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Supporting Materials

Synthesis of Regioregular Pentacene-containing Conjugated Polymers

Toshihiro Okamoto,[†] Ying Jiang,[†] Hector A. Becerril,[†] Sanghyun Hong,[†] Michelle L. Senatore,[†] Ming Lee Tang,[‡] Michael F. Toney[§], Theo Siegrist,[¶] and Zhenan Bao*[†]

[†] *Department of Chemical Engineering, Stanford University, Stanford, California 94305-5025*
[‡] *Department of Chemistry, Stanford University, Stanford, California 94305-5025*
[§] *Stanford Linear Accelerator Center, Menlo Park, California 94025*
[¶] *Department of Chemical and Biomedical Engineering, Florida State University, Tallahassee, FL 32306*

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1. General

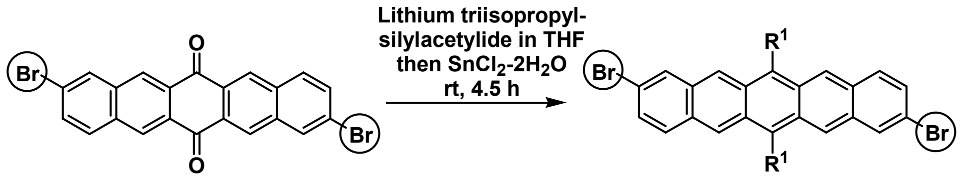
Chemical reagents: Common solvents were purchased from Sigma-Aldrich and used as received unless otherwise stated.

Instrument: ^{1}H and ^{13}C NMR spectra were recorded using Varian Inova 300, Merc 400 or Inova 500 in deuterated chloroform at 293 K. Electrochemical analysis of the compounds in *o*-dichlorobenzene (*o*DCB) was carried out by cyclic voltammetry using a CH Instruments Electrochemical Analyzer. The experiments were performed under a stream of argon in a saturated solution of 0.05 M tetra-*n*-butylammonium hexafluorophosphate (^{n}Bu$_4$NPF$_6$, from Strem Chemicals, Inc.) which was recrystallized from ethanol as a supporting electrolyte in anhydrous *o*DCB. The experiments were carried out using platinum electrodes at a scan rate of 100 mVs^{-1} against Ag wire as a pseudoreference electrode at room temperature. Ferrocene was used as a reference oxidation potential for all of our compounds. UV-vis spectra in *o*DCB were collected from a UV−vis spectrophotometer (model Cary 6000i) at room temperature using a quartz cuvette with a path length of 1 cm capped under argon prepared inside a glove box. Optical bandgaps (HOMO-LUMO gaps) were calculated from the edge of the visible-absorption bands. Ionization potentials of polymer thin films, drop-cast from chloroform onto glass, were measured in air using a photoelectron spectrometer (Model AC-2, Riken Keiki Co.). HOMO levels in the thin−film state were then estimated from the oxidation onset energies.

2. Synthesis

2.1 Synthesis of Compounds 2a and 2b

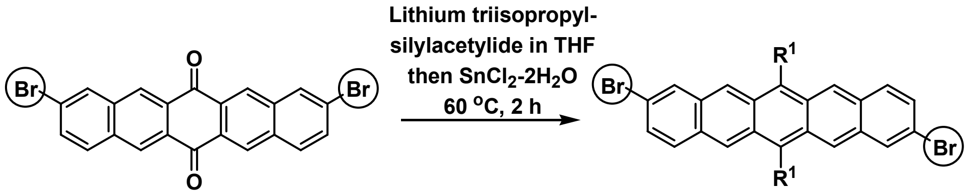
Compound 2a.



