Supplementary Material (ESI) for New Journal of Chemistry

Supplementary data

Organic Thin-Film Transistors Based on 2,6-Bis(2-arylvinyl)anthracene: High-Performance Organic Semiconductors

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1. Measurements

^{1}H NMR spectra were recorded in $CDCl_3$ and DMSO on a 300 MHz Bruker Spectrospin 300 with tetramethylsilane as an internal standard. TGA analyses were performed on a TGA Q50 TA instrument at 10 ºCmin^{-1} under a nitrogen atmosphere. DSC analyses were performed on a DSC2910 TA instrument at 10 ºCmin^{-1} under nitrogen flow. UV-vis absorption spectra were recorded on a BECKMAN COULTER DU 800 spectrophotometer using 2.5 cm path-length quartz cells. For solid-state measurements, oligomers were thermally evaporated in a vacuum chamber on quartz plates to form 300 Å thick films at the deposition rate of 0.5 Å s^{-1}. XRD analyses were carried out at room temperature with a Mac Science (M18XHF-22) diffraction meter using CuKα radiation as the X-ray source at 50 kV and 100 mA. Data were collected in the conventional θ-2θ configuration (3.2−30º) from thin films thermally evaporated in a vacuum chamber on SiO_2/Si substrates at 0.5 Å s^{-1} for 300 Å. AFM images of the same vacuum-deposited thin film were taken using a PSIA XE-100 Advanced Scanning Microscope. The voltammetric apparatus used was a CH Instruments model 700C electrochemical workstation. Cyclic voltammograms (CVs) were obtained at room temperature in a three-electrode cell with a working electrode (Au), a reference electrode (Ag/AgCl), and a counter electrode (Pt) in dichlorobenzene containing tetrabutylammonium hexafluorophosphate ($Bu_4N^+PF_6^-$, 0.1 M) as supporting electrolyte at a scan rate of 100 mV/s. All the potentials were calibrated with the standard

ferrocene/ferrocenium redox couple (E = +0.41 V measured). The field-effect measurements were carried out using top-contact FETs. TFT devices with 50 μm channel length (L) and 500 μm channel widths (*W*) were fabricated on thermally oxidized, highly n-doped silicon substrates. The SiO_2 gate dielectric was 300 nm thick. The organic semiconductor (300 Å) was evaporated (0.1 Å s^{-1}, at 1x10 $^{-6}$ torr) onto a non-pretreated or OTS-pretreated oxide surface. Gold source and drain electrodes were evaporated on top of the films through a shadow mask. All measurement were performed at room temperature using a 4155C Agilent semiconductor parameter analyzer, and mobilities (μ) were calculated in the saturation regime by using the relationship: $\mu_{sat} = (2I_{DS}L)/ (WC(V_g\text{-}V_{th})^2)$, where I_{DS} is the source-drain saturation current; *C* (1.18 x 10^{-8} F) is the oxide capacitance, V_g is the gate voltage, and V_{th} is the threshold voltage.

2. Synthetic Details

All chemicals were purchased from Aldrich and used without further purification.

2,6-Bis(cholormethyl)anthraquinone: A mixture of 2,6-dimethylanthraquinone (3.8 g, 16.09 mmol), SO_2Cl_2 (50 mL), and 2,2´-azobis(2-methylpropionitrile) (0.16 g, 0.96 mmol) was refluxed for 24 h. Excess SO_2Cl_2 was removed by distillation in vacuo. The solid residue was collected by filtration, washed several times with petroleum ether, dried, and recrystallized from DMF to yield 3.8 g (78%) of 2,6-bis(cholormethyl)anthraquinone. ^{1}H NMR (300 MHz, DMSO): δ 8.41 (m, 4H), 7.98 (s, 2H), 5.00 (s, 4H). High-resolution mass spectrometry (HRMS): Calcd. for $C_{16}H_{10}Cl_2O_2$ 304.0057. Found: 304.0034.

