

## Supporting Information

### High and balanced hole and electron mobilities from ambipolar thin film transistors based-on nitrogen containing oligoacences

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#### Experimental Details.

**General.** NMR(<sup>1</sup>H, <sup>13</sup>C) spectra were recorded on a Bruker ADVANCE III 400MHz or a Varian 300MHz spectrometer at room temperature. The <sup>1</sup>H and <sup>13</sup>C chemical shifts (δ) are reported in parts per million and the TMS was used as an internal standard. UV-Vis absorption spectra were recorded using a T6 UV-Vis spectrometer. Single crystal x-ray diffraction measurements were made on a Bruker X8 APEX diffractometer with graphite monochromated Mo-Kα radiation. Fluorescence measurements were conducted using a PE LS55 fluorescence spectrometer. The electrochemical measurement was conducted using a CHI660B electrochemistry work station. Thermogravimetric analysis (TGA) was carried out on a PERKIN ELMER TGA7. A heating rate of 10 °C min<sup>-1</sup> under flowing N<sub>2</sub> was used with runs being conducted from room temperature to high temperature. Melting points were recorded

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(uncorrected) on a Thomas-Hoover Capillary Melting Point Apparatus. High resolution mass spectral data (HRMS) were obtained on a Bruker APEX II FT-MS and APEX QE FT-MS mass spectrometer.

**FET Device Fabrication.** Top contact devices were made according to a literature procedure<sup>1</sup>. A thermally grown dry silicon dioxide layer (400nm) with a capacitance per unit area of  $9.0 \times 10^{-9}$  F/cm<sup>2</sup> functioned as the dielectric, while a heavily n-doped silicon substrate functioned as the gate electrode. Firstly, the substrates were cleaned by immersion in freshly prepared “piranha solution” (3:1 mixture of sulfuric acid and 30% hydrogen peroxide) for 45 minutes. Octadecyltrimethoxysilane (OTS) treatment was done by spin-coating a 3mM solution of OTS in trichloroethylene on a piranha cleaned wafer, then placing the substrate in an environment saturated with ammonia vapor for 12 hours. Shadow masks with W/L of 20 (W = 3000 $\mu$ m, L = 150 $\mu$ m) were used after the evaporation of the organic semiconductor to deposit the gold drain and source electrodes. The organic semiconductors were deposited at a rate of 0.2-0.3 $\text{\AA}$ /s under a pressure of  $10^{-6}$  Torr to a final thickness of 40nm as determined in-situ by a quartz crystal monitor. FET measurements were performed in the argon glove box using a Keithley 4200 semiconductor parameter analyzer.

**Synthesis.** Chemical reagents were purchased from Aldrich Chemical Co, TCI America, Lancaster, or Alfa Aesar and were used as received without further purification.

**6,13-Anthradipyridinequinone.** EtOH (50 mL) was added to 1.35 g (10 mmol) 2,3-pyridinedicarbaldehyde in a 100 mL flask and heated with stirring at 60 °C. After the dicarboxaldehyde was dissolved, 0.56 g (5.0 mmol) 1,4-cyclohexane dione was added and stirred until it was dissolved. A 15 % NaOH solution (0.5 mL) was added and the resulting precipitate was stirred for 1 h at 60 °C. The mixture was then cooled to room temperature and the brown precipitate (0.65 g, 42 %) was filtered, rinsed with water and acetone and used directly in the next reaction, M.p. > 320 °C. This compound is very insoluble, such that even proton NMR could not be measured.

**1-Azapentacene-6,13-quinone.** 1,4-anthraquinone (105 mg, 0.5 mmol),  $\alpha,\alpha,\alpha'\alpha'$ -tetrabromo-o-xylene (317 mg, 0.75 mmol) and NaI (225 mg, 1.5 mmol) were placed in a flask under argon. Anhydrous DMF (5 ml) were added and the mixture was heated and stirred at 75 °C for 24 hrs. After cooling to room temperature, the precipitated was filtered, washed with water, CH<sub>2</sub>Cl<sub>2</sub> and acetone and dried under vacuum. The 1-azapentacene-6,13-quinone was obtained as a deep yellow solid (70 mg, 45%), M.p. > 320 °C. This compound is very insoluble, such that even proton NMR could not be measured.

