Controlling the dimensionality of charge transport in organic thin-film transistors

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Electrolyte-gated organic thin-film transistors (OTFTs) can offer a feasible platform for future flexible, large-area and low-cost electronic applications. These transistors can be divided into two groups on the basis of their operation mechanism: (i) field-effect transistors that switch fast but carry much less current than (ii) the electrochemical transistors which, on the contrary, switch slowly. An attractive approach would be to combine the benefits of the field-effect and the electrochemical transistors into one transistor that would both switch fast and carry high current densities. Here we report the development of a polyelectrolyte-gated OTFT based on conjugated polyelectrolytes, and we demonstrate that the OTFTs can be controllably operated either in the field-effect or the electrochemical regime. Moreover, we show that the extent of electrochemical doping can be restricted to a few monolayers of the conjugated polyelectrolyte film, which allows both high current densities and fast switching speeds at the same time. We propose an operation mechanism based on self-doping of the conjugated polyelectrolyte backbone by its ionic side groups.

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ncorporation of electronics into paper, plastic, and other flexible, lightweight, thin and low-cost substrates can enable realization of a multitude of large-area electronic applications such as e-textiles, e-paper, lighting, photovoltaics, and sensors (1). In the field of organic electronics, considerable effort has been devoted to study organic thin-film transistors (OTFTs), which are regarded as the central components in each of the above mentioned applications (2). OTFTs must meet a wide range of specifications to provide a feasible technology platform: They must be solution processable, operate at low voltages, consume only a little power, and switch fast to enable fast signal processing. A promising solution to this problem is to use electrolytes as the gate "insulator" material (3-6). Upon applying a gate potential, electrolytes can rapidly form electric double layers near the electrolyte-semiconductor interface, which gives rise to high switching speeds, high electric fields, and high charge carrier densities already at relatively low voltages. Polymer electrolytes and polyelectrolytes in particular are ideal due to their additional filmforming characteristics and ease of processing from solutions. More recently, a question on the operating mechanism of electrolyte-gated OTFTs has sparked a lively discussion as to whether the gating is purely field-induced or electrochemical (7–9). In the former case, ions of the electrolyte migrate close to the semiconductor interface while charge carriers of opposite charge accumulate on the semiconductor side. The latter mechanism, on the other hand, is typically characterized by mass transport of ions across the electric double layer and involves electrochemical doping of the semiconductor bulk. Even if identification of the mechanism can be ambiguous, absorption (7, 10), Fourier transform (8), and impedance spectroscopy (11) as well as signatures in the electrical characteristics (12) have been used as evidence to judge the mode of operation. Electrochemical doping is most often (but not always) undesirable due to its deteriorating effect on the transistor performance such as considerably slower switching speed and large hysteresis in the electrical characteristics (13).

Therefore, several different techniques have been suggested to avoid electrochemical doping in electrolyte-gated OTFTs and include the use of highly crystalline semiconductors, immobile polyanions (13), and blocking layers between the semiconductor and the electrolyte (14). Despite this drawback, electrochemical transistors have proven particularly useful for, e.g., electrochromic displays that require high current densities to switch a pixel (15, 16). An attractive approach is to combine the advantages of both field-effect and electrochemical transistors into one transistor that would both switch fast and carry a high current density.