2,6-Bis(hydroxymethyl)anthraquinone: A suspension of 2,6-bis(chlorormethyl)anthraquinone (3.5g , 11.47 mmol) in 300 mL of water and 400 mL of DMSO was refluxed with vigorous stirring. Upon heating for 4 h, a clear solution was obtained. The reaction mixture was refluxed for 38 h and then cooled to room temperature. The crystalline product was collected by filtration and recrystallized from DMF to give 3.0 g (98%) of 2,6-bis (hydroxymethyl)anthraquinone. ^{1}H NMR (300 MHz, DMSO): δ 8.17 (m, 4H), 7.85 (d, 2H, J = 10.7 Hz), 5.57 (s,

2H), 4.70 (s, 4H). High-resolution mass spectrometry (HRMS): Calcd. for $C_{16}H_{12}O_4$ 268.0735. Found: 268.0749.

2,6-Bis(hydroxymethyl)anthracene: To a solution of 2,6-bis(hydroxymethyl)anthraquinone (2.8 g 10.43 mmol) in concentrated ammonium hydroxide (70 mL) was added zinc powder (6.0 g). The reaction mixture was refluxed overnight. The insoluble material was removed by filtration and washed with hot DMSO. The solution was precipitated in 200 mL of 1 N HCl. The product was collected by filtration to give 1.86 g (75%) of 2,6-bis(hydroxymethyl)anthracene. ^{1}H NMR (300 MHz, DMSO): δ 8.49 (s, 2H), 8.04 (d, 2H, J = 8.7 Hz), 7.94 (s, 2H), 7.46 (d, 2H, J = 8.7 Hz), 5.40 (t, 2H, J = 5.6 Hz), 4.69 (d, 4H, J = 5.6 Hz). High-resolution mass spectrometry (HRMS): Calcd. for $C_{16}H_{14}O_2$ 238.0994. Found: 238.1003.

2,6-Bis(bromomethyl)anthracene: Phosphorus tribromide (4.4 g, 16.30 mmol) was added dropwise to a suspension of 2,6-bis(hydroxymethyl)anthracene (1.5 g, 6.29 mmol) in DMF (30 mL) at 0 ºC. Upon formation of yellow precipitation, the mixture was warmed to room temperature and stirred for 4 h. The solids were collected by filtration and were washed with water and hexane to give rise to 2,6-bis(bromomethyl)anthracene as a yellow solid (2.2 g, 98%). The product was further purified by recrystallization from DMF. ^{1}H NMR (300 MHz, DMSO): *δ* 8.56 (s, 2H), 8.15 (s, 2H), 8.12 (d, 2H, J = 11.5 Hz), 4.93 (s, 4H). High-resolution mass spectrometry (HRMS): Calcd. for $C_{16}H_{12}Br_2$ 361.9306. Found: 361.9277.

2,6-Bis(diethylphosphorylmethyl)anthracene: 2,6-bis(bromomethyl)anthracene (2.2 g, 6.04 mmol) was added to triethyl phosphite (50 mL), and the resulting solution was refluxed for 12 h. The solvent was removed in vacuo, and the residue was purified by column chromatography on silica gel using ethyl acetate/dichloromethane (2:1) as the eluent. Yield (90%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.35 (s, 2H), 7.97 (d, 2H, J = 8.7 Hz), 7.90 (s, 2H), 7.46 (d, 2H, J = 8.7 Hz), 4.03 (m, 8H), 3.39 (d, 4H, J = 21.8 Hz), 1.26,(t, 12H, J = 7.0 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): 131.54, 130.83, 128.75, 128. 61, 128.39, 127. 84, 125. 67, (62.26, 62.16), (35.10, 33.27), (16.44, 16.30). MS(EI) *m/z*: (M^+) calcd for $C_{24}H_{32}O_6P_2$ 478.16; found 478.