**8,9,10,11-Tetrafluoro-1-azapentacene-6,13-quinone.** 1,4-anthraquinone (105 mg, 0.5 mmol),  $\alpha,\alpha,\alpha'\alpha'$ -tetrabromo-o-xylene (317 mg, 0.75 mmol) and NaI (225 mg, 1.5 mmol) were placed in a flask under argon. Anhydrous DMF (5 ml) were added and the mixture heated and stirred at 75 °C for 24 hrs. After cooling to room temperature, the precipitated was filtered, washed with water, CH<sub>2</sub>Cl<sub>2</sub> and acetone and dried under

vacuum. The 1-azapentacene-6,13-quinone was obtained as a deep yellow solid (70 mg, 45%), M.p. > 320 °C. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>) δ: 7.64-7.68 (m, 1H), 8.46-8.48 (d, 1H), 8.99 (s, 1H), 9.18-9.21 (m, 4H).

**6,13-Bis-(triisopropylsilylethynyl)-anthradipyridine (1).** In a oven-dried 2 necked flask with a condenser, triisopropylsilylacetylene (1.0 mL, 4.4 mmol) and dry 5 mL THF were added, then n-BuLi (1.41 mL, 2.84 M in hexanes, 4.0mmol) was added dropwise to this stirring solution at 0 °C under argon. The reaction mixture was stirred for a further 40 min at 0 °C, and then compound **6,13-anthradipyridinequinone** (310 mg, 1.0 mmol) was added to the solution, followed by 10 mL of dry THF. The mixture was heated to 60 °C for 4 hrs and then quenched with saturated ammonium chloride aqueous solution. Extraction with ethyl acetate (20 ml), washed with saturated ammonium chloride (2 × 20 ml), dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>. After evaporation of the solvent, the residue was filtered over silica gel using hexane/ethyl acetate (v/v, 5:1) to yield the corresponding diol (420 mg, 0.62 mmol, 62 % yeild). The crude diol was, without further characterization, dissolved in dry THF (10 mL) and SnCl<sub>2</sub>·2H<sub>2</sub>O (423 mg, 1.87 mmol) under argon. The mixture was heated to reflux for 2 h. After cooling to room temperature, DCM (100 mL) was added to the mixture and washed with water (3 × 100 mL). The combined organic layers were dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>. After evaporation of the solvent, the solids were further purified by chromatography on silica gel using CH<sub>2</sub>Cl<sub>2</sub> solvent. Compound **1** (166 mg, 26% yield, two steps) was isolated as deep blue solid. M.p. 251–253 °C, <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ: 9.55-9.59 (d, 2H), 9.29-9.35 (d, 2H), 9.01-9.02 (s, 2H), 8.27-8.30 (d,

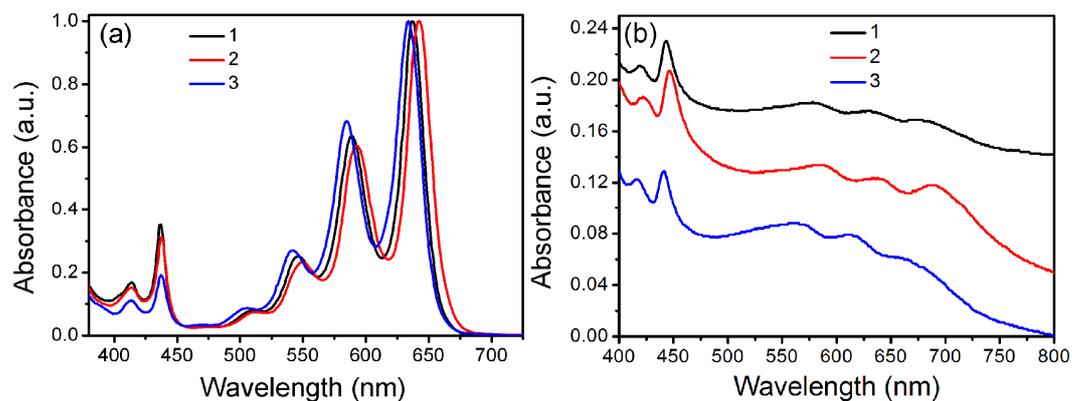
2H), 7.32-7.34 (m, 2H), 1.35-1.37 (42H).  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 153.23, 144.69, 144.59, 136.81, 136.71, 132.60, 132.32, 130.96, 130.67, 127.85, 127.79, 127.72, 127.59, 127.49, 121.17, 119.95, 119.46, 118.91, 109.25, 108.66, 108.03, 104.24, 104.00, 103.75, 19.03, 19.01, 18.97, 11.66, 11.63, HRMS (ESI) calcd for  $\text{C}_{42}\text{H}_{52}\text{N}_2\text{Si}_2$  ( $\text{MH}^+$ ) 641.3742; found: 641.3750.

