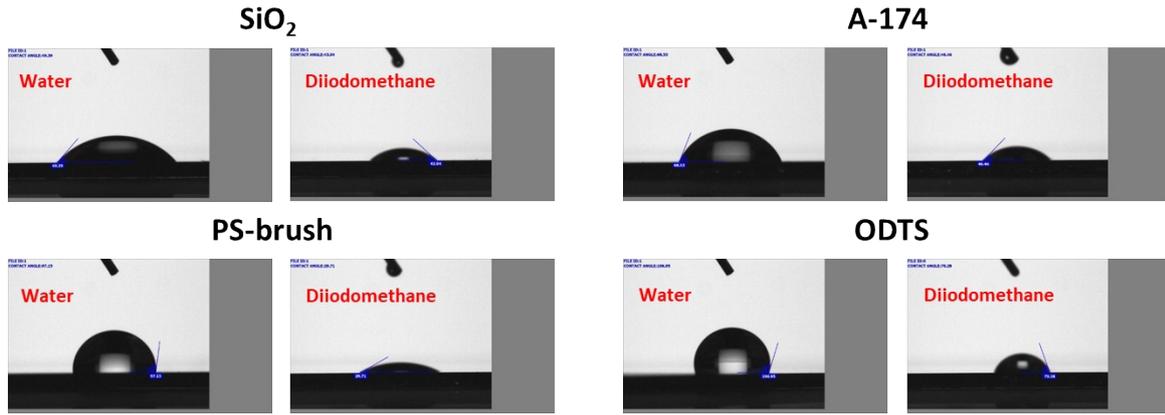


Figure S12. Captured optical images showing the seeding of water and diiodomethane droplets on as-cleaned, PS-brush-treated, A-174-treated, and ODTS-treated SiO₂/Si substrates.

Table S2. Surface energy of as-cleaned, PS-brush-treated, A-174-treated, and ODTS-treated SiO₂/Si substrates.

Surface	Contact Angle		γ_s^p [mJ m ⁻²]	γ_s^d [mJ m ⁻²]	γ_s [mJ m ⁻²]
	Water	Diiodomethane			
SiO ₂	49.39	43.04	4.95	5.24	51.87
A-174	68.53	46.46	3.37	5.43	40.79
PS-brush	97.15	29.71	-0.06	6.83	46.62
ODTS	106.95	70.28	0.44	4.78	23.06

The total surface energies (γ_s) of as-cleaned, PS-brush-treated, A-174-treated, and ODTS-treated SiO₂/Si substrates were calculated from the sum of the dispersion force component of the surface energy (γ_s^d) and the polar force component of the surface energy (γ_s^p), and the measured contact angles (θ) of water and diiodomethane with the following equation,^{S7}

$$1 + \cos \theta = \frac{2(\gamma_s^d)^{1/2}(\gamma_l^d)^{1/2}}{\gamma_l} + \frac{2(\gamma_s^p)^{1/2}(\gamma_l^p)^{1/2}}{\gamma_l}, \quad (1)$$

where γ_l is the surface energy of water (72.2 mJm⁻²) or diiodomethane (50.8 mJm⁻²), γ_l^d is the dispersion force component of the surface energy (γ_l^d of water = 22.0 mJm⁻², γ_l^d of diiodomethane = 48.5 mJm⁻²), and γ_l^p is the polar force component of the surface energy (γ_l^p of water = 50.2 mJm⁻², γ_l^p of diiodomethane = 2.3 mJm⁻²).