2a

A dry two-neck round bottom flask under argon was charged with triisopropylsilyl acetylene (0.73 mL, 3.24 mmol) in dry ether (22 mL) and then cooled down to 0 °C. To the solution was added *n*-butyl lithium in hexanes (1.59 M, 1.22 mL, 1.95 mmol) dropwise and then stirred for 30 mins at the same temperature. 2,9-Dibromopentacenequinone (303 mg, 0.649 mmol) and dry THF (9.2 mL) was added and the reaction mixture was allowed to rise to room temperature. After 21 h, the reaction mixture was quenched with wet ether and concentrated under reduce pressure. The resulting oil was dissolved with hexanes and flushed with hexanes on a silica gel short column to remove the excess amount of triisopropylsilyl acetylene. The column was then flushed with ethyl acetate as the eluent to collect the diol products. The solution was concentrated under reduced pressure to a give yellow solid. The resulting solids were dissolved with a mixture of THF and acetonitrile and $SnCl_2$-$2H_2O$ (2.93 g, 13.0 mmol) was added. After stirring for 4.5 h, the reaction mixture was concentrated under reduced pressure. The solids was dissolved with hexanes and filtered off by celite to remove tin residues. The crude product was subjected to a silica gel column chromatography with hexanes to obtain the desired product (366 mg, 71% yield) as a dark blue crystal. ^{1}H NMR (500 MHz, $CDCl_3$): 9.27 (s, 2H), 9.17 (s, 2H), 8.12 (s, 2H), 7.84 (d, 2H, *J*=9.0 Hz), 7.45 (d, 2H, *J*=9.0 Hz), 1.44–1.34 (m, 42H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.79, 130.91, 130.87, 130.50, 130.48, 130.26, 129.83, 127.00, 125.61, 120.58, 118.86, 108.10, 104.17, 19.09, 11.70. MS (TOF-MS) 797.20. Anal. Calcd for $C_{44}H_{52}Br_2Si_2$: C, 66.32; H, 6.58; Br, 20.05. Found: C, 66.26; H, 6.81; Br, 20.33.

Compound 2b.

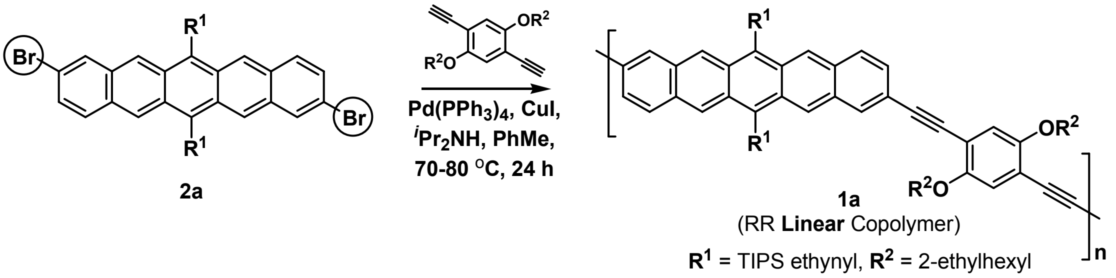


2b

A dry two-neck round bottom flask under argon was charged with triisopropylsilyl acetylene (1.08 mL, 4.83 mmol) in dry ether (32 mL) and then cooled down to 0^{o}C. To the solution was added n-butyl lithium in hexanes (1.60 M, 1.81 mL, 2.90 mmol) dropwise and then stirred for 40 min at the same temperature. 2,10-Dibromopentacenequinone (450 mg, 0.965 mmol) and dry THF (14 mL) was added and the reaction solution was allowed to rise to room temperature. After 13 h, to the reaction mixture was added a small amount of water, followed by $SnCl_2$-$2H_2O$ (4.36 g, 19.3 mmol, 20 mol amt.) as a crystal and then heated at 60 ^{o}C for 2 h. The reaction mixture was filtered off by celite and washed with chloroform to give a blue filtrate, which was then concentrated under reduced pressure. The resulting solids were dissolved with hexanes and then filtered off with a combination of celite and sodium sulfate to obtain dark blue green solids. The crude products were subjected to be silica gel column chromatography with hexanes as the eluent to give the desired product **2b** (428 mg, 56% yield) as a dark blue solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.25 (s, 2H), 9.19 (s, 2H), 8.13 (s, 2H), 7.83 (d, 2H, *J*=9.0 Hz), 7.45 (dd, 2H, *J*=9.0 Hz, 0.9 Hz), 1.42−1.34 (m, 42H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 132.87, 131.14, 130.63, 130.48, 130.41, 130.24, 129.78, 127.03, 125.56, 120.63, 119.02, 118.69, 108.18, 108.02, 104.24, 104.11, 19.10, 19.06, 11.70. MS (TOF-MS) 797.20. Anal. Calcd for $C_{44}H_{52}Br_2Si_2$: C, 66.32; H, 6.58; Br, 20.05. Found: C, 66.57; H, 6.60; Br, 19.78.