**6,13-Bis-(triisopropylsilylethynyl)-1-azapentacene (2).** In a oven-dried 2-necked flask with a condenser, triisopropylsilylacetylene (0.3 mL, 1.32 mmol) and dry 4 mL THF were added, then n-BuLi (0.42 mL, 2.82 M in hexanes, 1.2mmol) was added dropwise to this stirring solution at 0 °C under argon. The reaction mixture was allowed to warm to room temperature and stirred for a further 40 min, and then **1-azapentacene-6,13-quinone** (62 mg, 0.2 mmol) was added to the solution, followed by 6 mL of dry THF. The mixture was heated to 60 °C for 4 hrs and then quenched with saturated ammonium chloride aqueous solution. Extraction with ethyl acetate (10 ml) was washed with saturated ammonium chloride (2 × 10 ml), and dried with anhydrous  $\text{Na}_2\text{SO}_4$ . After evaporation of the solvent, the residue was filtered over silica gel using hexane/ethyl acetate (v/v, 5:1) to yield the corresponding diol (84 mg, 0.12 mmol, 62 % yeild). The crude diol was, without further characterization, dissolved in THF (5 mL) and  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  (81 mg, 0.36 mmol) under argon. The mixture was heated to reflux for 6 h. After cooling to room temperature, ethyl ether (100 mL) was added to the mixture and washed with water (3 × 100 mL). The combined organic layers were dried with anhydrous  $\text{Na}_2\text{SO}_4$ . After evaporation of the solvent, the solids were further purified by chromatography on silica gel using a

hexane/CH<sub>2</sub>Cl<sub>2</sub> (v/v, 1:1) solvent mixture. Compound **2** (31 mg, 24% yield, two steps) was isolated as deep blue solid. M.p. 248–250 °C, <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ: 9.55 (s, 1H), 9.38(s, 1H), 9.29-9.32 (d, 2H), 9.00-9.01 (d, 1H), 8.28-8.31 (d, 1H), 7.97-8.00 (dd, 2H), 7.43-7.45 (dd, 2H), 7.26-7.34 (m, 1H), 1.36-1.38 (42H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ: 152.83, 132.62, 132.54, 132.19, 131.11, 130.82, 130.55, 128.71, 128.64, 127.50, 126.58, 126.38, 126.31, 120.87, 119.24, 118.71, 108.34, 107.70, 104.47, 104.21, 19.04, 18.99, 11.69, HRMS (ESI) calcd for C<sub>43</sub>H<sub>53</sub>NSi<sub>2</sub> (MH<sup>+</sup>) 640.3795; found: 641.3789.