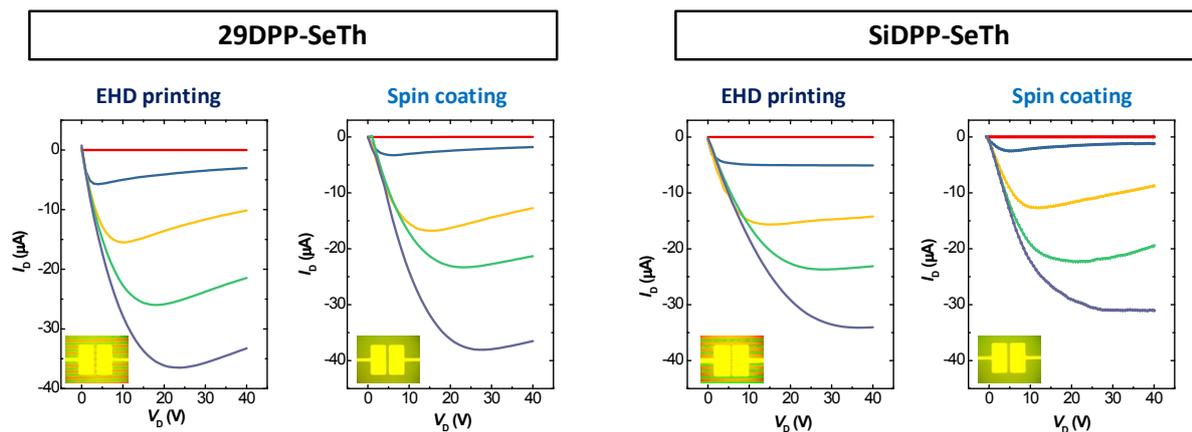


Figure S13. Output characteristics of the OFETs prepared with (left) EHD-printed and spin-coated 29DPP-SeTh and (right) EHD-printed and spin-coated SiDPP-SeTh. Before EHD jet printing of semiconductors, the dielectric surface was modified with ODTs.

