Supporting Information

Synthesis, Characterization, and Field-Effect Transistor Performance of Carboxylate Functionalized Polythiophenes with Increased Air Stability

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Experimental Section

Materials. All chemicals were purchased from Aldrich and used without further purification unless otherwise noted. Toluene was distilled over Na/benzophenone and pyridine from calcium hydride just prior to use. The N,N′-dimethylformamide used was anhydrous grade packed under N_2. All reactions were performed under dry N_2 unless otherwise noted. All extracts were dried over anhydrous Na_2SO_4 and solvents were removed by rotary evaporation with vacuum assist. Flash chromatography was performed using Merck Kieselgel 60 (230-400 mesh) silica.

Characterization. ^{1}H NMR and ^{13}C NMR spectra were recorded with Bruker AMX-300, AM-400 or DRX-500 instruments using $CDCl_3$ as the solvent unless otherwise noted. High resolution electron impact (EIHR-MS) mass spectrometry and fast atom bombardment (FAB) experiments were performed at the UC Berkeley MS Facilities. Elemental analyses were performed at the UC Berkeley Microanalysis Laboratory. UV-Vis data were measured with a Varian Cary 50 spectrophotometer. Differential scanning calorimetry was performed using a Seiko Instruments ExSTAR 6000 DSC 6200.

Analytical size exclusion chromatography (SEC) in THF was performed at 35 °C at a nominal flow rate of a 1.0 mL/min on a chromatography line calibrated with linear polystyrene standards (162-2,100,000 Da) and fitted with three 7.5 x 300 mm PL gel columns (5-µm particle size). The columns have a pore size of 105, 103, and 500 Å, respectively. The SEC system consists of a Waters 510 pump, a Waters 717 autosampler, and a Waters 486 UV-Vis detector detecting at 254 and 450 nm. Polymer solutions were prepared by adding 100 µL of a 1 mg/mL solution of the polymer in *o*-DCB to 1 mL of THF, then filtering through 0.2 µm pore size PVDF filters (Whatman) before injection.

Electrochemical measurements were done by cyclic voltammetry (CV) using a Solatron 1285 potentiostat. Measurements were performed using a three electrode airtight cell under nitrogen. A 2 mm diameter Pt wire was used for both work and counter electrodes with an Ag wire as a pseudo-reference electrode. Polymer thin films were created by dipping the working electrode into the polymer solution with a concentration of 10 mg/mL (solvent was chloroform for P3HT (MW = 21K, PDI = 1.2) and 1,2-dichlorobenzene for polymer **5** and **9**). The electrolyte solution was 0.1 M Bu_4NBF_4 in dry acetonitrile, which had been distilled over CaH_2. Current vs. voltage measurements were recorded versus the Ag reference electrode, which had been calibrated by using a standard ferrocene/ferrocenium redox reaction (0.30 V vs. SCE). Four cycles were taken of each polymer at a scan rate of 100 mV/s.

XRD films were drop cast from 100 °C solutions of polymer in *o*-DCB onto silicon substrates in a Petri dish heated to 120 °C. The Petri dish was kept closed to saturate the solvent environment and increase the film formation time. The drop casting procedure was then repeated to increase the film thickness. Resulting films were 5-10 microns thick. XRD measurements were made with a Phillips Expert x-ray diffractometer.

2-Bromothiophene-3-Carboxylic Acid (1) was prepared from thiophene-3-carboxylic acid using a published precedure.[25]