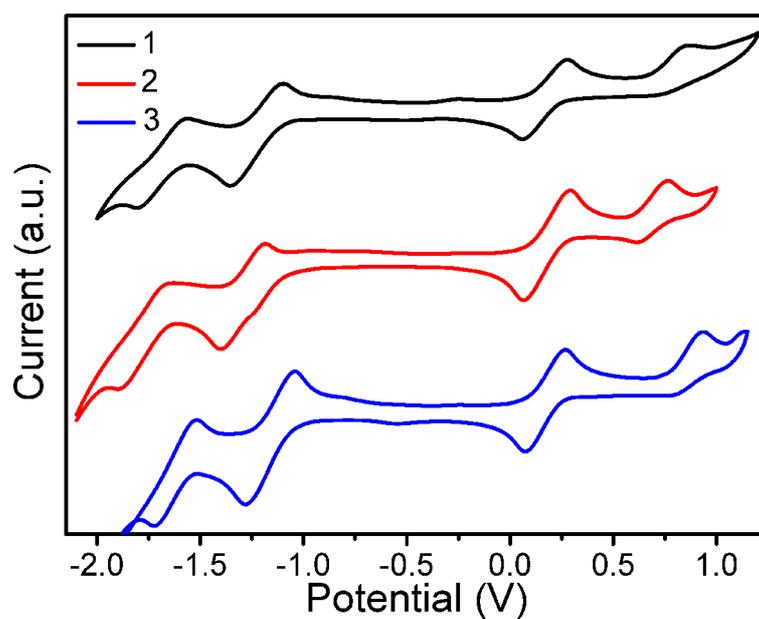
**8,9,10,11-Tetrafluoro-6,13-bis-(triisopropylsilylethynyl)-1-azapentacene (3).** **3** was prepared by the reaction of triisopropylsilylacetylene (0.3ml, 1.32 mmol) and **8,9,10,11-tetrafluoro-1-azapentacene-6,13-quinone** (76mg, 0.2 mmol). With the similar procedure as the synthesis of compound **2**, **3** was obtained as a deep blue solid (36 mg, 25% yield). M.P. 304–306 °C, <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ: 9.61 (s, 1H), 9.55-9.57 (d, 2H), 9.29 (s, 1H), 9.04-9.05(d, 1H), 8.31-8.32 (d, 1H), 7.35-7.38 (dd, 1H), 1.36-1.37 (d, 42H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ: 153.50, 144.83, 136.81, 132.58, 130.89, 130.63, 130.37, 128.15, 127.86, 127.75, 121.45, 120.40, 119.98, 119.67, 119.48, 109.82, 109.20, 103.51, 103.30, 18.94, 18.90, 11.57, HRMS (MALDI) calcd for C<sub>86</sub>H<sub>99</sub>N<sub>2</sub>Si<sub>4</sub>F<sub>8</sub> (2MH<sup>+</sup>) 1423.6758; found: 1423.6752.

## UV-Vis spectra.



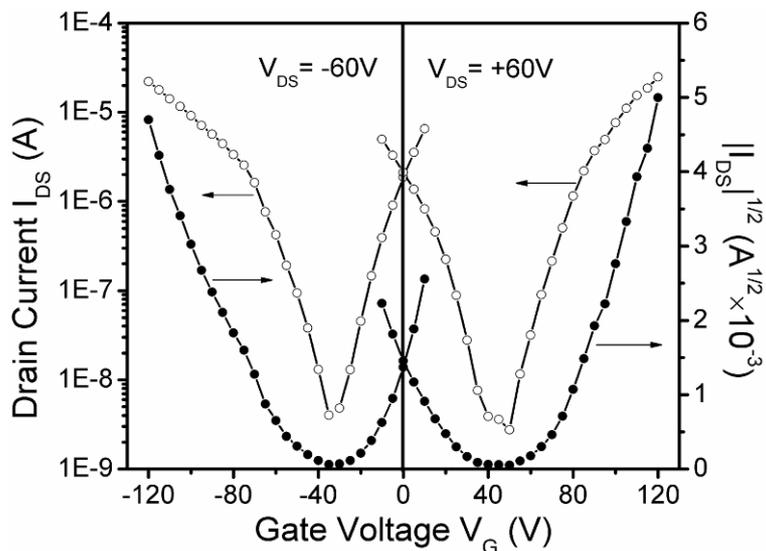
**Figure 1.** UV-Vis of **1** (black line), **2** (red line) and **3** (blue line) in a dilute toluene solution (left) and a 40nm thin film on quartz (right) made under device conditions.

