

Threshold-Voltage Shifts in Organic Transistors Due to Self-Assembled Monolayers at the Dielectric: Evidence for Electronic Coupling and Dipolar Effects

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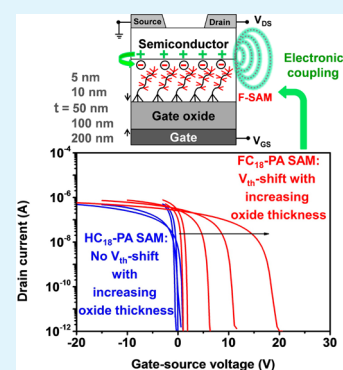
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S Supporting Information

ABSTRACT: The mechanisms behind the threshold-voltage shift in organic transistors due to functionalizing of the gate dielectric with self-assembled monolayers (SAMs) are still under debate. We address the mechanisms by which SAMs determine the threshold voltage, by analyzing whether the threshold voltage depends on the gate-dielectric capacitance. We have investigated transistors based on five oxide thicknesses and two SAMs with rather diverse chemical properties, using the benchmark organic semiconductor dinaphtho[2,3-b:2',3'-f]thieno[3,2-b]thiophene. Unlike several previous studies, we have found that the dependence of the threshold voltage on the gate-dielectric capacitance is completely different for the two SAMs. In transistors with an alkyl SAM, the threshold voltage does not depend on the gate-dielectric capacitance and is determined mainly by the dipolar character of the SAM, whereas in transistors with a fluoroalkyl SAM the threshold voltages exhibit a linear dependence on the inverse of the gate-dielectric capacitance. Kelvin probe force microscopy measurements indicate this behavior is attributed to an electronic coupling between the fluoroalkyl SAM and the organic semiconductor.

KEYWORDS: organic transistors, self-assembled monolayers, Kelvin probe force microscopy, gate-dielectric capacitance, threshold-voltage shift



1. INTRODUCTION

Substantial improvements in the performance and stability of organic thin-film transistors (TFTs) have made them a potential choice for flexible, large-area electronic and optoelectronic applications. A robust way of enhancing the electrical characteristics of bottom-gate organic TFTs is the chemical modification of the interface between the gate oxide and the organic semiconductor thin film by a self-assembled monolayer (SAM). It has been shown that the passivation of the gate-oxide surface with a highly ordered SAM can significantly reduce the density of charge traps at the oxide/SAM interface and thereby provide an enhancement of the charge-carrier field-effect mobility for both p-channel¹ and n-channel organic TFTs.² The beneficial effects of the passivation of the gate oxide with a SAM in organic TFTs have been reported for a variety of oxides, including SiO₂,^{3–6} Al₂O₃,^{7,8} HfO₂,^{9–12} ZrO₂,^{13–15} ZrTiO_x,¹⁶ and TiO₂,¹⁷ and for a variety of SAMs, most notably alkylsilane SAMs^{4,18} and alkylphosphonic acid SAMs.^{19–21} Enhanced field-effect mobility has also been associated with improvements in the thin-film morphology of the organic semiconductor layer, presumably induced by the surface energy of the SAM-functionalized oxide surfaces.⁵

Another important aspect of functionalizing the gate-oxide surface of organic TFTs with a SAM is the modification of the threshold voltage of the transistors over a range of a few volts to several tens of volts. Kobayashi et al. were among the first to introduce this effect by using various SAMs on a SiO₂ gate dielectric in combination with pentacene and C₆₀ as the semiconductors in p-channel and n-channel organic TFTs.²² In a similar study, Pernstich et al. showed that functionalizing the SiO₂ gate dielectric with different SAMs induces different threshold voltages in pentacene-based TFTs.²³ The physical mechanism responsible for this phenomenon has been under debate, and different explanations have been suggested.

Kobayashi et al. proposed that the threshold-voltage shift is related to the dipolar character of the SAM molecules, arguing that the built-in electric field of the SAM is compensated by the electric field externally applied across the gate dielectric. The electric field inside the SAM is expressed as the electrostatic potential difference across the SAM divided by its thickness

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($E_{\text{SAM}} = V_{\text{SAM}}/t_{\text{SAM}}$), with V_{SAM} given by the Helmholtz equation:

$$V_{\text{SAM}} = \frac{N_{\text{SAM}}P_z}{\epsilon_0\epsilon_{\text{SAM}}} \quad (1)$$

where N_{SAM} is the molecular density of the SAM (the number of molecules per unit area), P_z is the perpendicular component of the dipole moment of the SAM, ϵ_0 is the vacuum permittivity, and ϵ_{SAM} is the relative permittivity of the SAM. Following this line of argumentation, and assuming that the density of the dipole-induced charges accumulated at the semiconductor–dielectric interface is given by $Q_{\text{SAM}} = V_{\text{SAM}}C_{\text{SAM}}$, a general relation between the electrostatic potential of the SAM and the SAM-induced change in the threshold voltage (V_{th}) has been proposed:^{23–26}

$$V_{\text{th}} = -\frac{C_{\text{SAM}}V_{\text{SAM}}}{C_{\text{diel}}} + \varphi \quad (2)$$

with C_{diel} being the capacitance per unit area of the oxide capacitor and the SAM capacitor connected in series ($C_{\text{diel}} = (1/C_{\text{ox}} + 1/C_{\text{SAM}})^{-1}$). Thus, for large oxide thicknesses, when $C_{\text{diel}} \ll C_{\text{SAM}}$, V_{th} can be drastically larger than V_{SAM} . The term φ is introduced here to account for any contribution to the threshold voltage arising from parameters not related to the gate dielectric, such as the difference in work function between the gate electrode and the semiconductor.²⁷ In organic TFTs, φ is usually much smaller than the first term in eq 2, and therefore, it is often ignored. Any additional contribution from residual carriers or trapped charges are also assumed to be negligible in eq 2.²⁵

A conceptually different interpretation was proposed by Possanner et al., who argued that two different physical effects of the SAMs must be taken into account. According to this interpretation, the effect of a SAM composed of dipolar molecules is a shift of the threshold voltage (approximately) equal to the absolute value of the electrostatic potential of the SAM, but opposite in sign, a situation equivalent to achieving flat-band condition:²⁸

$$V_{\text{th}} = -V_{\text{SAM}} \quad (3)$$

This view, which is shared by Chung et al.,²⁹ cannot account for the fact that the threshold voltages of TFTs based on certain SAMs can be several tens of volts,^{22,23,26} while values for V_{SAM} are never greater than a few volts.^{26,30} The second effect therefore discussed by Possanner et al. is the SAM-induced formation of a space-charge layer at the semiconductor–dielectric interface that is compensated by a gate-source voltage $V_{\text{GS}} = V_{\text{th}}$ with the following value:

$$V_{\text{th}} = -\frac{\sigma}{C_{\text{diel}}} \quad (4)$$

The interfacial charge density σ can originate from a chemical reaction between the SAM and either the organic semiconductor or the oxide^{31–33} or from a modification of the density of states in the semiconductor,³⁴ and it may include a contribution from interface trap states.

