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Supporting Information

Influence of the substrate surface chemistry on the performance of top-gate organic thin-film transistors

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FET Device Fabrication and Measurements

**FET Fabrication.** Corning Eagle 2000 glass slides were used as substrates after cleaning them in an ultrasonic bath with acetone for 10 min. Titanium (adhesion layer, 5nm) and Gold (30nm) were deposited by plasma vapor deposition. Using conventional photolithography, the source and drain electrodes were patterned. Gold was etched using a KI₂ solution, and Titanium was etched using a SF₆ plasma treatment. These devices have a channel width of 1cm and a channel length of 100 μm. A N,N-dialkylsubstituted-(1,7&1,6)-dicyanoperylene-3,4:9, 10-bis(dicarboximide) derivative (Polyera ActivInk™ N1400) bought from Polyera Corporation was diluted in 1,2-dichloro-benzene at a concentration of 6mg/mL. Poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine] (PTAA) from was also used as the active layer at a concentration of 16mg/mL in toluene. Both solutions were spin-coated at 1000 rpm followed by a curing time of 5 minutes at 100°C. Cytop™ dielectric was then spin-coated on top of the semiconductors and cured at 100 °C for 20 min. The thickness of the layer was measured with a profilometer around 1.2μm. To promote adhesion of the gate electrode on the highly hydrophobic insulating layer, solution of Nafion diluted at 30 mg/mL in isopropanol was spin-coated at 1000 rpm. Finally an Ag ink gate electrode was printed by ink-jet using a Dimatix set up.

**Self-Assemble Monolayer Deposition.** The surface of glass was activated using a oxygen plasma. N-[3-(trimethoxysilyl)propyl]-aniline (PhAPrTMS, 1), (N,N'-dimethyl-aminopropyl)trimethoxysilane (DmetAPrTMS, 2), octyltrimethoxysilane (OctTMS, 3), Ethyltrimethoxysilane (EtTMS, 4), (3-chloropropyl)trimethoxysilane (ClPrTMS, 5), (3-bromopropyl) trimethoxysilane (BrPrTMS, 6) were bought from Sigma-Aldrich. 10mM solutions in toluene were prepared, in which samples were immersed at room temperature for a period of 16h. They were then rinsed thoroughly with pure toluene and dried in a N₂ gas stream at 100 °C. To minimize contact resistance in the devices, 4-methoxythiophenol (for n-channel transistors) and 4-fluorothiophenol (for p-channel transistors) were grafted on gold following the experimental procedure of [1].
**TFT Measurements.** Electrical measurements were performed at room temperature in air by using a parameter analyser (HP4145, Hewlett-Packard). The transfer characteristics in the saturation regime \( V_D = 80 \text{V} \) was measured on devices with a channel length of \( L = 100 \mu \text{m} \). The threshold voltage and saturation mobility were extracted from the linear extrapolation of the \( I_D^{1/2} - V_D \) curves. Typical Output characteristics are given in figure S1 and S2 for N1400 and PTAA respectively.

**SAMs Characterization**

To characterize the presence of the SAMs on glass, we measured the contact angle with water of glass modified with the different molecules USING Kruss DSA100 equipment. The contact angle of a sample after the surface activation with a plasma oxygen is also reported. As a reference, an activated glass substrate was immersed in toluene during the same time that for the SAMs. Results are given in table S1. After activation with the plasma, the contact angle drops from 61.5° to 4° reflecting a hydroxyl group rich surface, promoting the reaction with the SAMs. Immersion in toluene has practically no effect on the substrate surface as reflected by the measured contact angle of 8.7°. The higher values measured after immersion in the different SAMs indicates the presence of the molecules on glass. Interestingly, the different SAMs give close contact angles, expect for OctTMS which leads to a more hydrophobic surface. To further investigate and prove that the grafting of the SAMs was effective, XPS analyses have been achieved on different samples. A flood gun was used to minimize the charge effects induced by the highly insulating nature of the glass; 10 eV electrons allowed to fix this issue and obtain correct and useable spectra. Figure S3 shows representative XPS spectra measured for SAMs ClPrTMS and BrPrTMS.

**Numerical Simulations**

As discussed in the main text, similar threshold voltage shifts were reported for bottom-gate transistors by Kobayashi et al. in reference [2], in which the dielectric surface was functionalized with different SAMs. (see figure S7). The authors attributed the variation
of $V_T$ to the dipolar effect of the SAM. Using COMSOL multiphysics, we numerically simulated these effects when a SAM is grafted on the substrate of a top gate transistor. To modelize the molecule and its dipole moment, we introduced two charged plan of opposite signs, and with a thickness of 1nm under the semiconductor layer. The same principle was previously used in reference [3], in the case of the interface between the dielectric and the semiconductor. The 2D structure we employed is given in figure S8. Device channel dimensions are $L=100 \ \mu m$ and $W=1 \ \text{cm}$, as the ones used in the experiment. We choose thicknesses of 30 nm for electrodes, 100 nm for the semiconductor layer, 1 μm for the dielectric, 50 nm for the gate electrode and 1 nm for the charged plan representing the SAM. Dielectric constant was fixed as 3 for the semiconductor, 3.5 for the SAM, and 2 for the dielectric. The example shown below is for n-channel transistors, with a doping level $N_D=10^{12} \ \text{cm}^{-3}$, according to other reports [4]. Mobility was fixed at $1.10^{-2} \ \text{cm}^2/\text{Vs}$ in agreement with the experimental results.