2,6-Bis(2-naphthalen-2-yl-vinyl)anthracene (DNVAnt): LDA (1.5 M in cyclohexane, 4.35 mL, 7.83 mmol) was added dropwise to a stirred solution of 2,6-bis(diethylphosphorylmethyl)anthracene (1.5 g, 3.13 mmol) in anhydrous THF (50 mL) at -78 ºC under nitrogen. The mixture was stirred for 1 h and then naphthalene-2-carbaldehyde (1.22 g, 7.83 mmol) in THF (10 mL) was added dropwise over a period of 10 min. After the mixture was stirred for 2 h at -78 ºC and for 12 h at room temperature, 5 mL of water was added and the solvent was evaporated. The residue was washed with water and MeOH. The desired product was separated by sublimation. High-resolution mass spectrometry (HRMS): calcd. for $C_{38}H_{26}$ 482.2034; found 482.2032. Anal. Calcd: C, 94.57; H, 4.43; Found : C, 94.66; H, 4.33.

2,6-Bis(2-thianaphtene-2-yl-vinyl)anthracene (DTNVAnt): LDA (1.5 M in cyclohexane, 4.86 mL, 8.76 mmol) was added dropwise to a stirred solution of 2,6-bis(diethylphosphorylmethyl)anthracene (1.4e g, 2.92 mmol) in anhydrous THF (50 mL) at -78 ºC under nitrogen. The mixture was stirred for 1 h and then benzo[b]thiophene-2-carbaldehyde (1.42 g, 8.76 mmol) in THF (40 mL) was added dropwise over a period of 10 min. After the mixture was stirred for 2 h at -78 ºC and for 12 h at room temperature, 5 mL of water was added and the solvent was evaporated. The residue was washed with water and MeOH. The desired product was separated by sublimation. High-resolution mass spectrometry (HRMS): calcd. for $C_{34}H_{22}S_2$ 494.1163; found 494.1162. Anal. Calcd: C, 82.55; H, 4.48; S, 12.96; Found: C, 82.45; H, 4.49; S, 13.03.

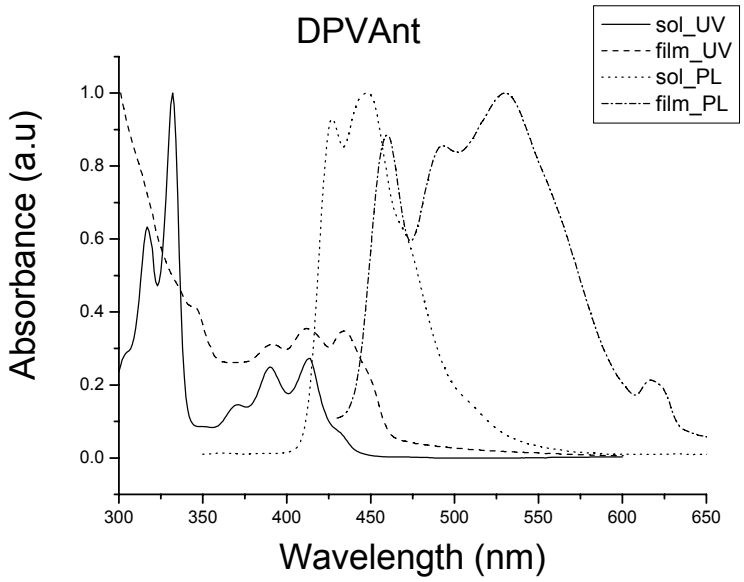

Figure S1. UV-vis absorption spectra and PL emission spectra of DPVAnt in xylene.