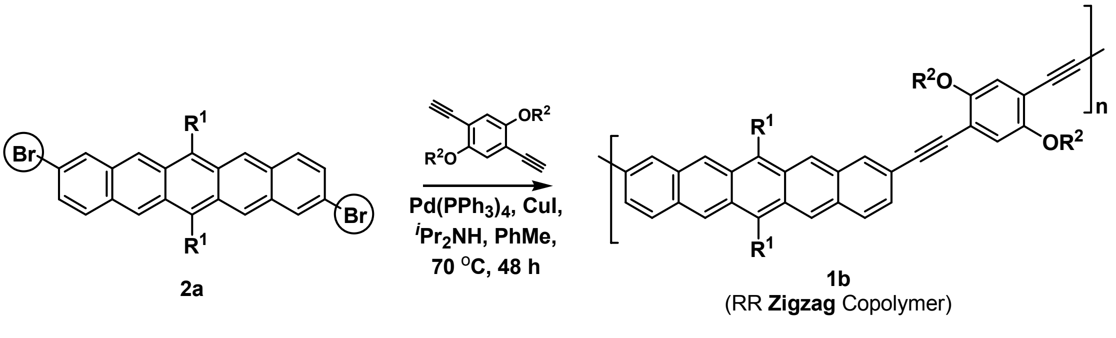
2.2 Preparation of Regioregular Pentacene-diethynylphenyl Copolymers (1a (*RR Linear*), 1b (*RR Zigzag*) and 1c (*RRa*).

1a (*RR Linear*).



A mixture of dry diisopropylamine (4.5 mL) and dry toluene (9.0 mL) was placed in a 25 mL Schlenk tube with a stirring bar. The flask was evacuated and back-filled with argon five times, followed by the addition of $Pd(PPh_3)_4$ (14.4 mg, 0.0125 mmol), CuI (1.7 mg, 8.75×10^{-3} mmol), **2a** (100 mg, 0.1255 mmol) and diethynylphenyl (52.8 mg, 0.138 mmol) under an argon atmosphere. The mixture was stirred at 70-80°C for 24 h. The reaction mixture was poured into methanol (300 mL) to give a dark brown solid which was collected and then washed with methanol, acetone and hexanes thoroughly. Finally, the polymers were dissolved in chloroform and filtered off with a syringe filter (0.25 um pore size) to give a dark green solution which was precipitated into methanol to give the desired polymer as a black solid in 82% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.29–9.26 (m, 4H), 8.19–8.17 (m, 2H), 7.96–7.94 (m, 2H), 7.52–7.47 (m, 2H), 7.17 (s, 2H), 4.06–3.93 (m, 4H), 1.95–1.25 (m, 60H), 1.09–0.88 (m, 12H). Anal. Calcd for $(C_{70}H_{88}O_2Si_2)_n$: C, 82.62; H, 8.72. Found: C, 79.55; H, 8.13.

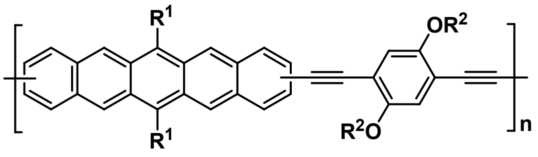
1b (*RR Zigzag*).



The same procedures as those used to obtain **1a** were used to obtain **1b**. ^{1}H NMR

(500 MHz, $CDCl_3$): δ 9.29–9.26 (m, 4H), 8.19–8.17 (m, 2H), 7.96–7.94 (m, 2H), 7.51–7.49 (m, 2H), 7.17 (s, 2H), 4.08–3.92 (m, 4H), 1.95–1.25 (m, 60H), 1.08–0.87 (m, 12H). Anal. Calcd for $(C_{70}H_{88}O_2Si_2)_n$: C, 82.62; H, 8.72. Found: C, 79.04; H, 8.09.

1c (*RRa Copolymer*).