In this article, we develop polyelectrolyte-gated OTFTs based on a carboxyl-functionalized poly(3-hexylthiophene) (P3CPT; Fig. 1B). P3CPT belongs to a group of conjugated polyelectrolytes whose intriguing properties stem from the combination of a hydrophobic π -conjugated backbone with the physicochemical properties of a hydrophilic ionic side group (17). Previously, this class of polymers has been used in organic photovoltaics (18), as gate dielectric material in transistors (19), or to improve the electrical contacts between electrodes and another semiconducting material (20). Bao and coworkers demonstrated the use of carboxyl-functionalized polyalkylthiophenes in field-effect transistors (21), but the transistors showed only poor electrical and structural characteristics most probably due to the short alkyl spacer (18) and the low dielectric constant of the gate insulator. Our hypothesis is that the dual nature of the conjugated polyelectrolyte can allow bulk transport in an OTFT because the polarons in the conjugated backbone can be stabilized by the neighboring ionic side groups throughout the bulk of the semiconductor layer. Here, we first distinguish between the different operational regimes and compare the transistor characteristics of the P3CPT based transistor to its well-studied unmodified precursor poly (3-hexylthiophene) (P3HT, Fig. 1B). We show that polyelectrolyte-gated OTFTs comprising P3CPT operate either in the fieldeffect (Fig. 1A, Regime I) or electrochemical regime, depending on the applied gate voltage. Furthermore, we report two distinct switching processes in the electrochemical regime, which are attributed to fast interfacial and slow bulk electrochemical doping, respectively (Fig. 1A, Regime II and III). An operation mechanism based on self-doping of the conjugated backbone by the ionic side groups is proposed.

Results and Discussion

The chemical structures of the two conjugated polymers used in this study are shown in Fig. 1*B*. They differ with respect to the terminal group of the side chain of the polymer—either a methyl (-CH₃) or a carboxyl group (-COOH). As an example, the hydrophobic alkyl side chains of P3HT give rise to a water contact angle

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Fig. 1. Device architectures and chemical structures of the materials used in this study. (A) Schematic diagram of a capacitor structure and a polyelectrolyte-gated OTFT under a negative gate voltage illustrating three different operational regimes: field-effect (Regime I) and interfacial and bulk electrochemical (Regimes II and III, respectively). The chemical structures of (B) regioregular poly(3-hexylthiophene) (P3HT), poly(3-carboxypentylthiophene) (P3CPT) and (C) poly(vinylphosphonic acid-co-acrylic acid) (P(VPA-AA)). Profiles of water droplets on (D) P3HT and (E) P3CPT surfaces with contact angle of 105° and 49°, respectively.

of 105° on a P3HT thin film whereas on a P3CPT film, water droplets show a considerably lower contact angle of 49° due to the hydrophilic carboxyl groups of P3CPT (Fig. 1 D and E). The hydrophobicity of P3HT constitutes a great problem for fabrication of top-gate/bottom-contact polyelectrolyte-gated OTFTs (Fig. 1A) where the hydrophilic polyelectrolyte film needs to be deposited from an aqueous solution on top of the hydrophobic semiconductor surface. Inkjet printing of the polyelectrolyte on top of P3HT has turned out to be very challenging, and even spin-coating of the polyelectrolyte is not straightforward. Two different approaches have been explored to reduce the water contact angle and to facilitate spin-coating of the polyelectrolyte on P3HT—namely, use of a surfactant (22) or a binary solvent mixture (13). However, the better wettability of P3CPT could solve these manufacturing challenges.

Maps of the Electrochemical Activity. Previously, impedance spectroscopy has been employed to survey polarization mechanisms of electrolytes under an electric field (23). Here our aim was to use impedance spectroscopy to map the boundary between fieldeffect and electrochemical regimes in OTFTs. For this purpose thin films of a polyelectrolyte poly(vinylphosphonic acid-coacrylic acid) (P(VPA-AA), Fig. 1C) together with either P3CPT or P3HT were sandwiched between Ti and Au electrodes to give capacitor structures (Fig. 1A), which were characterized by impedance spectroscopy. In addition to a small AC voltage ($V_{AC,rms} = 0.1$ V), we also applied a DC voltage bias ($V_{DC} = 0...$ -1.5...0 V) to the capacitors in order to explore the influence of a gate voltage, V_G , on the impedance characteristics. The phase angle plots (Θ vs. frequency, Fig. 2A) can be divided into two parts depending on the value of Θ . Capacitive behavior is predominant when $\Theta < -45^\circ$, whereas resistive behavior dominates when $\Theta > -45^{\circ}$.

When a low gate voltage was used ($|V_{\rm DC}|<0.6$ V), the capacitor structures comprising P3CPT (Fig. 24) exhibited resistive behavior at high frequencies (>30 kHz) due to dissociation and migration of protons from the polyelectrolyte chains, whereas capacitive behavior was more dominant at lower frequencies (<30 kHz), which can be attributed to the formation of electric double layers along the Ti/P(VPA-AA) and P3CPT/P(VPA-AA) interfaces (13, 23). As a comparison, the P3HT-based capacitors gave very similar results when $|V_{DC}| < 0.6$ V (see Fig. S1). However, when the DC bias was increased further ($|V_{DC}| > 0.9$ V), striking differences between P3HT and P3CPT were revealed. In P3CPT-based capacitors, the phase angle showed a significant increase that was accompanied by a simultaneous increase in the effective capacitance, suggesting a second mechanism by which the capacitor becomes more charged at low frequencies (Fig. 2). As an example, at $V_G = -1.5$ V the capacitors showed resistive behavior almost throughout the entire frequency range together with very high capacitance, thus implying that migration of ions dominate in this voltage range. We interpret these results as an indication of electrochemical doping of P3CPT, which takes place at high voltages and low frequencies. However, the symmetry in the phase angle and capacitance plots across $V_{\rm DC} = -1.5$ V suggests that the electrochemical doping processes were reversible.

Output and Transfer Characteristics. Next, top-gate/bottom-contact OTFTs were fabricated using a similar sandwiched structure as described above (Fig. 1A). Fig. 3 shows typical transfer (drain current I_D vs. gate voltage V_G) and output characteristics (I_D vs.



Fig. 2. Phase angle (A) and capacitance (B) plots as a function of frequency and applied DC bias for a capacitor structure of Au/P3CPT/P(VPA-AA)/Ti. The effective capacitance was calculated from the complex impedance by using an equivalent circuit comprising a resistor and a capacitor in parallel.



Fig. 3. Electrical characteristics of P3CPT-based OTFTs. (*A*) Transfer and (*B*) output curves under low gate voltage ($V_{G, \min} = V_{D, \min} = -0.5$ V). (*C*) transfer and (*D*) output curves under high gate voltage ($V_{G, \min} = V_{D, \min} = -1.5$ V).

drain voltage V_D) of the OTFTs comprising P3CPT and P(VPA-AA) semiconductor and polyelectrolyte layers, respectively. Current-voltage characteristics showed negligible hysteresis when the OTFTs were operated at low voltages ($|V_G| < 0.5$ V), which implies that the electric double layers were formed rapidly and which also rules out the possibility of extensive electrochemical doping of the semiconductor bulk (see Fig. 3 *A* and *B*). The field-effect mobility was calculated from a ($-I_{D,sat}$)^{1/2} vs. V_G plot by fitting a straight line for $V_G < -0.4$ V and using the following equation

$$\mu = \frac{2L}{WC_i} \left(\frac{\partial}{\partial V_G} \sqrt{-I_{D,\text{sat}}} \right)^2, \qquad [1]$$

where $C_i = 4 \ \mu\text{F/cm}^2$ (Fig. 2B) is the capacitance per unit area of the gate insulator layer, $W = 1,000 \ \mu\text{m}$ and $L = 3 \ \mu\text{m}$ the channel width and length and the last term gives the slope of the fitted line. The resulting mobility is $\mu = 2 \cdot 10^{-4} \ \text{cm}^2 \ \text{V}^{-1} \ \text{s}^{-1}$.

The situation was very different at higher gate voltages, $|V_G| > 1.0$ V (see Fig. 3 C and D). As compared to the former regime, a much higher output current, on-off ratio, and a high degree of hysteresis were observed. We will refer to these two regimes as Regime I and III (Fig. 1A) and will show further evidence that they are represented by a field-effect and an electrochemical mode of operation, respectively.