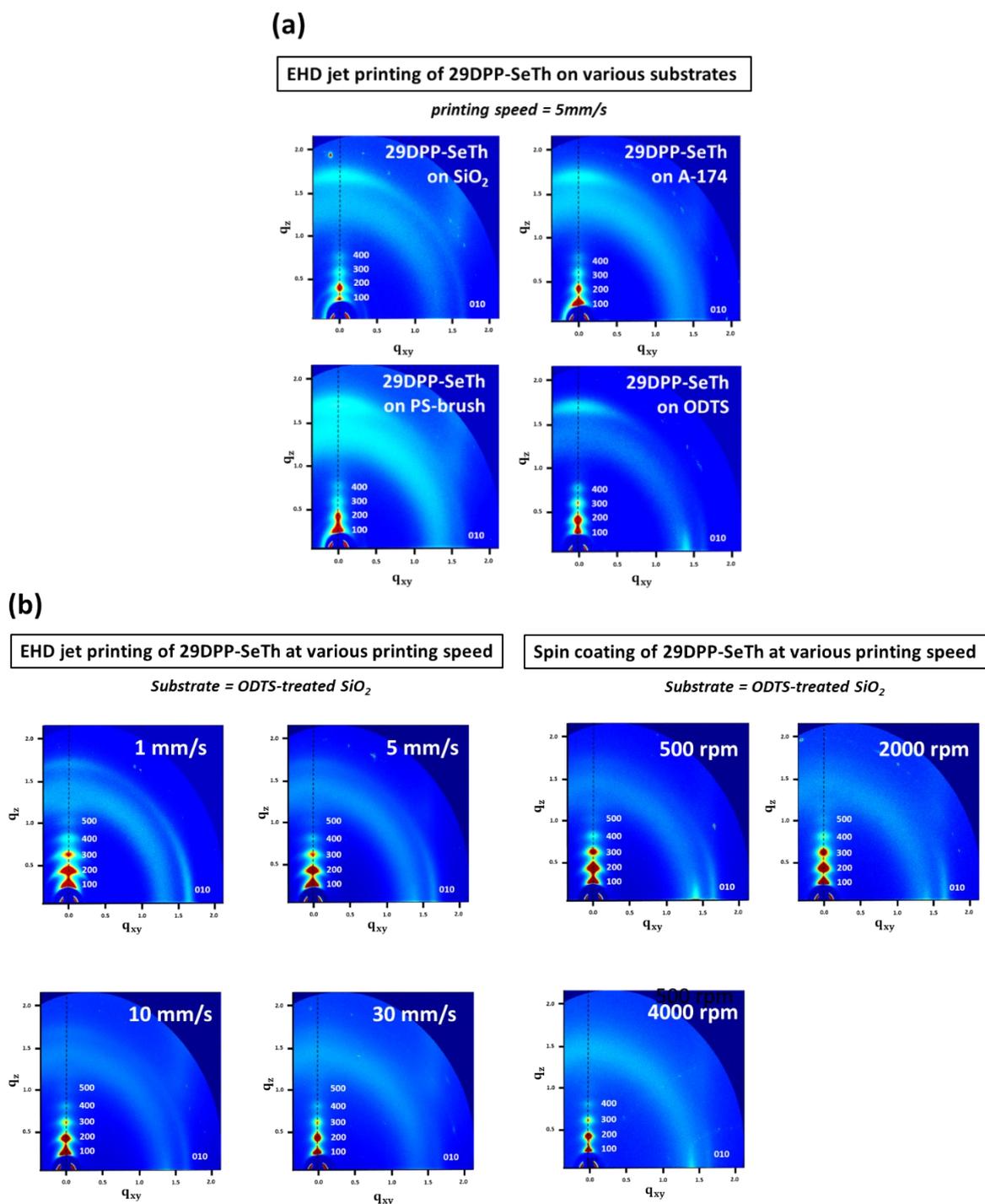
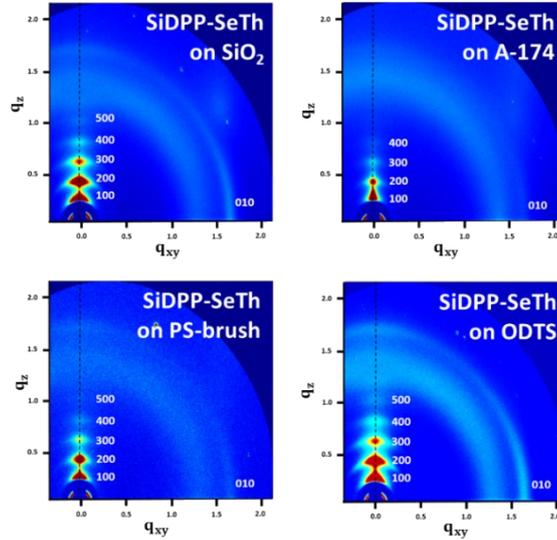


Figure S14. (a) 2D-GIXD patterns of 29DPP-SeTh prepared from EHD jet printing (5 mm/s of printing speed) on as-cleaned, PS-brush-treated, and A-174-treated SiO₂/Si substrates. (b) 2D-GIXD patterns of 29DPP-SeTh prepared from EHD jet printing (1 mm/s, 5 mm/s, 10 mm/s, and 30 mm/s of printing speed, respectively) and spin-coating (500 rpm, 2000 rpm, and 4000 rpm, respectively) on ODTS-treated SiO₂/Si substrates.

(a)

EHD jet printing of SiDPP-SeTh on various substrates

printing speed = 5 mm/s



(b)