1c
(**Regiorandom** Copolymer)
R¹ = TIPS ethynyl, **R²** = 2-ethylhexyl

The same procedures as those used to obtain **1a** were used to obtain **1c**. Polymer characterization could be found in a previous publication.[1]

Table S1. Molecular Weight of Polymer **1a**, **1b** and **1c**

Compound	**M_n (g mol^{-1})**	**PDI**
1a (*RR Linear*)	11200	1.5
1b (*RR Zigzag*)	15600	2.0
1c (*RRa*)	20200	1.6

3. X-ray Crystallographic Analysis of 2a and 2b

Single crystals of **2a** and **2b** suitable for X-ray crystal analysis were obtained by two-layer diffusion between dichloromethane as a good solvent and ethanol as a poor solvent. Crystals were in general small, and thus affected the quality of the data collection. Additionally, the observed structural phase transition at approximately 125K is leading to large atomic displacement factors, even at a temperature of 150K. The appearance of a phase transition at this low temperature indicates that the packing is not as stable, with the TIPS moiety on one side of the dibromopentacene backbone undergoing a large displacement. Thus, any discussion on the electronic overlap could use that structure.

Intensity data were collected on a Oxford Diffraction Xcalibur2 CCD Diffractometer with $\mathrm{Mo_{K\alpha}}$ radiation (λ = 0.7107 Å) and graphite monochrometer. A total of 25038 reflections were measured at a maximum 2Θ angle of 50° at a temperature of 120 K, of which 4535 were indepenent reflections ($R_{\mathrm{int}} = 0.08$). The structure was solved by direct methods (CRYSTALS) and refined by the full-matrix least squares on F^2. All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were placed by using geometrical considerations and Difference Fourier methods. The crystal data are as follows: $C_{11}H_{12}Br_{0.50}Si_{0.50}$; M_r = 796.88, crystal size 0.12 × 0.07 × 0.15 mm^3, triclinic, *P-1*, a=10.5231(8), b=10.9713(8), c=17.445(2) Å, α=90.807(8)°, β=89.922(8)°, γ=91.961(6)°, V=2012.6(3) Å^3, Z=4, ρ_{calcd}=1.315 g cm^{-3}. The refinement converged to $R_1 = 0.049$, w$R_2 = 0.054$ [$I > 1$s(I)], GOF = 1.0662.

The **2a** high-temperature polymorph was measured at a temperature of 200 K, a total of 14859 Reflections were collected to a maximum 2Θ angle of 50°, of which 3688 were independent (0.034). The crystal data are as follows: $C_{11}H_{12}Br_{0.50}Si_{0.50}$; M_r = 796.88, crystal size 0.12 × 0.05 × 0.15 mm^3, triclinic, *P-1*, a = 10.477(2), b = 11.226(2), c = 18.066(3) Å, α= 85.06(2)°, β = 80.46(2)°, γ = 81.59(2)°, V=2068.7(7) Å^3, Z = 4, ρ_{calcd} = 1.28 g cm^{-3}. The refinement converged to $R_1 = 0.088$, w$R_2 = 0.166$ [$I > 0.5$s(I)], GOF = 1.5358.

For **2b**, a total of 31889 reflections were measured at a maximum 2Θ angle of 50° at a temperature of 150 K, of which 9954 were independent reflections ($R_{\mathrm{int}} = 0.04$). The crystal data are as follows: $C_{11}H_{12}Br_{0.50}Si_{0.50}$; M_r = 796.88, crystal size 0.04× 0.13× 0.15 mm^3, triclinic, *P-1*, a = 8.5917(5), b = 14.2392(14), c = 17.7698(16) Å, α = 95.665(10)°, β = 98.824(10)°, γ = 103.551(10)°, V = 2067.8(3)Å^3, Z = 4, ρ_{calcd} = 1.28 g cm^{-3}. The refinement converged to $R_1 = 0.042$, $wR_2 = 0.104$ [$I > 1s(I)$], GOF = 0.7655.

CCDC 734417 and 734418 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif/.

4. OTFT Fabrication and OTFT Current-Voltage Characteristics of 1a, 1b, and 1c

Surface modification of SiO substrates with OTS.

We used 2×2 cm pieces of highly doped n-type (100) Si wafers (< 0.004 Ωcm) with a 300 nm dry thermal oxide gate dielectric (capacitance C_i=10 nFcm^{-2}) as device substrates. These wafers were cleaned in piranha solution (highly corrosive and oxidizing 7:3 mixture of H_2SO_4 and H_2O_2) for 30 min, rinsed with dionized water and dried under a nitrogen stream. For OTS treatment, a 0.1% solution of octadecyltrimethoxysilane (Gelest Inc., Morrisville, PA) in trichloroethylene (EMD Chemicals Inc., Darmstadt, Germany) was spin-coated on the cleaned wafers and allowed to react overnight at room temperature in the presence of ammonia vapor. Excess silane was removed by ultrasonication in toluene, followed by rinsing with toluene, acetone and isopropyl alcohol, and drying under a stream of nitrogen. OTS-treated wafers typically showed contact angle ~ 102°. sonicated with fresh toluene, rinsed with toluene, acetone and isopropanol and dried with nitrogen.