Dodecyl 2-bromothiophene-3-carboxylate (2). A mixture of 5.0 g (24 mmol) of **1** and 20 mL $SOCl_2$ was heated at reflux for 12 hours. The solution was cooled and the excess $SOCl_2$ was evaporated to give a brown solid. A solution of 9.0 g (48 mmol) of dodecanol in pyridine (15 mL) was added dropwise to the acid chloride. The mixture was heated at 80 ºC for 12 hours, and then cooled to room temperature. The reaction mixture was poured into a 1M HCl/ice slurry, and the product was extracted with ethyl acetate. The organic layer was then washed with sat. $NaHCO_3$ and brine, dried, and the solvent was evaporated. The product was purified by silica gel flash chromatography using 1:5 ethyl acetate/hexanes as the eluent. The solvent was evaporated and the product was dried *in vacuo* to give 7.25 g (80%) of a light orange oil. ^{1}H NMR (400 MHz): δ 7.36 (d, J = 5.6 Hz, 1H), 7.20 (d, J = 5.6 Hz, 1H), 4.26 (t, J = 6.4 Hz, 2H), 1.71-1.78 (m, 2H), 1.39-1.43 (m, 2H), 1.19-1.38 (m, 16H), 0.86 (t, J = 6.8 Hz, 3H). ^{13}C NMR (125 MHz): δ 14.16, 22.73, 26.07, 28.64, 29.27, 29.38, 29.55, 29.61, 29.67, 31.63, 31.95, 65.21, 119.60, 125.79, 129.48, 131.39, 162.10. HRMS (FAB) *m/z* calc for ($C_{17}H_{28}O_2SBr$) 375.0993; found 375.1000. Anal. Calcd for $C_{17}H_{28}O_2SBr$: C, 54.40; H, 7.25; S, 8.54. Found C, 54.79; H, 7.57; S, 8.23.

Didodecyl 5,5'-dibromo-2,2'-bithiophene-4,4'-dicarboxylate (3). To a screw-capped glass tube equipped with a magnetic stirring bar was added 1.5 g (4 mmol) of **2**, 20 mL DMSO and 46 mg (0.12 mmol) $Pd(PhCN)_2Cl_2$. To the resulting mixture 1.02 g (8.0 mmol) AgF was added and the whole mixture was stirred at 35 ^{o}C for 2 days. The mixture was diluted with chloroform (150 mL) and was successively washed with water. The organic layer was dried over anhydrous sodium sulfate and concentrated under reduced pressure. Purification by chromatography on silica gel using 1:5 ethyl acetate/hexane as the eluent afforded a light yellow solid that contained small amount of dodecyl 2-bromothiophene-3-carboxylate. This starting material contamination in the crude solid was removed by Kugelrohr distillation under vacuum (170 ^{o}C, 0.05 mmHg) to afford 1.02 g (69%) of a white solid, mp 101-102 ^{o}C. ^{1}H NMR ($CDCl_3$): δ 7.36 (s, 2H), 4.30 (t, J = 7 Hz, 4H), 1.76 (quintet, J= 7 Hz, 4H), 1.5-1.20 (m, 36H), 0.89 (t, J = 7 Hz, 6H). Anal. Calcd. for $C_{34}H_{52}O_4S_2Br_2$: C, 54.31; H, 6.97; S, 8.53. Found: C, 54.46; H, 7.06; S, 8.45.

5,5'-Bis(trimethylstannyl)-2,2'-bithiophene (4) was synthesized using a published procedure.[44]

Poly(didodecyl 2,2'-bithiophene-4,4'-dicarboxylate-*co*-2,2'-bithiophene) (5). A mixture of 0.37 g (0.5 mmol) of **3**, 0.25 g (0.5 mmol) of **4**, 40 mL toluene, and 8 mL DMF were combined in a 100 mL flask equipped with condenser. To this mixture was added 29 mg (0.025 mmol) of $Pd(PPh_3)_4$. The mixture was heated to 110 ^oC and stirred at that temperature for 24 hours. The solution was cooled to room temperature, and was poured into 100 mL of methanol. After filtration, the precipitate was dried, and then Soxhlet-extracted using chloroform. This chloroform solution was cooled to room temperature, and was poured into 300 mL of methanol. The precipitate was recovered by filtration followed by drying, and was then washed by Soxhlet extraction with dichloromethane to give 0.27 g of a dark purple polymer (73%). ^{1}H NMR (*o*-DCB-d_4): δ 7.84 (s, 1H), 7.75 (d, 1H), 7.36 (d, 1H), 4.55 (t, J = 7 Hz, 2H), 1.97 (t, J = 7 Hz, 2H), 1.60 (quintet, J = 7 Hz, 2H), 1.6-1.30 (m, 18H), 1.07 (t, J = 7 Hz, 3H). Anal. Calcd. for $C_{42}H_{58}O_4S_4$: C, 66.80; H, 7.74; S, 16.98. Found: C, 66.43; H, 7.56; S, 17.01. THF-SEC: Mn = 5984, Mw = 7464, PDI = 1.24.