In this model, we solved Poisson equation in the different media:

$$\frac{d^2 V}{dx^2} + \frac{d^2 V}{dy^2} = -\frac{\rho}{\varepsilon} \quad \quad (1)$$

Where $\rho$ is the density of charge in the materials, and $\varepsilon$ its dielectric constant. For the dielectric and the air, with fixed $\rho = 0 \ \text{C/cm}^3$. For the semiconductor, we used:

$$\rho = -e(n - N_D) \quad \quad (2)$$

Where $n$ is the density of charge carrier. We used a current density null in the semiconductor layer, since $V_D=V_S=0$. Drift diffusion equation is given by:

$$j = e n \mu E + e D \text{grad} n \quad \quad (3)$$

Where $j$ is the current density, $E$ the electric field and $D$ the diffusion coefficient. Einstein relationship is given by:
\[ D = \frac{kT}{e} \mu \]  

(4)

With \( j=0 \), we found a solution of (3):

\[ n = N_D \exp\left(\frac{eV}{kT}\right) \]  

(5)

We used (5) to solve Poisson equation in the semiconductor layer. To simulate the interface dipole due to the SAMs, we used two identical surface charge density \( \sigma_{dip} \) with opposite signs, separated by a distance \( d_{dip} \), as proposed in [3]. Charges are fixed and represent the internal molecule field. The dipole density \( \gamma_{dip} \) is equal to:

\[ \gamma_{dip} = d_{dip} \sigma_{dip} = \frac{\mu_{dip}}{A} \]  

(6)

Where \( A \) is the surface of a single molecule on glass, and \( \mu_{dip} \) its dipolar moment. To estimate the charge density \( \rho \) used to resolve Poisson’s equation, we write:

\[ \rho = \frac{\sigma_{dip}}{t_{SAM}} = \frac{\mu_{dip}}{A d_{dip} t_{SAM}} \]  

(7)

For instance, using a dipole moment equals to 4D, a surface of the molecule equal to 10 Å², a distance between charged plan of 0.5 nm and a SAM thickness of 1 nm, we found \( \rho = e \times 1.7 \times 10^{21} \text{ C/cm}^3 \).

Note, for conditions at limits between materials, we supposed that there were no potential barrier between electrodes and semiconductor, and that Fermi levels are aligned. The same was used at the interface gate/dielectric. At other interfaces, we used continuity:

\[ \tilde{n} \cdot (\varepsilon_1 \tilde{E}_1) = \tilde{n} \cdot (\varepsilon_2 \tilde{E}_2) \]  

(8)
Table S1. Contact angles with water for the different SAMs.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Contact angle [°]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cleaned Glass</td>
<td>61.5±2.4</td>
</tr>
<tr>
<td>Activated glass</td>
<td>4.0±2.1</td>
</tr>
<tr>
<td>Activated glass + immersion in toluene</td>
<td>8.7±1.7</td>
</tr>
<tr>
<td>Activated glass + ClPrTMS</td>
<td>74.2±0.8</td>
</tr>
<tr>
<td>Activated glass + BrPrTMS</td>
<td>61.8±1.2</td>
</tr>
<tr>
<td>Activated glass + EtTMS</td>
<td>59.7±1.1</td>
</tr>
<tr>
<td>Activated glass + OctTMS</td>
<td>97.3±0.5</td>
</tr>
<tr>
<td>Activated glass + PhAPrTMS</td>
<td>60.2±1.1</td>
</tr>
<tr>
<td>Activated glass + DMetAPrTMS</td>
<td>58.1±0.8</td>
</tr>
</tbody>
</table>
Figure S1. XPS Spectra measured on glass samples modified with (a) BrPrTMS and (b) ClPrTMS. Signature of bromine and chlorine are circled.

Figure S2. High resolution XPS Spectra measured on glass samples modified with (a) BrPrTMS and (b) ClPrTMS. Spectra emphasize on Bromine and Chlorine region respectively.
**Figure S3.** Optical microscope images of N1400 layers on an hydrophilic (A) and hydrophobic (B) substrates.

**Figure S4.** Top. AFM images of N1400 films (~100 nm) on monolayes of type 1,2 (A), 3,4 (B), and 5,6 (C). These are 5x5 micrometer images. Bottom. AFM images of N1400 films (~10 nm) on the indicated SAM type.
Figure S5. XRD plots of N1400 films (~10 nm) on the indicated SAMs.

Figure S6. Representative output characteristics of N1400 with (a) ClPrTMS, (b) EtTMS, (c) DMAPrTMS.

Figure S7. Representative output characteristics of PTAA with (a) ClPrTMS, (b) EtTMS, (c) DMetAPrTMS.
Figure S8. Transfer characteristics reported by Kobayashi and al in reference [2] for (a) pentacene and (b) PCBM.

Figure S9. Schematic of the simulated device.
References:


