Supporting information

Low-Dimensional Arylacetylenes for Solution-Processable High-Mobility Field-Effect Transistors.

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**General remarks.** Melting points were determined on a Buchi melting point apparatus and are uncorrected. Adsorption chromatography was performed on Riedel de Haën silica gel (230-400 mesh ASTM). NMR spectra were recorded on a Varian Associates VXR-400 multinuclear instrument (internal Me₄Si). UV-Vis spectra were recorded on a Cary Model 1 UV-Vis spectrophotometer. Commercially available reagents were purchased from Sigma-Aldrich Co. and utilized without further purification, unless otherwise noted. Petroleum ether as 40°-60°C boiling fraction was used. Electrochemistry was performed on a C3 Cell Stand Electrochemical Station equipped with BAS Epsilon software (Bioanalytical Systems, Inc., Lafayette, IN) in an electrolyte solution of 0.1M tetrabutylammonium hexafluorophosphate (Bu₄N+PF₆⁻) in dry dichloromethane. Platinum wire or carbon electrode were used as working electrodes, platinum wire was used as counter electrodes, and a silver wire was used as the pseudo-reference electrode. A ferrocene/ferrocenium redox couple was used as an internal standard and the potential values obtained in reference to the silver electrode were converted to the vacuum scale. TGA analyses were performed under nitrogen on a Thermogravimetric Analyzer (TGA) Q50 (scan rate 10°C/min). Thin films were analyzed by wide-angle X-ray film diffractometry (WAXRD) on a Rikagu ATX-G instrument with Cu Kα radiation and a monochromator using standard 0-20 techniques. All 0-20 scans were calibrated in situ with the reflection of the Si (100) substrates.

**OFET device fabrication and Thin Film Characterization.**
Prime grade n-doped silicon wafers (100) having a 300 nm thermally grown oxide layer (Process Specialties Inc.) were used as device substrates. These were rinsed with water and methanol before film deposition. Trimethylsilyl and octadecylsilyl functionalization of the Si/SiO₂ surface was carried out by exposing the silicon wafers to hexamethyldisilazane (HMDS) or n-octadecyltrichlorosilane (OTS) vapor at room temperature in a closed container under nitrogen overnight. The compounds 1 and 2 were spin-coated from 5 mg/mL solutions in chloroform and then annealed under nitrogen at 80°C for 2.5h. Spin-coated films were 25-30 nm-thick as assessed
by profilometry. For FET device fabrication, top-contact electrodes (500 Å) were deposited by evaporating gold (pressure $< 10^{-5}$ Torr); channel dimensions were 25/50/100 μm (L) by 1.0/2.0/5.0 mm (W). The capacitance of the insulator is $1 \times 10^{-8}$ F/cm² for 300 nm SiO₂. TFT device measurements were carried out in a customized vacuum probe station ($8 \times 10^{-5}$ Torr) or in air. Coaxial and/or triaxial shielding was incorporated into Signatone probes to minimize the noise level. TFT characterization was performed with a Keithley 6430 subfemtoammeter and a Keithley 2400 source meter, operated by a locally written Labview program and GPIB communication.

Material synthesis.