## Cyclic voltammograms.

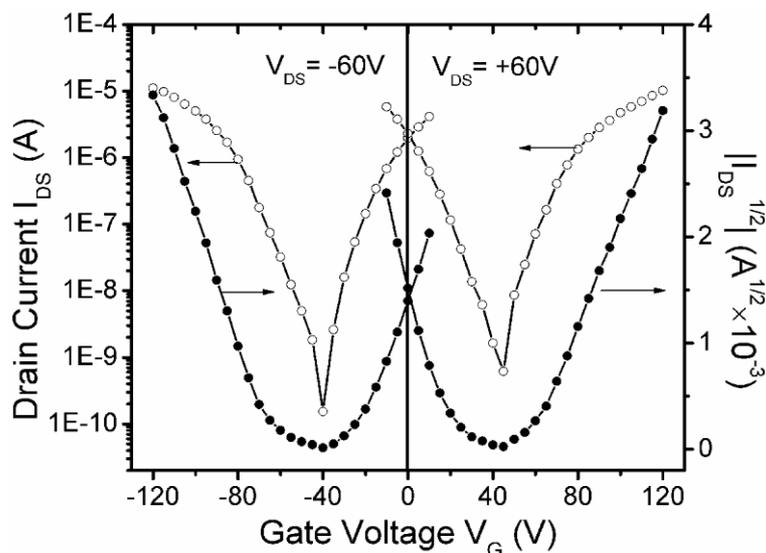


**Figure 2.** Cyclic voltammograms of compound **1**, **2** and **3** as solutions in  $\text{CH}_2\text{Cl}_2$  solution (0.1 M  $\text{Bu}_4\text{NBF}_4$  electrolyte), Pt electrode. Scan rate: 100 mV/s.  $\text{Fc}/\text{Fc}^+$  (-4.8 eV to vacuum) as internal reference.

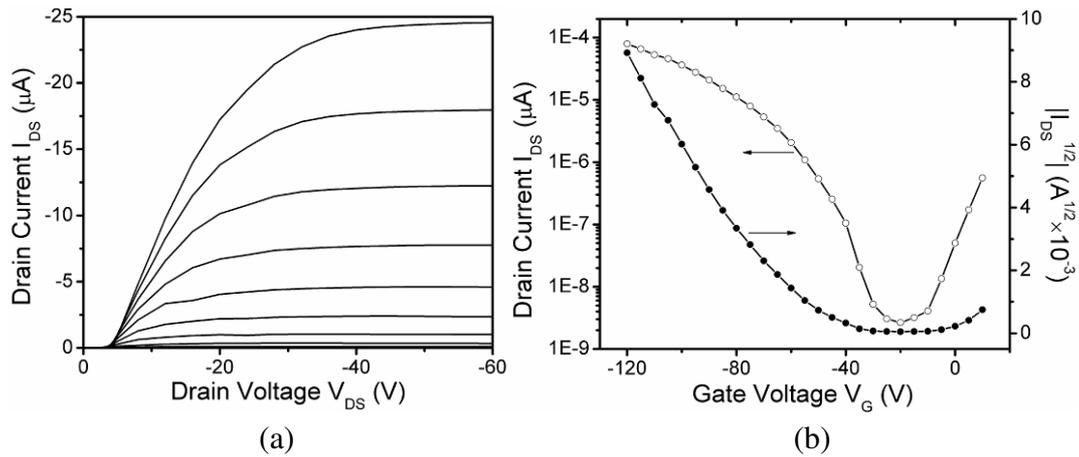
**FET characteristics.**



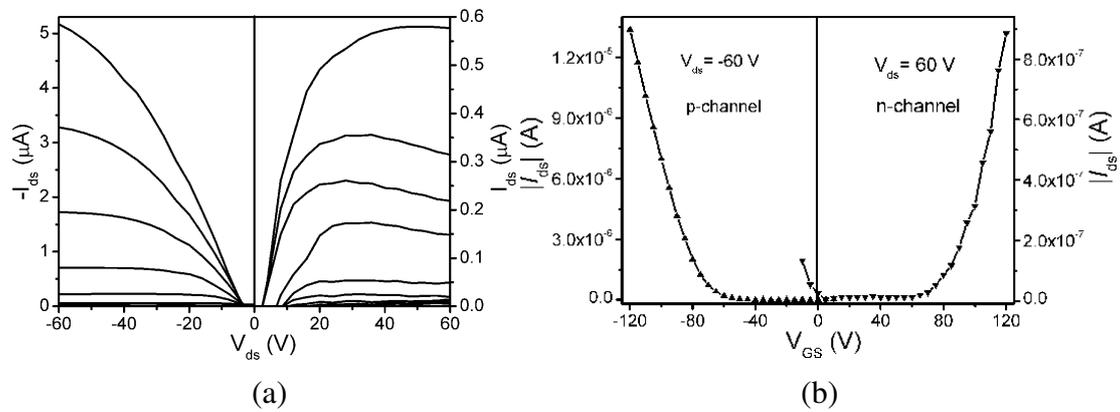
**Figure 3.** Typical transfer curves for **1** deposited at 80°C on OTS-treated SiO<sub>2</sub> for L=150 μm, W/L=20. The gate voltage ranges from -120 to 120 V.