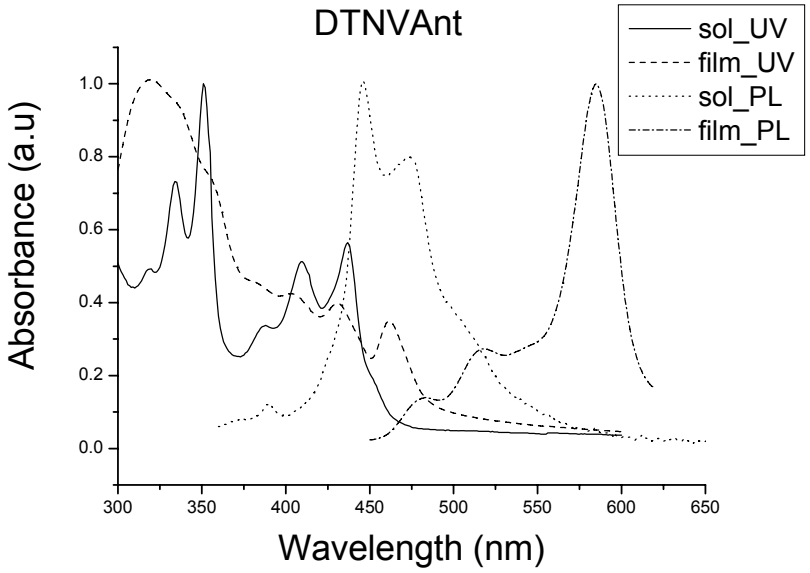

Figure S2. UV-vis absorption spectra and PL emission spectra of DTNVAnt in xylene.

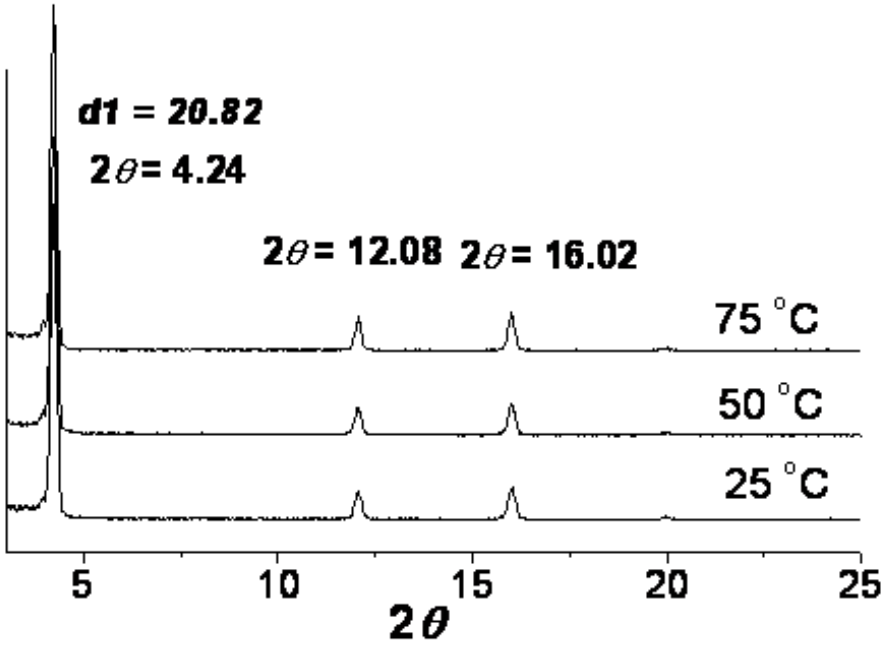

Figure S3. XRD pattern of DPVAnt thin films vacuum-deposited on OTS-treated SiO_2/Si at T_{sub} = 25, 50, 75 °C.

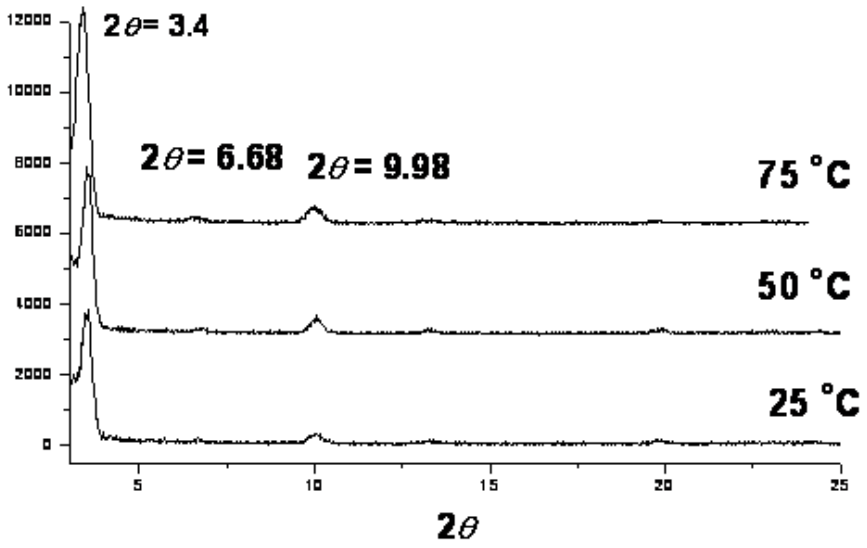

Figure S4. XRD pattern of DNVAnt thin films vacuum-deposited on OTS-treated SiO_2/Si at T_{sub} = 25, 50, 75 °C.