Transistor fabrication and testing.

We prepared 3.0 mg/mL solutions of the 3 different polymers in chloroform, stirred at room temperature overnight, heated to 70 °C for 30 min and filtered them through a 0.45 μm and a 0.2 μm pore PTFE syringe filter. About 40% of the material was lost upon filtering. We applied enough solution (~1.8 mg/mL) to cover the modified SiO_2 substrates, and enclosed them in a glass chamber saturated with chloroform vapor, to achieve slow evaporation (~20 min). The films were then dried in a hot plate at 80 °C for 30 min. After drying, films were further annealed at different temperatures and for different amounts of time. Films destined for device fabrication had 40 nm gold contacts evaporated through a shadow mask (W/L = 20, L= 50 μm), while those for GIXD studies did not. All fabrication procedures from solubilization to electrode evaporation were performed inside a N_2 glovebox.

Characterization of polymer thin films.

Tapping mode AFM investigation of the films was done using a Multimode Nanoscope III with Extender electronics (Digital Instruments/Veeco Metrology Group, Santa Barbara, CA). GIXD measurements were taken at the Stanford Synchrotron Radiation Laboratory using a plate detector and X-rays with 0.9752 Å wavelength. Spectra were corrected for geometrical deformation using an in-house written routine. UV-Vis spectroscopy was accomplished on thin-films deposited on quartz slides using a Carey 6000 UV-Vis-NIR spectrophotometer in transmission mode.

Characterization of OTFT performance.

OTFT characteristics were recorded using a Keithley 4200 semiconductor parametric analyzer (Keithley Instruments, Cleveland OH). Devices were measured both under a dry N_2 atmosphere inside a glovebox or in ambient air. Devices were transferred back and forth several times and behavior in and out of the glovebox was consistent and did not appear to degrade over the period of testing (several days).

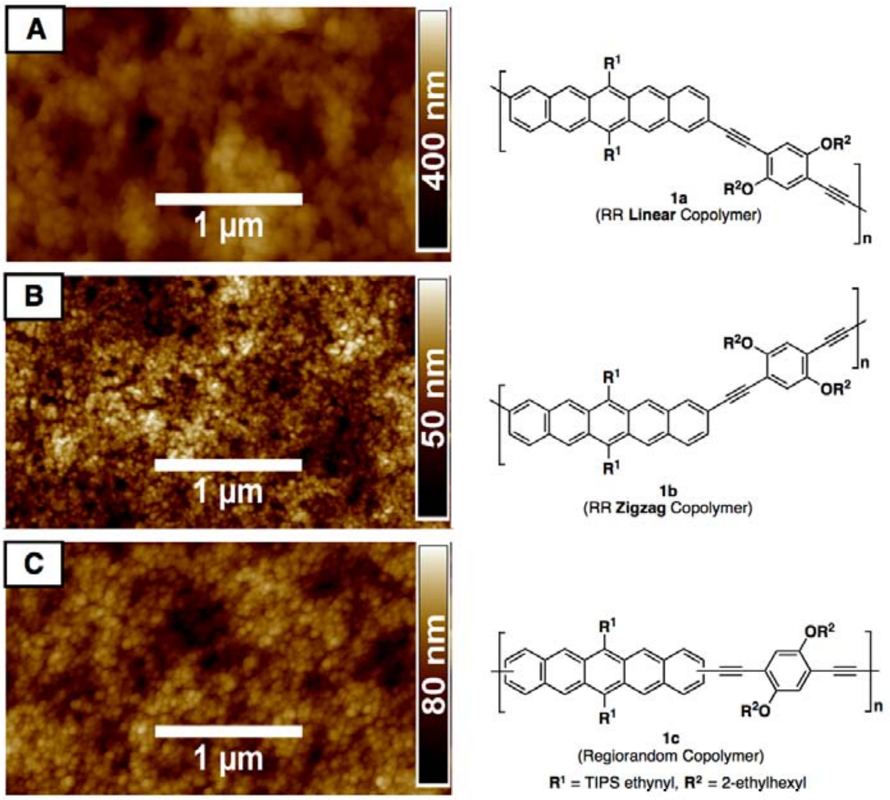


Figure S1. Morphology of polymer thin-films. **A**, **B, C** are Tapping-mode AMF height images of **1a**, **1b** and **1c** thin-films respectively. The root-mean-square roughness of the films is **A**: 46.92 nm; **B**: 8.72 nm; **C**: 10.98 nm. Mean particle size and its standard deviation are **A**: 98.88 nm, 24.0 nm; **B**: 31.46 nm 12.0 nm; **C**: 40.81 nm, 13.2 nm.