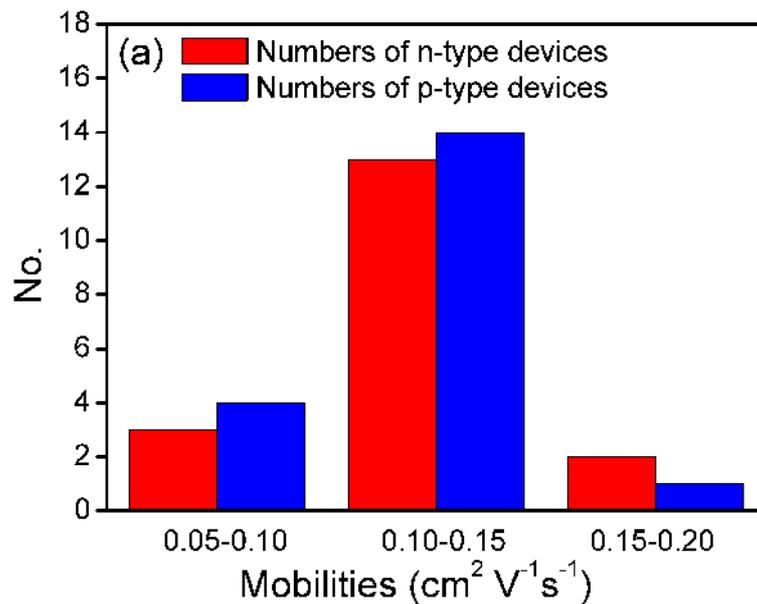
**Figure 4.** Typical transfer curves for **3** deposited at 80°C on OTS-treated SiO<sub>2</sub> for L=150 μm, W/L=20. The gate voltage ranges from -120 to 120 V.