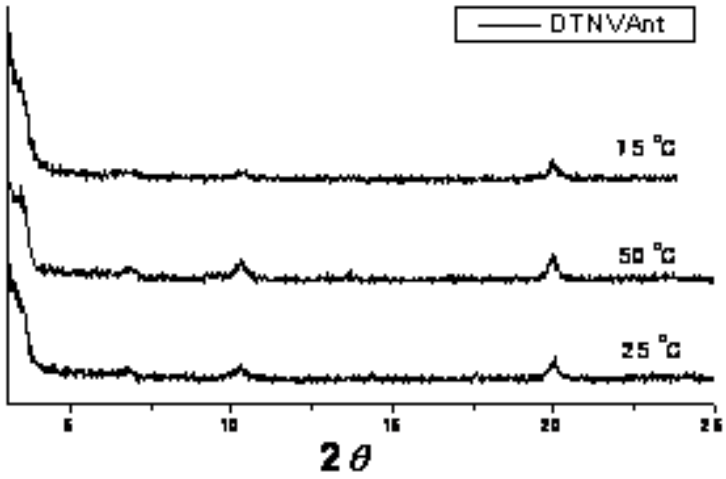

Figure S5. XRD pattern of DTNVAnt thin films vacuum-deposited on OTS-treated SiO_2/Si at T_{sub} = 25, 50, 75 °C.

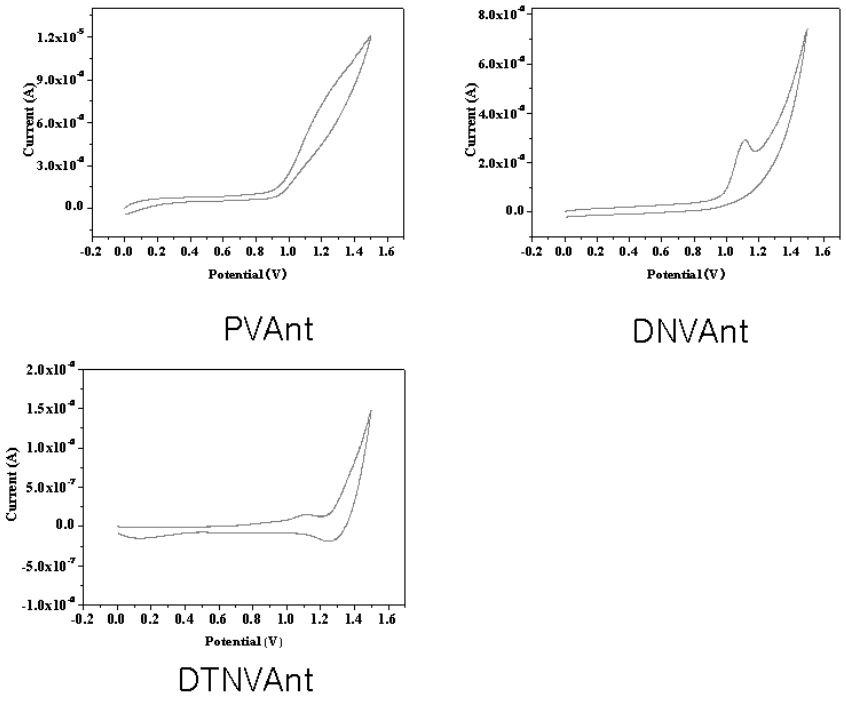

Figure S6. Cyclic voltammograms of DPVAnt, DNVAnt and DTNVAnt.