Table S2 summarizes the transistor performance of our devices. Averages quoted are over of six devices, sometimes more. The relative standard deviation for each average given is displayed in parenthesis. Figure S2 shows typical transfer curves from these devices.

Table S2. OTFT Performance of **1a**, **1b** and **1c**

Sample	Average I_{DS} (rsd) [nA]	Average mobility (rsd) [cm^2/Vs]	I_{On}/I_{Off} (rsd)	V_{th} (rsd) [V]
1c in N_2	3.50 (0.6)	1.09E-06 (0.3)	20200 (0.5)	10.2 (0.7)
1a in N_2	77.98 (0.1)	2.01E-04 (0.1)	310 (0.6)	41.7 (0.1)
1b in N_2	15.75 (0.1)	3.76E-05 (0.7)	250 (0.2)	42.5 (0.6)
1c in Air	No TFT			
1a in Air	40.22 (0.2)	6.29E-05 (0.3)	160 (0.2)	-55.8 (0.1)
1b in Air	19.47 (0.4)	1.90E-05 (0.2)	55200 (0.7)	-41.6 (0.1)

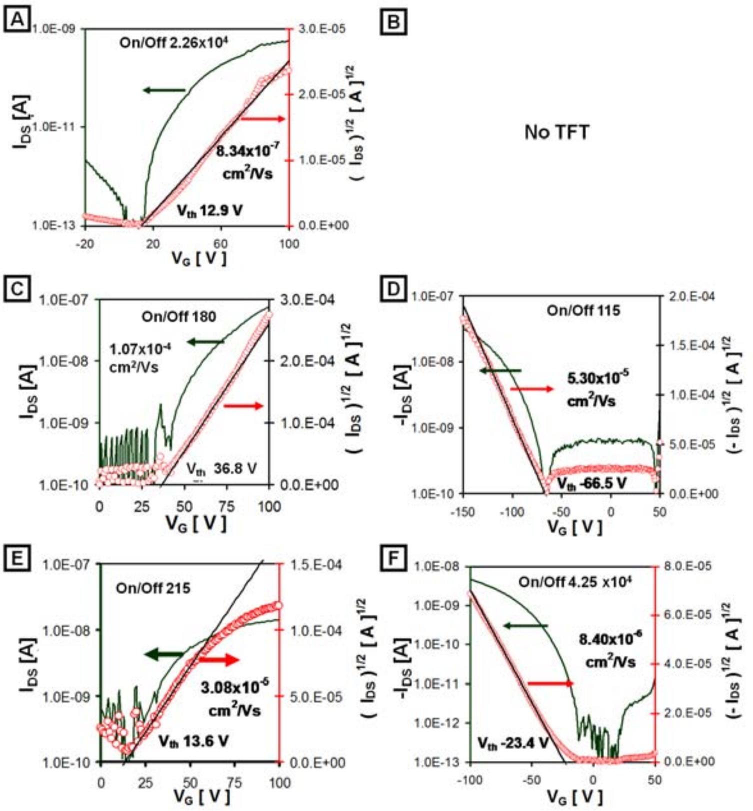


Figure S2. Performance of top-contact thin-film transistors fabricated from **1c** (**A-B**), **1a** (**C-D**) and **1b** (**E-F**). Plots **A**, **C** and **E** were measured inside a nitrogen environment, while the rest were measured in ambient conditions. Mobility is higher and threshold voltage is closer to zero for devices tested in nitrogen. W/L is 20 and L = 50 µm in all cases. The drain-source voltage, V_{ds} is + 100.0 V for panels **A**,**C** and **E**, is -150.0 V for panel **D** and -100.0 for panel **F**.

5. Reference

(1) Okamoto, T.; Bao, Z. *J. Am. Chem. Soc.* **2007**, *129*, 10308-10309.