The presence of a space-charge layer implies the dependence of the threshold voltage on the capacitance of the entire gate dielectric ($V_{\text{th}} \propto 1/C_{\text{diel}}$), analogous to eq 2 and in stark contrast to eq 3. But unlike eqs 2 and 3, eq 4 does not include an explicit relation with the dipolar character of the SAM. All of the above-mentioned interpretations are based on the common ground

that the SAM changes the carrier density in the semiconductor and thereby the threshold voltage. The controversy pertains to the physical or chemical mechanism(s) by which the SAM produces the observed changes in carrier density and threshold voltage, and to the question why the threshold voltage is in some experiments proportional to the inverse of the gate-dielectric capacitance (eqs 2 and 4), but in others independent of it (eq 3). A common approach to investigate the effect of the SAMs on the threshold voltage is to fabricate TFTs with SAMs based on more or less dipolar molecules and analyze the dependence of the threshold voltage on the calculated molecular dipole moment or the interfacial charge density expected from the calculated dipole moment.^{24–26,29,33,35} One limitation of this approach is that the actual dipole moment of a SAM may differ from the dipole moment calculated for an individual free molecule, where depolarization effects may be important. Another drawback is that more than one mechanism may be involved when SAMs having different characteristics (e.g., chain length, chemical nature of the anchor group and/or the functional group) are employed.

To ensure a reliable and comparative study, two different SAMs were chosen, namely, an alkyl- and a fluoroalkyl-phosphonic acid SAM with the same chain length. The different functional groups will lead to different dipole moments and may induce different carrier densities in the semiconductor by affecting the chemistry at the SAM/semiconductor interface, but by keeping the anchor groups and the processing conditions and thus the bonding to the gate oxide identical, the effects of the functional groups can be isolated from any secondary effects.³⁶ As the gate oxide, aluminum oxide (Al_2O_3) with thickness ranging from 5 to 200 nm was deposited by atomic layer deposition (ALD). ALD produces oxide films with a small defect density and a small surface roughness while providing excellent control of the oxide thickness. In addition, Al_2O_3 is an excellent template for the formation of high-quality SAMs based on alkylphosphonic acids.³⁷ The benchmark organic semiconductor dinaphtho[2,3-b:2',3'-f]thieno[3,2-b]thiophene (DNNT) was chosen for its excellent combination of large carrier mobility and long-term stability.^{38,39} Kelvin probe force microscopy (KPFM) was employed to measure the electrostatic potential originating from the SAMs as well as to get insight into the electronic interaction between the SAMs and the DNNT. In addition, atomic force microscopy (AFM) was used to confirm that the threshold voltage of the TFTs is independent of the SAM-induced semiconductor morphology.

The main conclusion from our results is that the above-mentioned relations between the SAM dipole moment and the threshold voltage cannot be generally applied. Moreover, we show that the relation between the threshold voltage and the gate-dielectric capacitance depends on the chemical nature of the SAM and the semiconductor.

2. EXPERIMENTAL SECTION

All experiments were performed using heavily doped silicon substrates onto which a layer of aluminum oxide (Al_2O_3) with a thickness of 5, 10, 50, 100 or 200 nm was deposited by ALD at a substrate temperature of 250 °C. Prior to the Al_2O_3 deposition, the native silicon dioxide was removed in dilute hydrofluoric acid. For this study, two different phosphonic acids were employed: *n*-octadecylphosphonic acid ($\text{HC}_{18}\text{-PA}$; purchased from PCI Synthesis) and 12,12,13,13,14,14,15,15,16,16,17,17,18,18,18-pentadecylfluoro-octadecylphosphonic acid ($\text{FC}_{18}\text{-PA}$; kindly provided by Matthias Schlörholz).⁴⁰ A successful SAM treatment results in a hydrophobic gate-dielectric surface, which provides the additional benefit of

preventing the adsorption of dipolar water molecules. Measurements of the water contact angle, which is a measure of the hydrophobicity of the surface, indicate that the SAM treatment with both types of SAMs results in hydrophobic surfaces (see Figure S1), and that the water contact angle is independent of the oxide thicknesses. This observation confirms that these substrates provide a good basis for comparison. In addition to the water contact angle measurements, hexadecane contact angle measurements (41° for the HC₁₈-PA SAM and 71° for the FC₁₈-PA SAM), which are in good agreement with the previously reported values in the literature,^{41,42} suggest the formation of closely packed SAMs of alkyl and fluoroalkyl molecules, exposing the CH₃ and the CF₃ groups respectively to the air/film interface.⁴²

For most of the experiments, the Al₂O₃-coated silicon substrates were immersed into a 2-propanol solution of either the alkyl- or the fluoroalkylphosphonic acid, resulting in a uniform coverage of the Al₂O₃ surface with one particular SAM. For some of the KPFM measurements, we also prepared substrates on which both SAMs are present. To obtain patterned substrates with both SAMs, we employed a combination of microcontact printing and immersion. In the first step, a pattern of the FC₁₈-PA SAM was produced on the Al₂O₃ surface by microcontact printing using a polydimethylsiloxane (PDMS) stamp.^{43–45} Those areas of the substrate not covered by the FC₁₈-PA SAM were then filled with the HC₁₈-PA SAM by immersing the substrate into a 2-propanol solution of the alkylphosphonic acid. Substrates were then rinsed with pure 2-propanol, blow-dried with nitrogen, and baked on a hot plate at a temperature of 100 °C for 10 min to stabilize the monolayers.⁴⁵

The organic semiconductor DNTT (purchased from Sigma-Aldrich) was deposited onto the SAM at a substrate temperature of 60 °C in a vacuum of about 10⁻⁶ mbar. The deposition rate and the nominal film thickness were monitored using a quartz crystal microbalance. For most of the experiments, the deposition rate was set to 0.03 nm s⁻¹ and the nominal film thickness was 25 nm. For some of the experiments in which the thin-film morphology of the semiconductor was investigated, a smaller deposition rate of 0.007 nm s⁻¹ was chosen, and in some experiments the nominal film thickness was 2 nm in order to obtain a partial surface coverage. Fabrication of bottom-gate, top-contact (inverted staggered) thin-film transistors was completed by the deposition of gold source and drain contacts by thermal evaporation in vacuum through a shadow mask onto the surface of the organic semiconductor layer. All TFTs have a channel length of 100 μm and a channel width of 200 μm. The gate dielectric is a combination of Al₂O₃ (deposited by ALD and having a thickness of 5, 10, 50, 100, or 200 nm) and either of the two SAMs (prepared by immersion into a 2-propanol of either the alkyl- or the fluoroalkylphosphonic acid). KPFM measurements were carried out in ambient air at room temperature using an Asylum Research Cypher equipped with conductive Ti/Ir-coated probe tips having a force constant of 1.7 N m⁻¹. Contact-mode AFM images were obtained using a Nanoscope III Multimode in ambient air using a soft cantilever ($K = 0.01 \text{ N m}^{-1}$). AFM and KPFM images were analyzed using the WsXM software.⁴⁶

Current–voltage measurements on the TFTs were carried out in ambient air at room temperature under yellow laboratory light, using a micromanipulator probe station and an Agilent 4156C semiconductor parameter analyzer, and using the heavily doped silicon substrate as a common gate electrode.

3. RESULTS AND DISCUSSIONS

3.1. Transistor Characteristics and Threshold Voltage.

The TFTs were fabricated in the bottom-gate, top-contact architecture on silicon substrates with an Al₂O₃/SAM gate dielectric with oxide thicknesses of 5, 10, 50, 100, or 200 nm. The oxide surface was functionalized with SAMs composed of either an alkyl- or a fluoroalkylphosphonic acid, both with a chain length of 18 carbon atoms.⁴⁰ The organic semiconductor DNTT was deposited in vacuum, and the source and drain contacts were patterned using a shadow mask. The schematic

cross section of the TFTs and the chemical structures of the organic semiconductor DNTT and the alkyl- and fluoroalkylphosphonic acids (HC₁₈-PA, FC₁₈-PA), are shown in Figure 1.

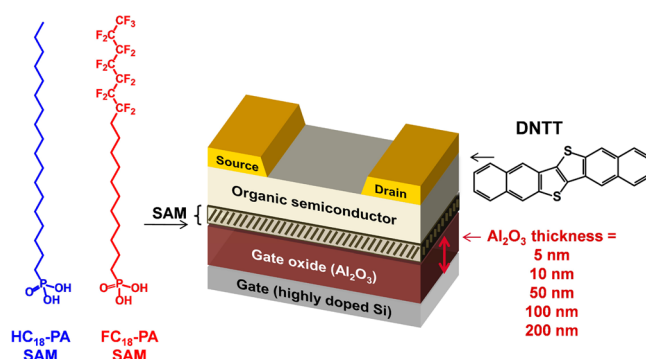


Figure 1. Schematic cross section of the TFTs, fabricated with five different Al₂O₃ thicknesses and two different phosphonic acid SAMs (HC₁₈-PA, FC₁₈-PA). Chemical structures of the organic semiconductor (DNTT) and the two phosphonic acids (HC₁₈-PA, FC₁₈-PA) are also shown.

The effect of the oxide thickness and the SAM type on the threshold voltage of the TFTs was analyzed by measuring the current–voltage characteristics of the devices. The measured transfer characteristics as well as a plot summarizing the corresponding carrier mobilities extracted from the linear regime of operation are shown in Figure 2. Regardless of the oxide thickness and the type of the SAM, all TFTs exhibit field-effect mobilities ranging from around 2 to 3.5 cm² V⁻¹ s⁻¹, similar to the highest field-effect mobilities reported for DNTT TFTs in the literature.^{38,47,48} Figure 2 also shows that independent of the oxide thickness, all TFTs in which the oxide surface was functionalized with the fluoroalkyl SAM have a more positive threshold voltage than the TFTs in which the oxide surface was functionalized with the alkyl SAM, which is consistent with previous reports.^{6,22,23,40,49}

To obtain the threshold voltages of the TFTs, the measured transfer curves were fitted to the basic field-effect transistor equation:

$$I_D = \frac{\mu \cdot C_{\text{diel}} W}{L} \left[(V_{\text{GS}} - V_{\text{th}}) V_{\text{DS}} - \frac{1}{2} V_{\text{DS}}^2 \right] \quad (5)$$

where μ is the field-effect mobility, W is the channel width, L is the channel length, V_{GS} is the gate-source voltage, and V_{DS} is the drain-source voltage (-0.1 V). The gate-dielectric capacitance (C_{diel}) was calculated as follows:

$$C_{\text{diel}} = \left(\frac{1}{C_{\text{ox}}} + \frac{1}{C_{\text{SAM}}} \right)^{-1} = \epsilon_0 \left(\frac{t_{\text{ox}}}{\epsilon_{\text{ox}}} + \frac{t_{\text{SAM}}}{\epsilon_{\text{SAM}}} \right)^{-1} \quad (6)$$

where t_{ox} is the oxide thickness, ϵ_{ox} is the relative permittivity of Al₂O₃ ($\epsilon_{\text{ox}} = 9$),⁵⁰ t_{SAM} is the thickness of the SAM (2.1 nm)⁵¹ and ϵ_{SAM} is the relative permittivity of the SAM ($\epsilon_{\text{SAM}} = 2.5$ for the HC₁₈-PA SAM, $\epsilon_{\text{SAM}} = 2.2$ for the FC₁₈-PA SAM).⁵² For the smallest oxide thickness (5 nm), the calculations were confirmed by frequency-dependent capacitance measurements (see Figure S2). The threshold voltages obtained for each TFT are indicated in Figure 2 and summarized in Table 1.

3.2. Electrostatic Potential Measurements. In order to understand the impact of the SAM on the threshold voltage, it

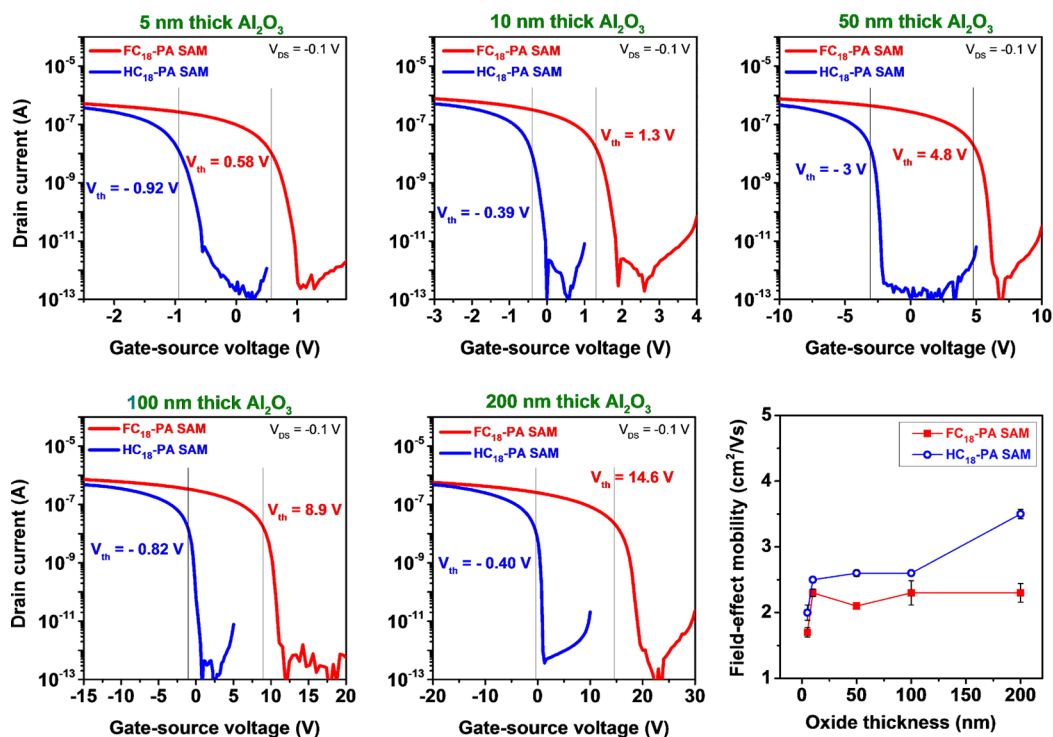


Figure 2. Measured transfer characteristics of DNTT TFTs based on five different Al_2O_3 thicknesses and two different SAMs (HC_{18} -PA, FC_{18} -PA), and field-effect mobilities extracted from the transfer characteristics of all 10 TFTs plotted as a function of the Al_2O_3 thickness (with statistical error bars). The field-effect mobilities were extracted from the linear regime ($V_{\text{DS}} = -0.1$ V). In each transfer curve, the threshold voltage is marked with a vertical line.

Table 1. Summary of the Gate-Dielectric Capacitances (Calculated Using eq 6) and the Threshold Voltages of DNTT TFTs (with Statistical Errors from Measuring Several TFTs) Based on Five Different Al_2O_3 Thicknesses and Two Different SAMs

Al_2O_3 thickness [nm]	SAM capacitance [nF cm^{-2}]		threshold voltage [V]	
	$\text{Al}_2\text{O}_3/\text{HC}_{18}$ -PA	$\text{Al}_2\text{O}_3/\text{FC}_{18}$ -PA	HC_{18} -PA SAM	FC_{18} -PA SAM
5	650 ^a	580 ^a	-0.92 ± 0.02	$+0.58 \pm 0.01$
10	450	430	-0.39 ± 0.03	$+1.3 \pm 0.01$
50	140	140	-3.0 ± 0.07	$+4.8 \pm 0.07$
100	74	73	-0.82 ± 0.07	$+8.9 \pm 0.18$
200	38	38	-0.40 ± 0.18	$+14.6 \pm 0.14$

^aFor the 5 nm thick oxide, the calculations were confirmed by frequency-dependent capacitance measurements (see Figure S2).

is important to have an experimental measure of the electrostatic potential generated by the SAM (V_{SAM}). Since the actual electrostatic potential may differ from the value predicted by eq 1 due to charge rearrangements, depolarization effects (dipole-dipole interactions) and substrate-molecule interactions,⁵³ we employed KPFM as a noninvasive method to obtain the electrostatic potential on the surface. Since KPFM measures the contact-potential difference between the surface and the probe tip, a quantitative determination of the electrostatic potential independent of any tip effects requires using a surface reference. Moreover, the same tip must be used for comparison between different KPFM measurements. We have measured a freshly cleaved highly oriented pyrolytic graphite (HOPG) surface subsequent to each measurement as a reference to make sure the probe tip has not changed. The histograms obtained from the surface potential maps of the bare Al_2O_3 surface as well as those obtained after the functionalization with the two SAMs are shown in Figure 3. From the surface potential histograms shown in Figure 3, electrostatic potentials (relative to the Al_2O_3 surface) of +0.87 V for the

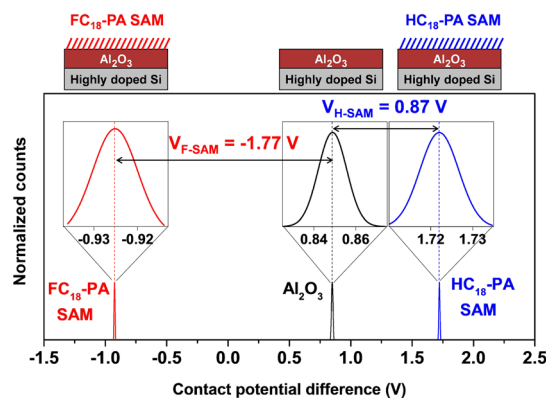


Figure 3. Surface potential histograms obtained from KPFM measurements on an Al_2O_3 surface without SAM (center), on an Al_2O_3 surface covered with the FC_{18} -PA SAM (left), and on an Al_2O_3 surface covered with the HC_{18} -PA SAM (right). The magnitude of the contact potential differences is marked with arrows between the magnified histograms shown as inset.