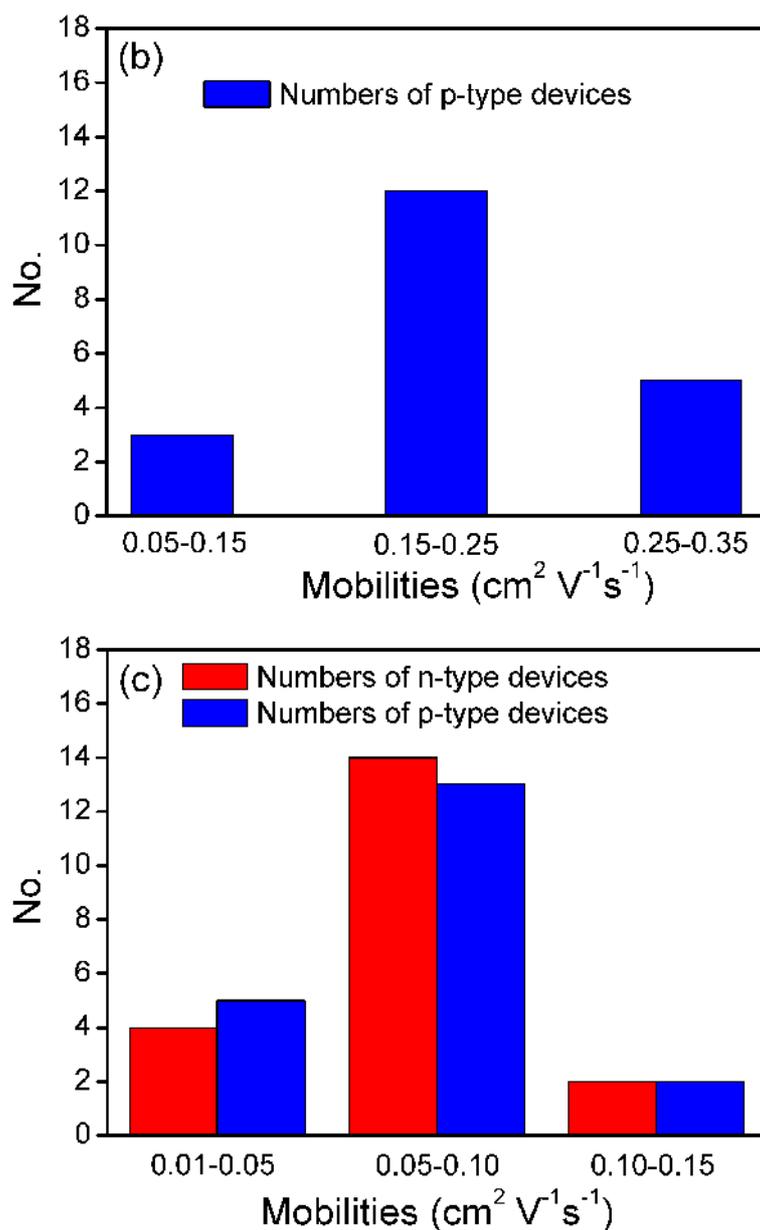


**Figure 5.** Typical output(a) and transfer(b) curves for **2** deposited at  $80^\circ C$  on OTS-treated  $SiO_2$  for  $L=150 \mu m$ ,  $W/L=20$ . The gate voltage ranges from -120 to 10 V.



**Figure 6.** Typical output(a) and transfer(b) curves for **2** deposited at  $80^\circ C$  on OTS-treated  $SiO_2$  with Ag as electrode material for  $L=150 \mu m$ ,  $W/L=20$ . The gate voltage ranges from -120 to 10 V.