4,7-bis(5-[[3,4-bis(hexyloxy)phenyl]ethynyl]thien-2-yl)-2,1,3-benzothiadiazole (2). Dry toluene (4.2 ml), diisopropylamine (1.8 ml), CuI (0.0025 g, 0.013 mmol), Pd(PPh₃)₄ (0.015 g, 0.013 mmol) and bis(bromothienyl)-benzothiadiazole (0.14 g, 0.306 mmol) were placed in a flask and degassed with argon at 0°C for 20 min. 3,4-(Bishexyloxy)-ethynylbenzene (0.312, 0.77 mmol) was then added and the mixture was kept at 55°C for 16 h. The solvent was then removed under reduced pressure and the residue was chromatographed on silica gel (elution: petroleum ether/chloroform 7:3) to give compound 2 (90% yield) as deep red solid; Anal.Calcd. for: C₅₄H₆₄N₂O₄S₃: C, 71.96; H, 7.16; N, 3.11; S, 10.67. Found: C, 71.57; H, 7.15; N, 3.09; S, 10.60; mp 126-127°C (ethyl acetate); ¹H-NMR (CDCl₃) δ 0.86 (m, 12H), 1.29 (m, 16H), 1.43 (m, 8H), 1.48-1.80 (m, 8H), 3.99 (m, 8H), 6.79 (d, 2H, J= 8.4 Hz), 6.99 (m, 2H), 7.04-7.07 (m, 2H), 7.27 (d, 2H, J= 3.96 Hz), 7.81 (s, 2H), 7.96 (d, 2H, J= 3.92 Hz); ¹³C-NMR (CDCl₃) δ 152.5, 150.0, 148.8, 140.0, 132.3, 127.5, 125.6, 125.5, 125.3, 124.9, 116.3, 114.8, 113.2, 95.7, 81.4, 69.3, 69.1, 31.6, 29.2, 25.7, 22.6, 14.0; UV-Vis (CHCl₃) [$λ_{max}$ nm (logε)] 359 (4.8), 503 (4.6).
Figure S1. CV curve of arylacetylene 2 in 0.1 M Bu$_4$N$^+$PF$_6$ solution in CH$_2$Cl$_2$ at a scan rate of 100 mV/s. Fc/Fc$^+$ was used as internal standard.

Figure S2. Absorption spectra of arylacetylenes 1 (A.) and 2 (B.) in solution (red line) and in film (black line).
Figure S3. TGA plot obtained for arylacetylene 2
Figure S4. FET transfer (A, C) and output (B, D) plots of arylacetylene 1 spin–cast onto HDMS- and OTS-treated substrates and annealed at 80°C. Devices measured in vacuum.
Figure S5. FET transfer (A, C, E) and output (B, D, F) plots of arylacetylene 2 spin-cast onto bare, HDMS and OTS-treated substrates and annealed at 80°C. Devices measured in vacuum.
Figure S6. FET transfer (A-C) and output (D-F) plots of arylacetylene 1 spin-cast onto bare, HDMS- and OTS-treated substrates and annealed at 80°C. Devices measured in air.
Figure S7. FET transfer (A-C) and output (D-F) plots of arylacetylene 2 spin-cast onto bare, HDMS- and OTS-treated substrates and annealed at 80°C. Devices measured in air.
Figure S8. XRD scans for film 1 spin cast from chloroform onto (A.) HDMS-treated and (B.) OTS-treated Si/SiO₂ substrates and annealed at 80°C

Figure S9. XRD scans for film 2 spin cast from chloroform onto (A.) HDMS-treated and (B.) OTS-treated Si/SiO₂ substrates and annealed at 80°C
Figure S10. AFM images (100 μm x 100 μm) showing the surface morphology of semiconductor 1 (A.) and 2 (B.) spin cast on HDMS-treated Si/SiO₂ substrates and annealed at 80°C.
Table S1. Average mobilities for semiconductors 1 and 2

<table>
<thead>
<tr>
<th>Surface treatment</th>
<th>μ (cm²V⁻¹s⁻¹)</th>
<th>Vacuum (x10⁻²)</th>
<th>Air (x10⁻²)</th>
</tr>
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<tbody>
<tr>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>1 bare</td>
<td>6.3 ± 0.7</td>
<td>7.0</td>
<td></td>
</tr>
<tr>
<td>HMDS</td>
<td>4 ± 1.0</td>
<td>3.2 ± 0.8</td>
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<tr>
<td>OTS</td>
<td>1.9 ± 1.1</td>
<td>1.5 ± 0.5</td>
<td></td>
</tr>
<tr>
<td>2 bare</td>
<td>1.6 ± 0.4</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td>HMDS</td>
<td>2.2 ± 0.8</td>
<td>1.7 ± 0.3</td>
<td></td>
</tr>
<tr>
<td>OTS</td>
<td>4 ± 1.0</td>
<td>3.5 ± 0.5</td>
<td></td>
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