2,5-Dibromothiophene-3-carboxylic acid (6) was prepared using a literature precedure.[25]

Dodecyl 2,5-Dibromothiophene-3-carboxylate (7). A mixture of 1.9 g (6.6 mmol) of compound **6** and 10 mL of $SOCl_2$ were heated at reflux for 5 h, then the excess $SOCl_2$ was removed by distillation to afford a light yellow solid. Subsequently, a solution of 1.86 g (10 mmol) of 1-dodecanol in 2 mL of pyridine were added to the flask. The mixture was stirred for 5 hours at 60 ^oC, cooled to room temperature and poured into an

1M HCl/ice slurry. The aqueous solution was washed with ether, and the organic phase was combined and washed with saturated $NaHCO_3$ and dried over $MgSO_4$. The ether was removed with a rotary evaporator, and the crude product was purified by flash chromatography using ethyl acetate/hexane and afforded a greasy solid containing small amount of 1-dodecanol. The 1-dodecanol impurity was removed by Kugelrohr distillation under vacuum to provide pure product as white solid, mp 46-47 ^{o}C. ^{1}H NMR ($CDCl_3$): δ 7.35 (s, 1H), 4.27 (t, J = 7 Hz, 2H), 1.73 (quintet, J = 7 Hz, 2H), 1.5-1.20 (m, 18H), 0.89 (t, J = 7 Hz, 3H). Anal. Calcd for $C_{17}H_{26}Br_2O_2S$: C, 44.95; H, 5.77; S, 7.06. Found: C, 44.99; H, 5.82; S, 7.00.

Poly(dodecyl thiophene-3-carboxylate-*co*-thiophene) (9). A mixture of 0.45 g (1 mmol) of **7**, 0.40 g (1 mmol) **8**, 50 mL toluene, and 10 mL DMF were combined in a 100 mL flask equipped with condenser. To this mixture was added 58 mg (0.05 mmol) $Pd(PPh_3)_4$ and the solution was heated to 110 ^{o}C and stirred at that temperature for 24 hours. The solution was cooled to room temperature, and was poured into 100 mL of methanol. After filtration, the precipitate was dried, and then Soxhlet-extracted using chloroform (130 mL). This chloroform solution was cooled to room temperature, and was poured into 300 mL of methanol. The precipitate was recovered by filtration and drying, and was then washed by Soxhlet extraction with dichloromethane to afford 0.35 g of a purple blue solid (93%). ^{1}H NMR (*o*-DCB-d_4): δ 7.87 (s, ~0.5 H), 7.82 (s, 1H), 7.74 (s, ~0.5H), 7.34 (s, ~ 0.5H), 7.25 (s, ~0.5H), 4.55 (t, J = 7 Hz, 2H), 1.96 (t, J = 7 Hz, 2H), 1.59 (quintet, J = 7 Hz, 2H), 1.6-1.30 (m, 18H), 1.07 (t, J = 7 Hz, 3H). Anal. Calcd. for $C_{21}H_{30}O_2S_2$: C, 66.62; H, 7.99; S, 16.94. Found: C, 66.22; H, 7.59; S, 17.03. THF-SEC: Mn = 4593, Mw = 6584, PDI = 1.43.

Thin Film Transistors. Low resistivity n-type silicon wafer substrates were used with the substrate acting as a back-gate. Both top and bottom contact geometry devices were constructed, both using a 1000 or 1250 Å silicon dioxide dielectric thermal oxide, grown at 900 °C from steam. The RMS roughness as measured by a Digital Instruments Nanoscope 3100 Atomic Force Microscope was < 0.20 nm, and the water contact angle as measured by a Karl Seuss Contact Angler Profiler was < 20°. Solvents used for casting were anhydrous and purchased from Aldrich. 3mg/mL solutions of the polymers in *o*-DCB were prepared in a scintillation vial, sonicated for 1 minute then heated to 80 °C on a hot plate to completely dissolve the polymers. Heated solutions were quickly spun onto the wafers at 1000 rpm for 30 seconds. Remaining solvent was removed under high vacuum for 30 minutes, then the films were annealed in a furnace oven at various temperatures for 30 minutes. Spin casting and all heating and annealing was performed in the air. For the devices using P3HT as the active layer, a 10 mg/mL solution of P3HT (MW = 21K, PDI = 1.2) in chloroform was spun cast at 1000 rpm for 30 seconds. Devices were placed under high vacuum for 30 minutes to remove any remaining solvent.