As a comparison, the electrical characteristics of the wellstudied P3HT-based OTFTs (13) showed clear current modulation and negligible hysteresis throughout the studied voltage range (see Fig. S2), supporting the earlier indications (13) that they operate mainly in the field-effect regime.

Switching Transients. The switching characteristics of a transistor can be used as a probe to determine whether the transistor operates in the field-effect or electrochemical regime. More precisely, fast switching speed (<ms) is characteristic for the former regime, whereas the switching of electrochemical transistors occurs more slowly (s) and is typically limited by the diffusion rate of ions in and out from the semiconductor film. Fig. 4 shows the source current switching characteristics of P3CPT-based OTFTs at two different gate voltage ranges when the OTFTs were switched on and off (Off \rightarrow On: $V_G = 0 \rightarrow -0.5/-1.5$ V and



Fig. 4. Switching characteristics of P3CPT-based OTFTs under (A) low gate voltage ($V_D = V_G = -0.5$ V) and (B) high gate voltage ($V_D = V_G = -1.5$ V).

On \rightarrow Off: $V_G = -0.5/ - 1.5 \rightarrow 0$ V in Fig. 4). A constant voltage and a square-wave voltage was applied to the drain and gate electrode, respectively, while the source current was monitored. A current that arises from the charging of the gate capacitor was removed from the transients by subtracting a response at $V_D = 0$ V from the response at $V_D \neq 0$ V (4). On and off switching times were defined as the time required to reach 90% and 10% of the on and off state, respectively (see Table 1).

P3CPT-based OTFTs showed fast switching characteristics at low gate voltage ($V_G = V_D = -0.5$ V, Fig. 4A), similar to the P3HT-based OTFTs (see Fig. S3), which suggests that they operate in the field-effect regime (Fig. 1A, Regime I). Surprisingly, at high gate voltage ($V_G = V_D = -1.5$ V; Fig. 4B) the source current of the P3CPT-based OTFTs first exhibited an intermediate on mode (Regime II), which was followed by a second, relatively slower rise (Regime III). Importantly, the P3CPT-based OTFTs could be continuously operated solely in Regime II without drifting to Regime III provided that the pulse length of the applied gate voltage was limited to less than 100 ms (Fig. S5). The second gradual rise (Regime III) can be attributed to electrochemical doping and charge transport in the *bulk* of P3CPT (Fig. 1A, Regime III), but further evidence is required to define the origin of the fast response (Regime II).

Current Versus Semiconducting Layer Thickness. It is generally agreed that in a field-effect transistor, the flow of charge carriers from source to drain is confined to the very first monolayers next to gate dielectric (24, 25). This gives that the output current of a field-effect transistor is more or less independent of the semiconductor layer thickness provided that the film morphology remains the same regardless of the thickness. In electrochemical transistors, on the contrary, the output current is expected to scale linearly with the active layer thickness due to that electrochemical doping and charge transport occur throughout the entire bulk of the active layer (26). Fig. 5 shows the channel current of the transistors as a function of the P3CPT film thickness. Each measurement point is an average over five different transit

Table 1. Switching times of the OTFTs

			Switching time	
Semiconductor	V _G	Regime*	on	off
P3HT	–0.5 V	I	1.9 ms	0.4 ms
P3HT	–1.5 V	1	1.7 ms	0.3 ms
P3CPT	–0.5 V	1	7.0 ms	2.4 ms
P3CPT	–1.5 V	II	9 ms	15 ms†
P3CPT	–1.5 V	111	3.4 s	0.3 s

*See Fig. 4, Fig. S3, and Fig. 1A.

¹Extracted from a switching off curve ($V_G = -1.5 \rightarrow 0$ V) after having been held at $V_G = V_D = -1.5$ V for 50 ms.