EHD jet printing of SiDPP-SeTh at various printing speed

Spin coating of SiDPP-SeTh at various printing speed

Substrate = ODTS-treated SiO₂

Substrate = ODTS-treated SiO₂

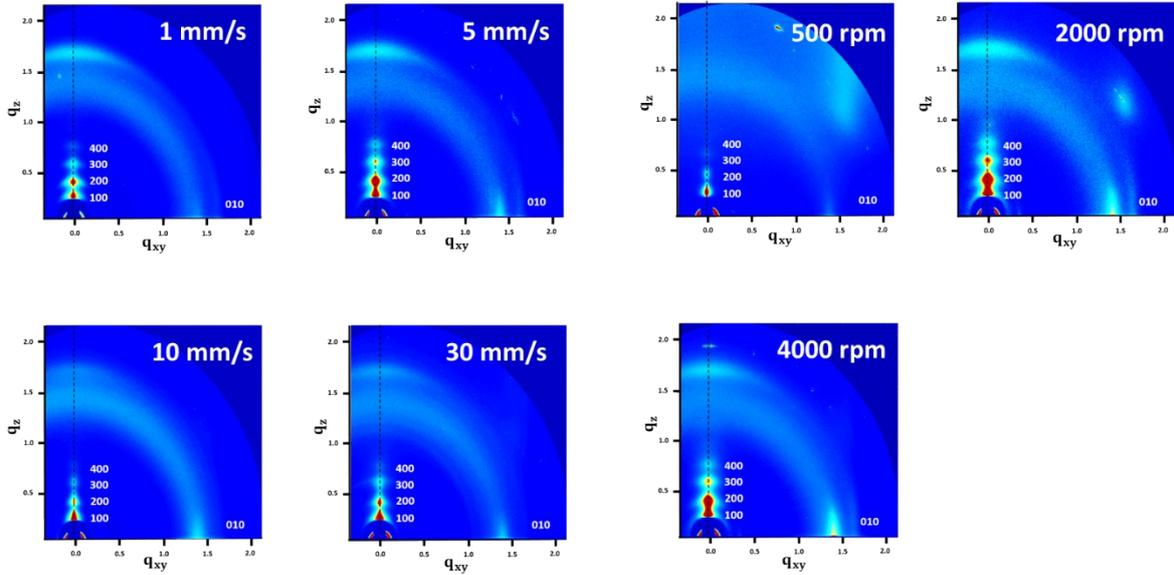


Figure S15. (a) 2D-GIXD patterns of 29DPP-SeTh prepared from EHD jet printing (5 mm/s of printing speed) on as-cleaned, PS-brush-treated, and A-174-treated SiO₂/Si substrates. (b) 2D-GIXD patterns of 29DPP-SeTh prepared from EHD jet printing (1 mm/s, 5 mm/s, 10 mm/s, and 30 mm/s of printing speed, respectively) and spin-coating (500 rpm, 2000 rpm, and 4000 rpm, respectively) on ODTS-treated SiO₂/Si substrates.

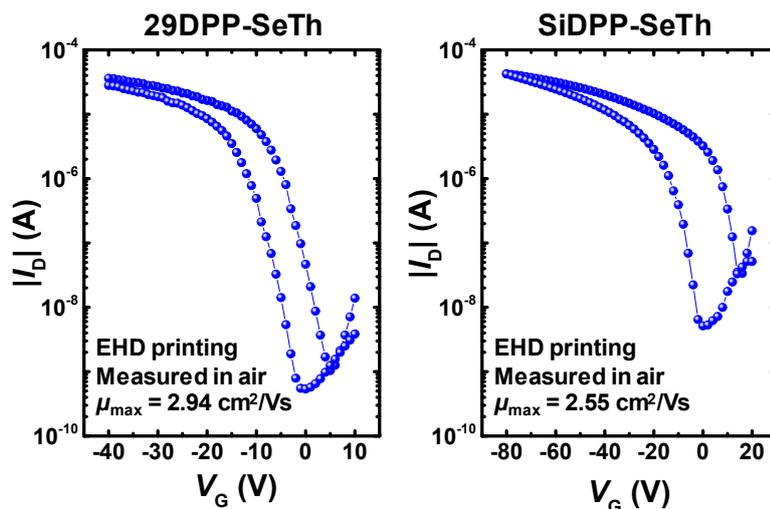


Figure S16. Transfer characteristics in the saturation regime ($V_D = -40$ V) of the OFETs with the EHD-printed 29DPP-SeTh and SiDPP-SeTh, both of which were measured in air condition.

ESI References

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