For top contact devices, shadow masks were used in conjunction with thermal evaporation to pattern electrodes on the top of the active layer. As shadowing effects often lead to device dimensions smaller than those fabricated on the mask itself, both AFM and scanning electron microscopy (SEM) were used to measure the effective dimensions patterned via shadow masking; resulting channel lengths measured from 5 µm to 40 µm. For gold electrode deposition, a base pressure of $< 2 \times 10^{-7}$ torr was used, with an evaporation rate of 0.5 nm/s. Overall gold thickness was 50 nm, and bottom contact devices used a 2.5 nm chrome adhesion layer.

To obtain a low surface energy interface, octadecyltrichlorosilane (OTS) was used to form a hydrophobic self-assembled monolayer (SAM) on top of grown thermal oxide. The RMS roughness of the OTS layer was < 0.8 nm, and the contact angle was > 110°. For SAM formation, 10 µL of OTS was added to 100 mL of heptane (99%, anhydrous) under atmosphere, and an oxidized wafer was immersed for one hour. After removal, the wafer was further sonicated in heptane for 30 minutes, and then rinsed in deionized water. Substrates treated in this manner were used for top contact devices only.

The electrical measurements were performed in nitrogen or ambient atmosphere using an Agilent 4156C Precision Semiconductor Parameter Analyzer. As the entire backside of the substrate was used as the gate electrode, the entire thin film was accumulated during device testing. To minimize gate leakage and improve isolation in this type of setup, the active layer was scratched via probe tips around groups of devices. Mobilities were calculated in the saturation regime using eq 1[45,46]

$$\mu = gm^2 / 2I_DC_{ox}(W/L) \qquad (1)$$

where gm is the transconductance, W is the channel width, L is the channel length, C_{ox} is the capacitance of the insulating layer, and I_D is the saturation current.

Atomic Force Microscopy (AFM) was done in tapping mode on a DI Nanoscope® Dimension 3100 equipped with a Nanoscope® IV controller.

^{1}H NMR spectra were taken with a DRX-500 instrument using 1,2-dichlorobenzene-d_4 as the solvent. Samples were heated to 70 °C during acquisition of the spectra.

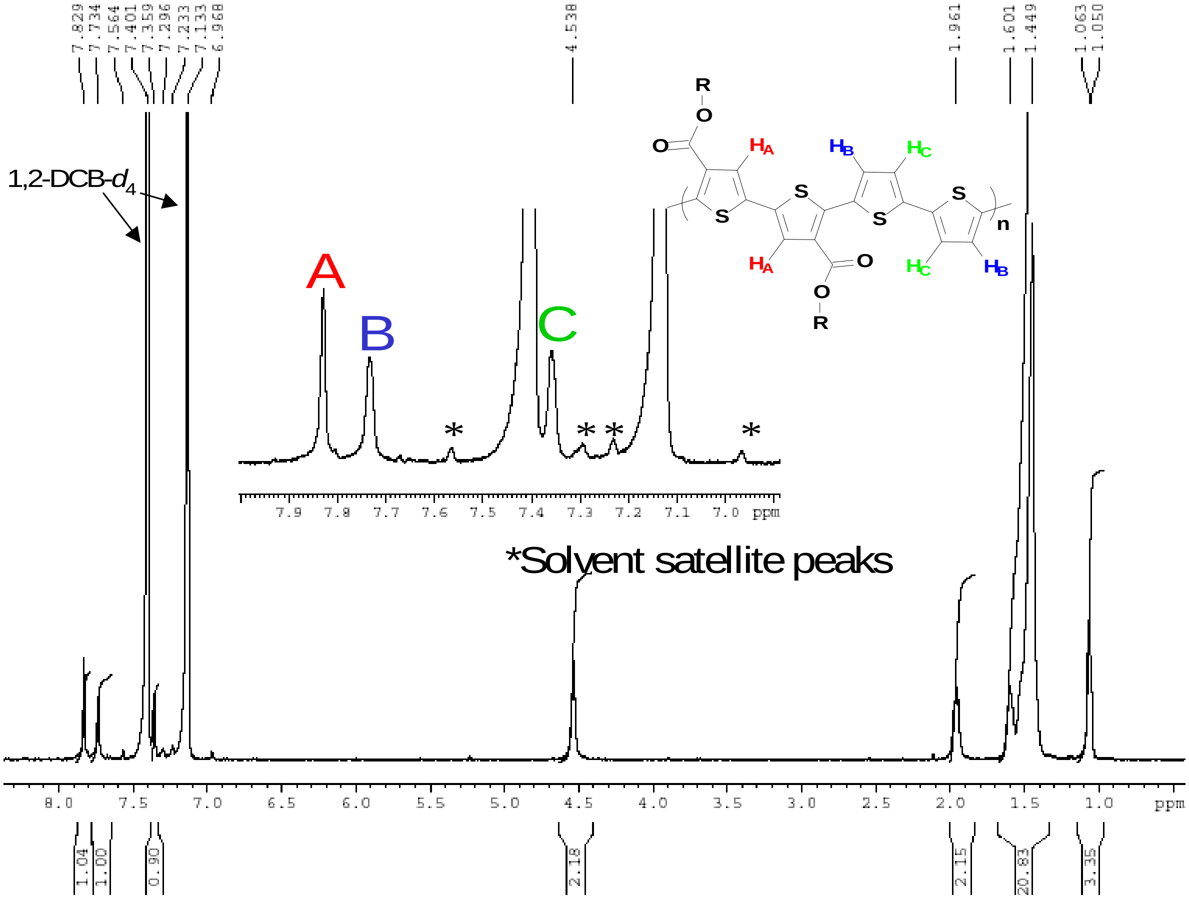

Figure S1. ^{1}H NMR spectrum of polymer **5**.

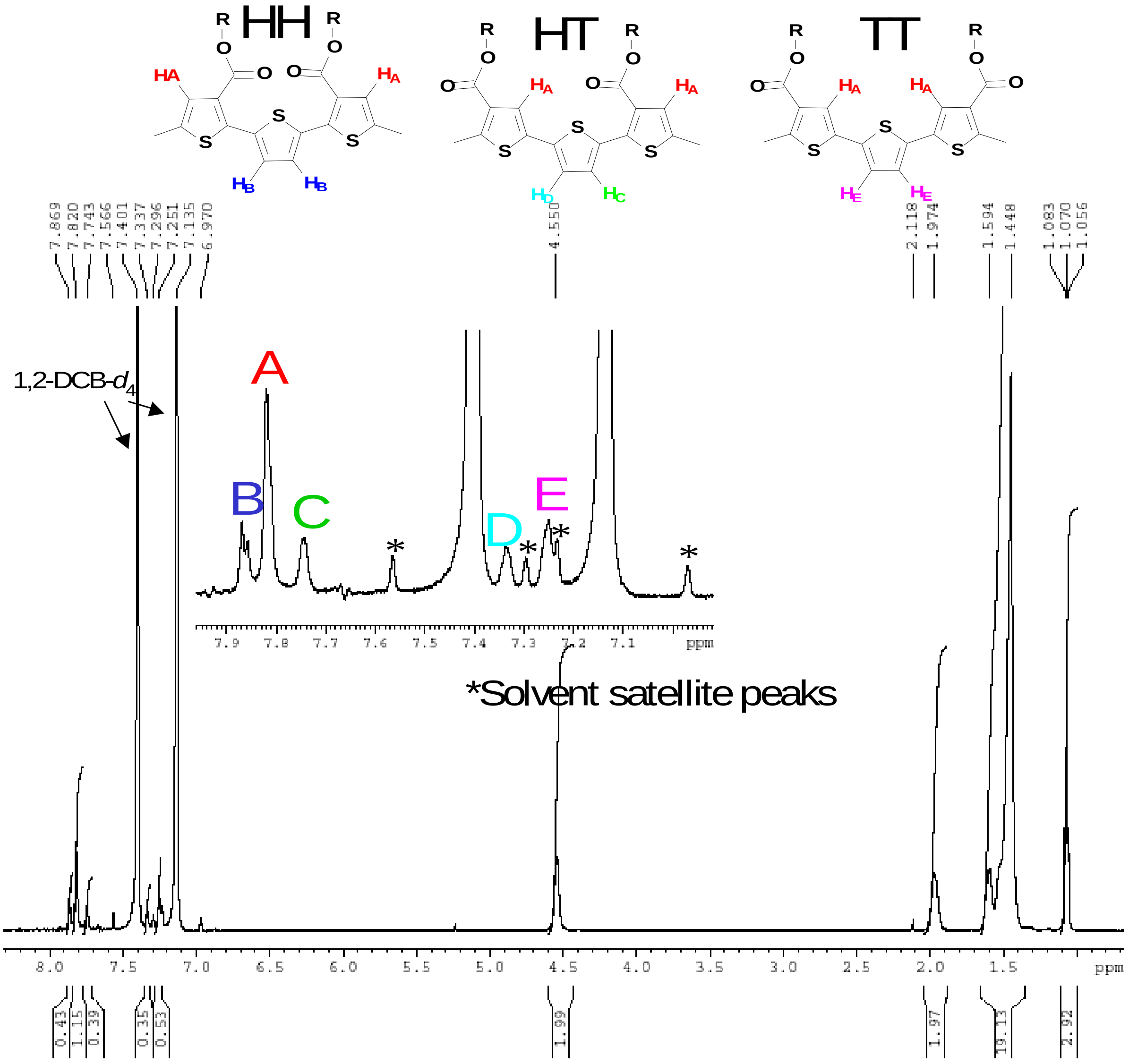

Figure S2. ^{1}H NMR spectrum of polymer **9**.

As noted in the text, the devices were generally tested under nitrogen, but when tested under ambient conditions only small deviations were observed as shown in Figure S3. Operation of these devices in air resulted in nearly identical threshold voltages, mobilities and on/off ratios ranging from 10^5 to 10^6. In some cases, such as that shown in Figure S3, the off-current was even lower in air than when the device was operated in nitrogen.

Over time a negative shift in the threshold voltage was seen, so devices were subjected to a positive gate and source-drain voltage (V_g = +35 V, V_{DS} = 0 to 35 V) before operation to see if the original threshold voltages could be recovered by reducing any traps that could have formed within the film. The effect is shown in Figure S3, where only a slight decrease in the threshold voltage was seen.

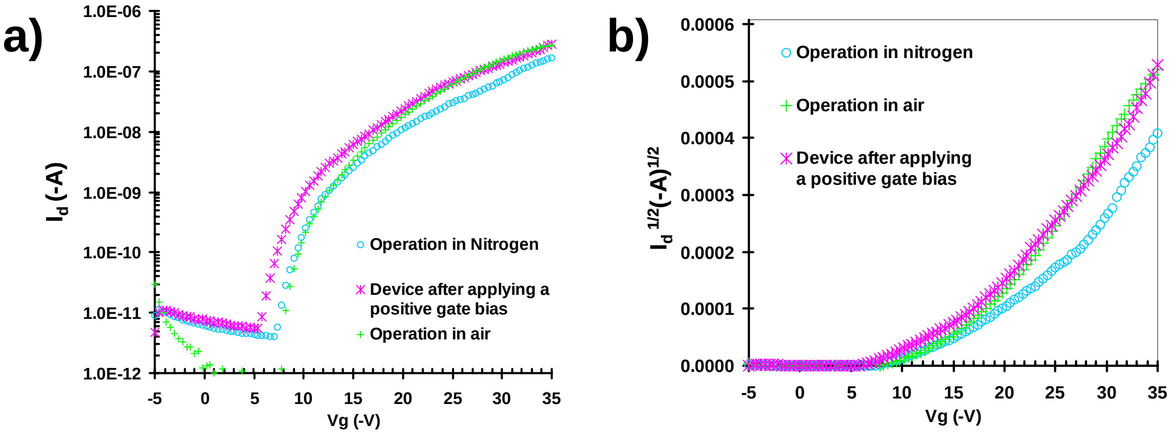

Figure S3. Transfer characteristics in the saturation regime for a device made with polymer **5** stored in air for 4 months then subjected to operation in nitrogen, air or after a reverse bias scan. Plots of a) V_g vs. I_d and b) V_g vs. $I_d^{1/2}$ for a bottom contact device with $L = 10\ \mu$m and $W = 300\ \mu$m at $V_d = -35$ V.