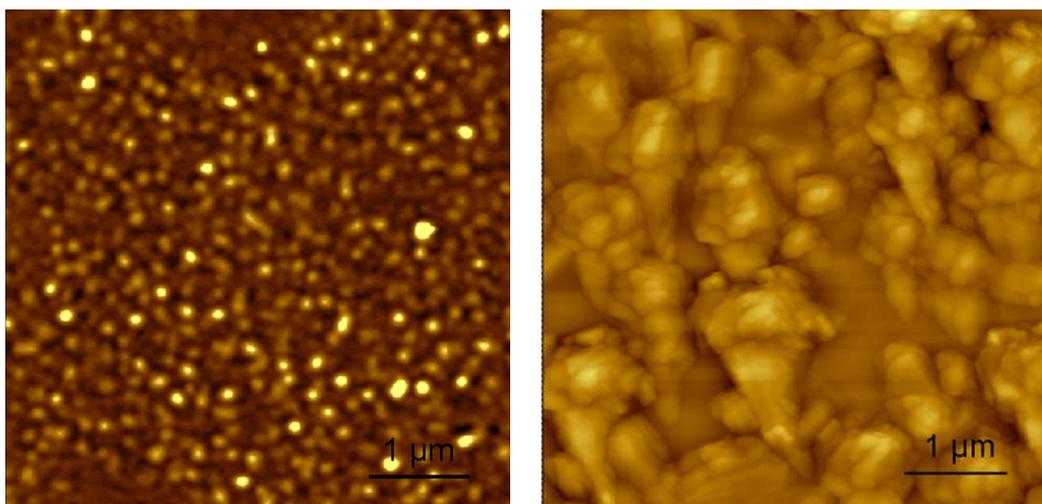




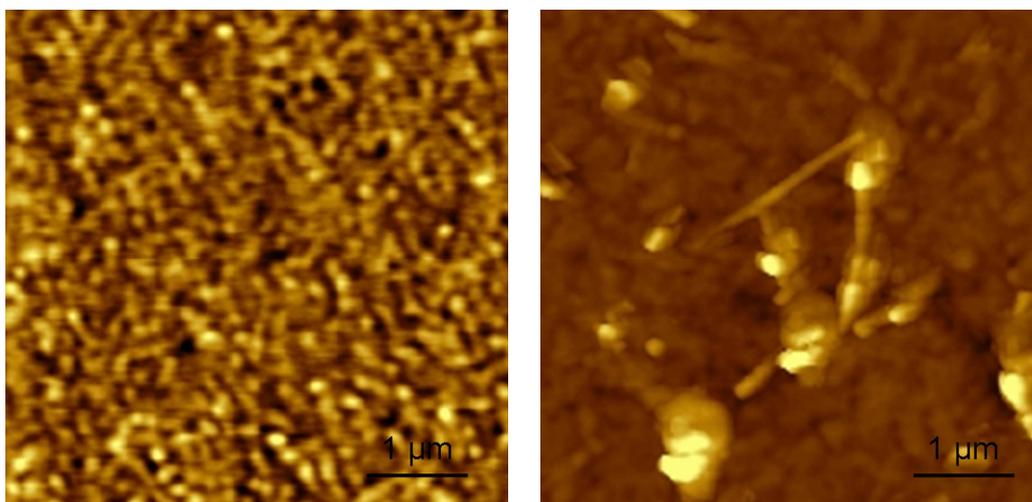
**Figure 7.** Statistical results of thin film transistor mobilities of compound 1 (a), 2 (b) and 3 (c). The organic layers were deposited at 80 °C.

**AFM images.** An Agilent 5500 scanning probe microscope was used to perform tapping mode AFM on the samples by a silicon tip with spring constant of 130N/m.

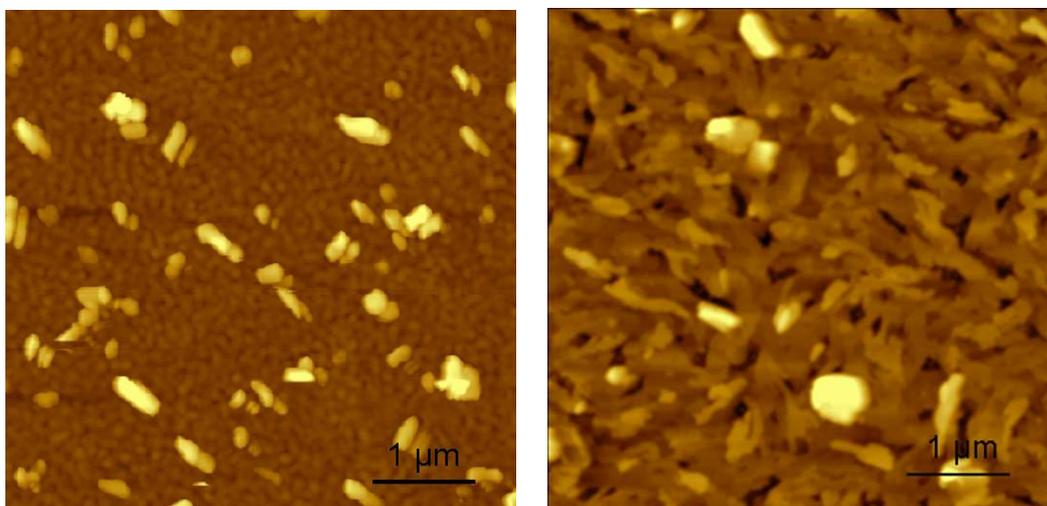
Picoview software was used to process the raw AFM images.



**Figure 8.** AFM images of **1** on OTS treated SiO<sub>2</sub> at substrate temperature of R.T. (left) and 80°C (right).



**Figure 9.** AFM images of **2** on OTS treated SiO<sub>2</sub> at substrate temperature of R.T. (left) and 80°C (right).



**Figure 10.** AFM images of **3** on OTS treated SiO<sub>2</sub> at substrate temperature of R.T. (left) and 80°C (right).

**Reference**

(1) Locklin, J.; Roberts, M. E.; Mannsfeld, S. C. B.; Bao, Z. *Journal of Macromolecular Science, Part C: Polymer Reviews* 2006, 46, 79-101.