Table 2. Dipole Moments of Individual HC₁₈–PA and FC₁₈–PA Molecules, and Molecular Densities, Relative Dielectric Constants, and Electrostatic Potentials of the HC₁₈–PA and FC₁₈–PA SAMs Predicted by eq 1 and Measured by KPFM^a

SAM type	molecular dipole moment [D]	molecular density of the SAM [cm ⁻²]	relative dielectric constant	electrostatic potential predicted by eq 1 [V]	electrostatic potential measured by KPFM [V]
HC ₁₈ –PA	-1.07	4.55 × 10 ¹⁴ [ref 29] to 5.4 × 10 ¹⁴ [ref 54]	2.5	+0.74 to +0.88	+0.87
FC ₁₈ –PA	2.79	3.33 × 10 ¹⁴ [ref 55] to 3.7 × 10 ¹⁴ [ref 56]	2.2	-1.6 to -1.77	-1.77

^aThe values for the dipole moments and relative dielectric constants are taken from Jedaa et al.,⁵² and the molecular packing densities are taken from the literature either directly or were calculated for a close hexagonal packing of the molecules using the van der Waals radius of the chains.

HC₁₈–PA SAM and -1.77 V for the FC₁₈–PA SAM are obtained. Table 2 shows that the experimentally determined V_{SAM} values measured by KPFM are in good agreement with the V_{SAM} calculated using eq 1 for the densest close-packing of the chains according to the literature.

A cross-check experiment was performed using grounded gold contacts on each SAM as an in situ reference for the calibration of the work function of the probe tip (see Figure S3).

By performing the KPFM measurements on substrates with various Al₂O₃ thicknesses, we also confirmed the reasonable and commonly made assumption that the electrostatic potential of a SAM is not affected by the thickness of the oxide underneath the SAM (see Figure S4). We can therefore use the V_{SAM} measured for an oxide thickness of 5 nm to analyze the correlation between the electrostatic potential of the SAM and the threshold voltage for all TFTs in this study, despite the different oxide thicknesses.

Comparing the measured threshold voltages (Table 1) with the measured electrostatic potentials of the SAMs (Table 2), it can be seen that the threshold voltages of the TFTs with the FC₁₈–PA SAM are significantly larger than the electrostatic potential of this SAM, at least when the oxide thickness is greater than a few tens of nanometers. For example, for an oxide thickness of 200 nm, the absolute value of the threshold voltage of the TFTs with the FC₁₈–PA SAM (~+15 V) is almost an order of magnitude larger than the absolute value of the measured electrostatic potential of this SAM (-1.77 V). This shows that for TFTs with the fluoroalkyl SAM, eq 3 does not hold.

3.3. Relationship Between Threshold Voltage and Gate-Dielectric Capacitance. In Figure 4, the measured and predicted threshold voltages (eq 2 using the measured electrostatic potentials listed in Table 2) are plotted for different gate-dielectric capacitances. As can be seen, for both SAMs, there is a significant disagreement between the measured and the theoretically predicted values. The threshold voltages of the TFTs with the HC₁₈–PA SAM exhibit an average value of -0.64 V without any systematic dependence on the gate-dielectric capacitance, in contrast to the predicted threshold voltages from eq 2 ($V_{\text{th}} \propto 1/C_{\text{diel}}$). This value is close to the measured electrostatic potential of the HC₁₈–PA SAM, but with opposite polarity ($V_{\text{th}} \approx -V_{\text{SAM}}$), a result that is in agreement with the dipole-layer scenario proposed by Possanner et al.²⁸ and the experimental results from Chung et al.²⁹ We infer from this observation that the main effect of the oxide functionalization with the HC₁₈–PA SAM is the passivation of the charge traps at the oxide surface.²

Unlike the threshold voltages of the TFTs with the HC₁₈–PA SAM, which are independent of the gate-dielectric capacitance, the threshold voltages of the TFTs with the FC₁₈–PA SAM show a linear dependence on the inverse of the

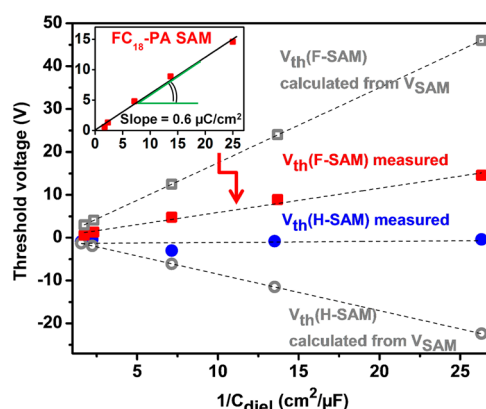


Figure 4. Measured threshold voltages (see Table 1) and threshold voltages calculated from V_{SAM} using eq 2 (using the electrostatic potentials measured by KPFM, i.e., +0.87 V for the HC₁₈–PA SAM and -1.77 V for the FC₁₈–PA SAM; see Table 2) plotted as a function of the gate-dielectric capacitance (see Table 1). For both SAMs, there is a significant disagreement between the measured and the theoretically predicted threshold voltages. The inset illustrates how the charge density σ is obtained from the slope of the linear fit using eq 4.

gate-dielectric capacitance ($V_{\text{th}} \propto 1/C_{\text{diel}}$). However, the slope of this linear relationship is only $0.6 \mu\text{C cm}^{-2}$, which is significantly smaller than the value predicted by eq 2 ($1.8 \mu\text{C cm}^{-2}$ for $C_{\text{SAM}} = 1 \mu\text{F cm}^{-2}$ and $V_{\text{SAM}} = -1.77 \text{ V}$).

Thus, for both SAMs, it is clear that eq 2 does not apply in practice, which raises the question whether there is a general relation between the dipole moment of the SAM and the threshold voltage of the TFTs, and whether this relation applies universally to all types of SAMs.

The linear relation between V_{th} and $1/C_{\text{diel}}$ for TFTs with the FC₁₈–PA SAM can be understood in terms of the space-charge layer described by eq 4. The interfacial charge density responsible for the observed $V_{\text{th}} \propto 1/C_{\text{diel}}$ dependence (see inset in Figure 4) is estimated to be $\sigma \approx -0.6 \mu\text{C cm}^{-2} = -3.5 \times 10^{12} \text{ e cm}^{-2}$, causing accumulation of holes in the channel, a value comparable to SAM-induced charge densities estimated experimentally for pentacene TFTs^{23,57} and also to theoretical simulations.²⁸

It is worth mentioning that, despite the different behavior of V_{th} , TFTs with the FC₁₈–PA SAM do not show hysteresis between the forward and backward sweeps of the transfer curves (shown in Figure S5) and exhibit a steep subthreshold swing which is compelling evidence that the interfacial charge density is not caused by shallow traps in the semiconductor.

The fact that the relationship between the gate-dielectric capacitance and the threshold voltage is so different depending on the choice of the SAM ($V_{\text{th}} \approx \text{const.}$ for the TFTs with the HC₁₈–PA SAM; $V_{\text{th}} \propto 1/C_{\text{diel}}$ for those with the FC₁₈–PA

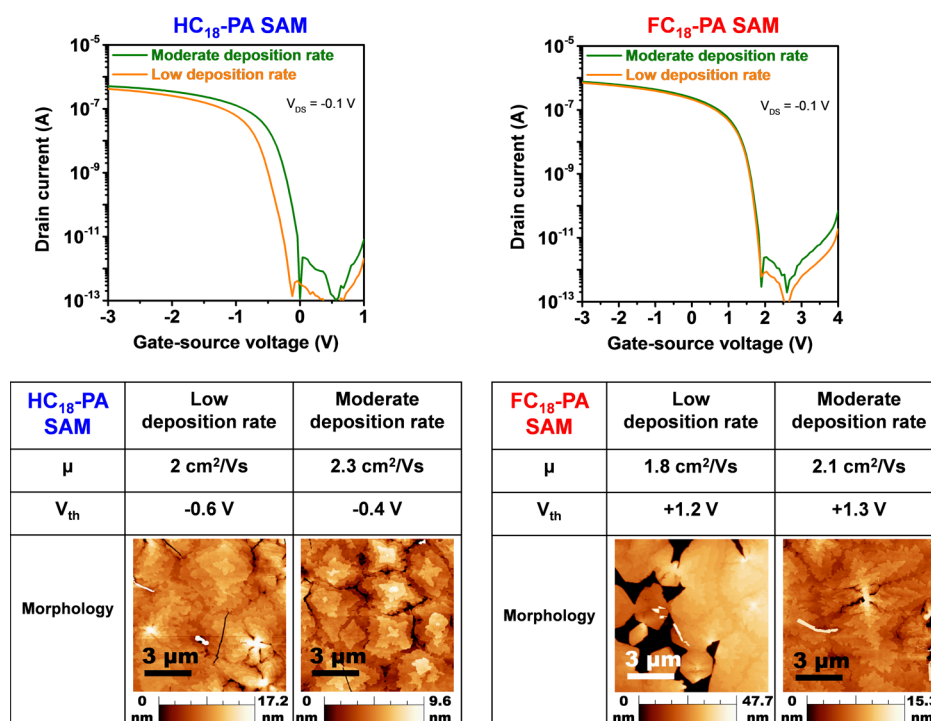


Figure 5. Transfer characteristics of DNTT TFTs fabricated using either of the two SAMs and with the DNTT layers deposited using either a moderate deposition rate of 0.03 nm s^{-1} or a low deposition rate of 0.007 nm s^{-1} . The Al_2O_3 gate-oxide layer has a thickness of 10 nm. The field-effect mobilities and the threshold voltages of the TFTs along with the morphology of the DNTT layers are also shown.

SAM) could be related to the presence of the strongly electronegative fluorine substituents in the FC_{18} -PA SAM. These substituents are located directly at the semiconductor/SAM interface and are likely to have a strong influence on the electronic characteristics of this interface. Before analyzing this matter, it is important to explore the possible influence of the selected SAMs on the semiconductor morphology.

3.3.1. Ruling out Semiconductor Morphology. Different SAMs can have different surface energies, which often has a significant influence on the thin-film morphology of the subsequently grown organic semiconductor layer. For many organic semiconductors, for example, pentacene, the morphology can affect the electrical TFT characteristics.^{58–60} We have therefore examined the extent to which the electrical properties of our DNTT TFTs are influenced by the thin-film morphology of the DNTT layers deposited onto the two studied SAMs. In the course of these experiments, we found that the DNTT growth mode and the resulting thin-film morphology are affected not only by the choice of the SAM, but also by the DNTT deposition rate, but that these differences do not have a noticeable effect on the electrical characteristics of the TFTs.

Figure 5 shows the measured transfer characteristics of four TFTs fabricated by depositing a nominally 25 nm thick layer of DNTT onto either of the two SAMs with either a moderate or a low deposition rate (0.03 or 0.007 nm s^{-1}), along with AFM topography images of the thin-film morphology of the corresponding DNTT layers. The AFM images indicate rather pronounced differences in the DNTT morphology depending on the choice of the SAM and the deposition rate. The significant influence of the deposition rate on the thin-film morphology is also seen in much thinner DNTT layers with partial surface coverage, as shown in Figure S6. But surprisingly, these differences in the semiconductor morphology do not have

a noticeable effect on the field-effect mobility or the threshold voltage of the TFTs.

Based on these observations, we rule out that the different morphology of the DNTT films on HC_{18} -PA and FC_{18} -PA functionalized substrates is responsible for the observed difference in the threshold voltage of the TFTs. Furthermore, the Al_2O_3 layer underneath the SAM is atomically smooth for all thicknesses and thus is unlikely to induce changes in the DNTT film morphology within the series of TFTs treated with the FC_{18} -PA SAM, which might cause the observed thickness-dependent V_{th} shift. In other words, neither the fact that the threshold voltages of the TFTs based on the FC_{18} -PA SAM are significantly more positive than those of the TFTs with the HC_{18} -PA SAM, nor the observation that the threshold voltage increases linearly with the inverse of the gate-dielectric capacitance in the case of the FC_{18} -PA SAM, but not in the case of the HC_{18} -PA SAM, can be explained with the different semiconductor morphologies on the two SAMs.

3.3.2. Electronic Coupling between the SAM and the Organic Semiconductor. We now turn to the question whether there are any electrostatic or electronic interactions between the SAM and the organic semiconductor that may play a role in determining the relationships between each particular SAM and the measured threshold voltages. Such possibility has been discussed in the context of charge transfer (i.e., chemical doping),^{28,61,62} charge trapping,⁶³ and electrostatic interactions between the organic semiconductor with the local electric field of the dipolar SAM.^{23,34} The latter has been proposed recently by Mityashin et al. as the mechanism responsible for the observation of a more positive threshold voltage for pentacene TFTs with fluoroalkyl-silane SAMs (in comparison to alkyl-silane SAMs) and this effect has been attributed to the accumulation of positive charge carriers due to broadening and shift of the density of states at the pentacene/SAM interface.³⁴

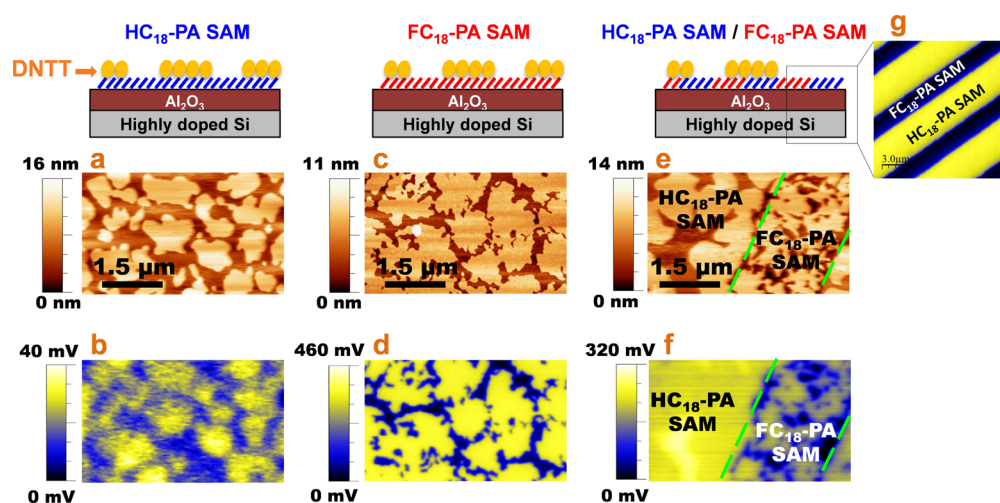


Figure 6. AFM topography images (first row) and KPFM electrostatic potential maps (second row) of a HC₁₈-PA SAM with partial DNTT coverage (a,b), of a FC₁₈-PA SAM with partial DNTT coverage (c,d), and of an array of both SAMs (produced by microcontact printing of the FC₁₈-PA SAM followed by immersion into the HC₁₈-PA molecules) with partial DNTT coverage (e,f). The contact potential difference maps have been rescaled for clarity to start from zero.

The electrostatic potential of the surface can be precisely measured by KPFM. Figure 6a–d shows AFM topography and KPFM electrostatic potential maps of a HC₁₈-PA SAM surface and of a FC₁₈-PA SAM surface, both decorated with individual, unconnected islands of DNTT (nominal DNTT thickness 2 nm).

As can be seen in Figure 6b, a small positive surface potential of about +40 mV is measured on the DNTT islands with respect to the surrounding HC₁₈-PA SAM. We presume that the positive sign is due to electronic polarization induced in the DNTT by the dipole moment of the HC₁₈-PA SAM.⁶⁴ The perpendicular components of the dipole moments of the HC₁₈-PA SAM and the FC₁₈-PA SAM point into opposite directions,⁵² so if the surface potential on the DNTT located on the FC₁₈-PA SAM was also due to electronic polarization by the SAM dipole, the surface potential would be negative, that is, in the KPFM surface potential maps the DNTT islands would appear darker than the surrounding FC₁₈-PA SAM.⁶⁵ However, as Figure 6d clearly shows, a relatively large positive contact potential difference of about +0.4 V is measured between the DNTT and the FC₁₈-PA SAM, which is an order of magnitude larger than that between the DNTT and the HC₁₈-PA SAM. This suggests that there is electronic coupling between the DNTT and the FC₁₈-PA SAM that produces an interface dipole with a negative surface potential on the surface of the FC₁₈-PA SAM and a positive surface potential on the DNTT islands.

As a cross-check experiment, we also prepared a substrate on which both SAMs are present, since a patterned substrate makes it possible to measure the electrostatic potentials on the two SAMs in a single uninterrupted measurement independent of the type and the condition of the probe tip. These substrates were prepared by a combination of microcontact printing (stamping of the FC₁₈-PA SAM) and immersion (filling of the remaining areas with the HC₁₈-PA SAM). The electrostatic potential map of this patterned surface without DNTT is shown in Figure 6g. The areas with the larger (smaller) electrostatic potential correspond to the alkyl (fluoroalkyl) SAM. The measured surface-potential difference between the two SAMs prepared on the same substrate is about 0.6 V (see Figure S4), which is significantly smaller than the potential

difference measured when both SAMs were prepared separately by immersion on different substrates (about 2.6 V; see Figure 3). This discrepancy is attributed to the smaller density of molecules in the microcontact-printed SAM compared to the solution-processed SAM. The potential map of the patterned surface partially covered by DNTT (Figure 6f) clearly shows a relatively large contact potential difference between the DNTT islands and the FC₁₈-PA SAM, in contrast to the small contact potential difference between the DNTT islands and the HC₁₈-PA SAM. This observation confirms the presence of a certain electronic interaction between the DNTT and the FC₁₈-PA SAM, but not between the DNTT and the HC₁₈-PA SAM. It is a priori not clear whether the interface dipole formed at the interface between the DNTT and the FC₁₈-PA SAM stems from charge transfer and/or electrostatic doping due to the electrostatic interaction between the DNTT and the FC₁₈-PA SAM. The large energy level mismatch between the highest occupied molecular orbital (HOMO) of DNTT (−5.4 eV)⁴⁷ and the lowest unoccupied molecular orbital (LUMO) of the SAM (∼−0.2 eV for octadecyltrichlorosilane SAMs with the same chain length as our FC₁₈-PA SAM)⁶⁶ makes direct charge transfer between DNTT and the SAM unlikely.

The positive electrostatic potential on the DNTT islands on the FC₁₈-PA SAM measured by KPFM (Figure 6d) implies the accumulation of positive charges in the DNTT layer. Having already ruled out polarization and direct charge transfer, we conclude that the positive charges in the DNTT are balanced by negative charges elsewhere in the device, most likely at one of the two interfaces between the DNTT, the SAM and the Al₂O₃ layer. Although the SAM is sufficiently thin for charges to tunnel from the DNTT to the interface between the SAM and the gate oxide,^{33,67} we believe that charge trapping at the SAM/Al₂O₃ interface is unlikely, since the hydroxyl groups (known to act as trap states) that are initially present on the Al₂O₃ surface are eliminated by the phosphonic acid SAM treatment. We therefore postulate that the negative charges are localized in the FC₁₈-PA SAM.

To determine whether the positive charges in the DNTT that form the space-charge layer are mobile or immobile, we will correlate the observed positive shift of the threshold voltage of the TFTs with the large positive electrostatic potential on

the DNTT islands measured by KPFM. Assuming that the positive surface potential on the DNTT islands in Figure 6d originates from immobile positive charges in the DNTT layer, that are compensated by immobile negative charges at the FC₁₈-PA SAM/DNTT interface, a small capacitance-independent shift of the threshold voltage would be expected. Such a situation would be similar to the effect of V_{SAM} in Equation 3 and is not consistent with the observed linear dependence of V_{th} on the inverse of the dielectric capacitance. On the other hand, if there were uncompensated immobile positive charges in the semiconductor, a more negative gate-source voltage would be required to accumulate mobile holes. This would imply a negative shift of V_{th} , which is the opposite of what we obtained in our devices; see Figure 4. Having ruled out all of the above scenarios, points to the accumulation of mobile holes in the DNTT layer in close proximity to the FC₁₈-PA SAM as the most likely explanation consistent with the KPFM results and with the positive threshold voltage shifts observed in our TFTs. The accumulation of mobile holes in the DNTT layer, which is the consequence of the presence of immobile negative charges (electrons or ions) in the fluorine substituents of the SAM molecules, resembles surface chemical doping. Figure 7

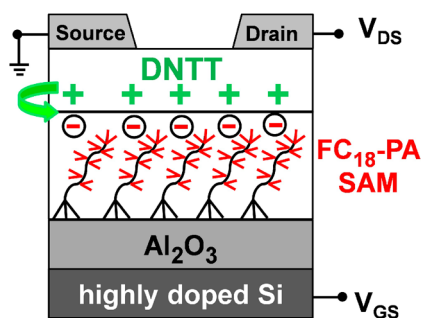


Figure 7. Schematic cross section of the DNTT TFTs with the FC₁₈-PA SAM indicating the accumulation of mobile positive charges in the DNTT layer and immobile negative charges in the SAM at the interface between DNTT and the FC₁₈-PA SAM.

illustrates that the space-charge layer, which is most probably the dominant mechanism behind the threshold voltage shifts observed in the TFTs with the FC₁₈-PA SAM, consists of mobile holes in the DNTT layer located at the interface between the DNTT and the fluorine substituents in the SAM.

A simple estimation of the charge density in the DNTT on the FC₁₈-PA SAM using a parallel plates capacitor model using $\sigma \approx C_{\text{DNTT}}V_{\text{DNTT}}$, with σ^+ and σ^- on the DNTT and the SAM surface respectively, yields a value of $\sigma \approx 2.7 \times 10^{12} \text{ e cm}^{-2}$ (with $C_{\text{DNTT}} = \epsilon_{\text{DNTT}}\epsilon_0/d_{\text{DNTT}} \approx 0.11 \mu\text{F cm}^{-2}$ and assuming $\epsilon_{\text{DNTT}} = 4$ as for pentacene,⁶⁸ $d_{\text{DNTT}} = 3.2 \text{ nm}$ (height of a double-layered island), and $V_{\text{DNTT}} = 0.4 \text{ V}$ from the KPFM measurement in Figure 6d). This value, which is comparable to the previously calculated charge density from the relationship between the threshold voltage and the inverse of the gate-dielectric capacitance (Figure 4), is a result of the electronic coupling at the interface between the dielectric and the DNTT.

It is important to note that the measured surface potential stems from intrinsic electronic effects at the SAM/DNTT interface and does not include charge injection from the contacts to form the TFT channel, as is the case in a transistor. The smaller value of the charge density estimated from the surface potential compared to that obtained from the V_{th} shifts ($\sigma \approx 2.7 \times 10^{12}$ vs $3.5 \times 10^{12} \text{ e cm}^{-2}$), is perhaps an indication

for an additional mechanism of trapping of immobile charges at the dielectric interface upon the operation of the TFTs, as reported by Gholamrezaie et al.⁶³

4. CONCLUSIONS

We have carried out a systematic investigation to unravel the mechanisms behind the shift of the threshold voltage of bottom-gate organic TFTs by the functionalization of the surface of the Al₂O₃ gate dielectric with two different SAMs. We have demonstrated that in TFTs based on a fluoroalkyl SAM, that is, a SAM with strongly electronegative fluorine substituents at the interface to the semiconductor, the threshold voltage exhibits a linear dependence on the gate-dielectric capacitance ($V_{\text{th}} \propto 1/C_{\text{diel}}$), while in TFTs based on an alkyl SAMs, the threshold voltage is independent of the dielectric capacitance and is determined mainly by the electrostatic potential generated by the SAM ($V_{\text{th}} \approx -V_{\text{SAM}}$).

To shed light on this dissimilar behavior, we have presented a detailed nanoscale investigation of the electrostatic potential of the SAM/organic semiconductor interface by means of KPFM. Our results provide evidence for an electronic coupling and the formation of a space-charge layer consisting of mobile holes at the interface between the DNTT and the fluoroalkyl SAM, which is responsible for the observed dependence of the threshold voltage on the gate-dielectric capacitance. In contrast, no evidence for such interfacial electrostatic interaction was detected for the combination of DNTT and the alkyl SAM. We thereby confirm the validity of the two vigorously debated cases ($V_{\text{th}} \propto 1/C_{\text{diel}}$ and $V_{\text{th}} \approx -V_{\text{SAM}}$) by showing that both of them are essential to explain the threshold-voltage shifts observed in organic TFTs due to SAMs at the semiconductor/dielectric interface. Our method of determining the electrostatic potential difference between the SAM and the semiconductor is thus a promising approach to select the proper combination of oxide thickness, SAM and organic semiconductor to tune the threshold voltage, which is an important aspect in the design of integrated circuits. We conclude that the mechanism by which the gate-dielectric modification with a SAM affects the threshold voltage of organic TFTs is ultimately related to the properties of the interface between the SAM and the organic semiconductor and can therefore not be ascribed solely to the dipole moment of the SAM.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b02747.

Water contact angle measurements on Al₂O₃ with five different thicknesses (Figure S1), frequency-dependent capacitance measurements on the 5 nm thick Al₂O₃ (Figure S2), KPFM electrostatic potential measurements on the SAMs with a grounded gold contact (Figure S3), KPFM measurements on the Al₂O₃ patterned with both SAMs (Figure S4), hysteresis-free transfer curves (forward and backward sweeps) of the TFTs functionalized with the FC₁₈-PA SAM (Figure S5), and AFM topography images of DNTT partial layer morphology and further discussions on the DNTT growth (Figure S6) (PDF)

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Notes

The authors declare no competing financial interest.

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