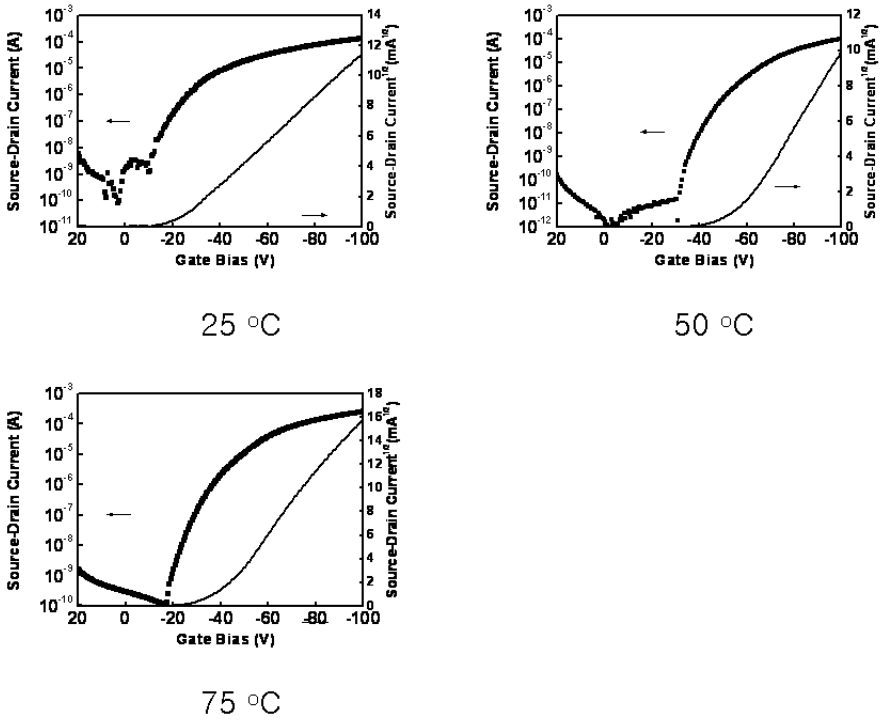

Figure S7. Output of DPVAnt thin films vacuum-deposited on OTS-treated SiO_2/Si at T_{sub} = 25, 50 and 75 °C.

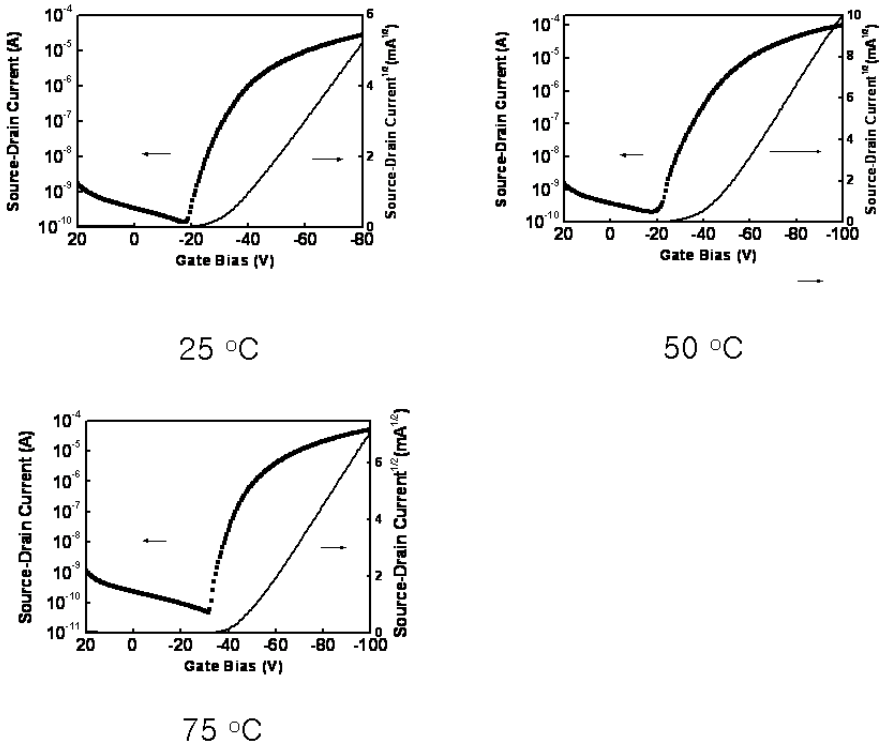

Figure S8. Output of DNVAnt thin films vacuum-deposited on OTS-treated SiO_2/Si at T_{sub} = 25, 50 and 75 °C.

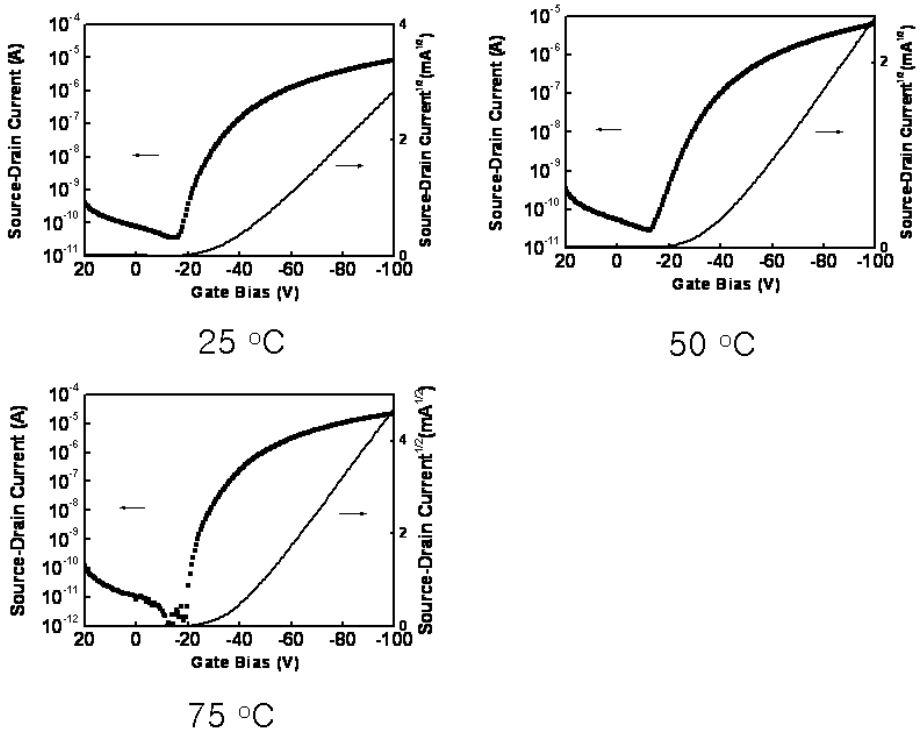

Figure S9. Output of DTNVAnt thin films vacuum-deposited on OTS-treated SiO_2/Si at T_{sub} = 25, 50 and 75 °C.

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Table 1. Field-effect mobility (μ_{TFT}), on/off current ratio (I_{on}/I_{off}), and threshold voltage (V_T) of DPVAnt, DNVAnt and DTNVAnt vacuum-deposited on a differently treated SiO_2 surfaces and at substrate temperatures (T_{sub}).

DPVAnt		Mobility (cm^2/Vs)	Threshold Voltage (V)	On/off ratio (I_{on}/I_{off})
OTS	25℃	0.301	-38.6	1.7×10^6
	50℃	0.599	-30.0	2.7×10^8
	75℃	1.008	-28.9	2.2×10^6
Bare	25℃	0.290	-23.4	1.3×10^9
	50℃	0.318	-38.8	1.9×10^8
	75℃	0.328	-16.2	9.0×10^7

DNVAnt		Mobility (cm^2/Vs)	Threshold Voltage (V)	On/off ratio (I_{on}/I_{off})
OTS	25℃	0.106	-34.4	4.8×10^5
	50℃	0.140	-35.6	1.9×10^5
	75℃	0.201	-39.2	1.1×10^7
Bare	25℃	0.065	-31.2	6.4×10^7
	50℃	0.077	-28.9	4.9×10^4
	75℃	0.133	-27.3	1.3×10^7

DTNVAnt		Mobility (cm^2/Vs)	Threshold Voltage (V)	On/off ratio (I_{on}/I_{off})
OTS	25℃	0.023	-24.0	2.3×10^5
	50℃	0.027	-25.9	1.9×10^6
	75℃	0.106	-29.4	2.4×10^7
Bare	25℃	0.007	-17.5	1.5×10^6
	50℃	0.020	-10.0	4.1×10^5
	75℃	0.101	-11.9	1.4×10^6

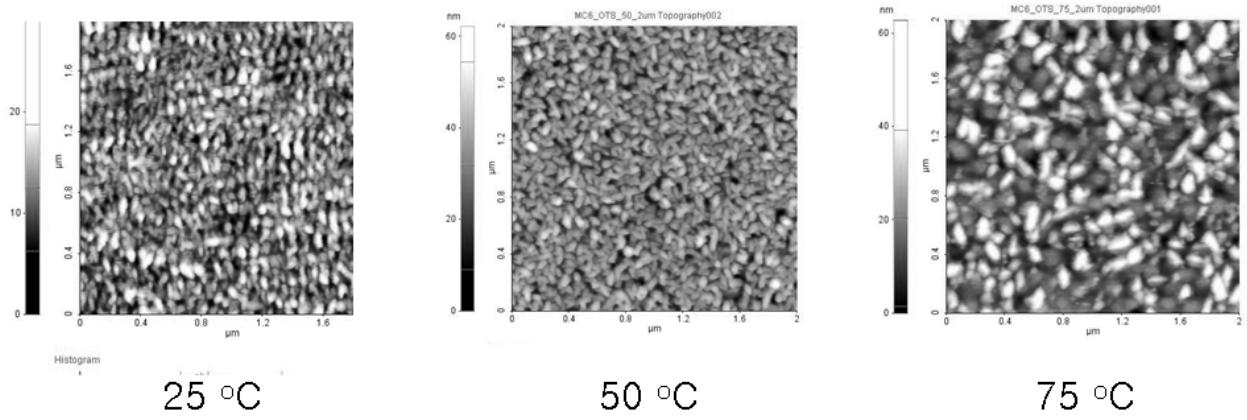

Fig. S10 noncontact mode AFM (topogaphy) image (2 x 2 um area) of DNVAnt and at 25, 50 and 75 ºC.

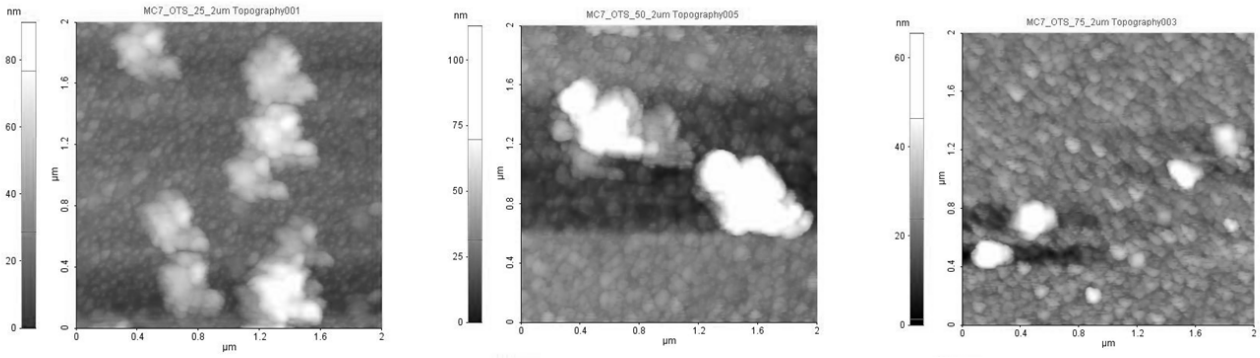

Fig. S11 noncontact mode AFM (topogaphy) image (2 x 2 um area) of DTNVAnt at 25, 50 and 75 ºC.