Fig. 5. Channel current as a function of P3CPT film thickness at low gate voltage (triangles) in Regime I and at high gate voltage in Regime II (circles) and in Regime III (squares). Each measurement point is an average over five different transistors, with the error bars indicating the highest and lowest measured current in the five transistors.

sistors, with the error bars indicating the highest and lowest measured current in the five transistors. The current values at low ($V_G = -0.5$ V) and high gate voltage ($V_G = -1.5$ V) were extracted from the transfer and switching characteristics, respectively. At low gate voltage ($V_G = -0.5$ V), the output current is independent of the P3CPT film thickness, suggesting that the doping and charge transport occurs exclusively at the interface of P3CPT rather than in the bulk (Fig. 1A, Regime I). At high gate voltage ($V_G = -1.5$ V), the transistors showed two different regimes, as was shown in the switching characteristics (Fig. 4B). Remarkably, the fast intermediate mode shows no current dependence on the P3CPT film thickness (Fig. 5, Regime II), which implies that the charge transport is confined to a thin layer of the semiconductor, next to the polyelectrolyte interface. Assuming surface transport, we can estimate the sheet conductance $\sigma_{\text{sheet}} = \frac{I}{V_D} \frac{L}{W} = 140 \text{ nS sq}^{-1}$, where $I = 70 \text{ }\mu\text{A}$ is the channel current (Fig. 5), $V_D = -1.5 \text{ V}$ is the drain voltage, $W = 1,000 \text{ }\mu\text{m}$, and $L = 3 \ \mu m$ the channel width and length, respectively. In the subsequent slow Regime III, the output current scales linearly with the P3CPT film thickness (Fig. 5) indicative of electrochemical bulk doping. The bulk conductivity in Regime III can be extracted from Fig. 5 by using $\sigma_{\text{bulk}} = \frac{f}{V_D} \frac{L}{Wd}$ where d is the P3CPT film thickness. This gives $\sigma_{\text{bulk}} = 0.2 \pm 0.05$ S/cm.

Operation Mechanism. Finally, we will discuss the probable operation mechanisms in each of the three observed regimes.

Regime I is characterized by negligible hysteresis (Fig. 3 A and B), fast switching speed (Fig. 4A), and thickness-independent channel current (Fig. 5). These different lines of evidence all point to purely field-induced gating (i.e., field-effect mode of operation). Here, the P(VPA-AA) polyanions alone balance the polarons in the semiconductor similar to the polyelectrolyte gated P3HT-based transistors (13).

Regime III is characterized by high current density (10^3 A/cm^2) , large hysteresis in the electrical characteristics (Fig. 3 *C* and *D*), slow switching speed (Fig. 4*B*), and a channel current linearly increasing with the semiconductor film thickness (Fig. 5). Moreover, the switching times of the P3CPT-based OTFTs increased with increasing P3CPT layer thickness (see Fig. S4). This is clear evidence that Regime III corresponds to electrochemical doping in the bulk of P3CPT and consequent 3D charge transport, with bulk conductivity of 0.2 S/cm.

Regime II is characterized by high current levels, fast switching speed (Fig. 4*B* and Fig. S5), and thickness-independent channel current (Fig. 5). Despite the fast switching speed, we deduce that electrochemical doping process governs the operation of the OTFTs in Regime II as well because of an exceptionally high

current level ($I_D > 50 \ \mu$ A). We can estimate the typical doping depth in Regime II by fitting two lines through the data points of Regime II and III in Fig. 5. It turns out that the lines cross at a film thickness of 1.5–8.4 nm, which correspond to a thickness of one to five monolayers (18). Assuming surface charge transport, we can estimate the mobility in Regime II by using $I_{\text{sat}} = \frac{W}{2L} \mu C_i$ ($V_G - V_T$)², where $I_{\text{sat}} = 70 \ \mu$ A (Fig. 5), $C_i = 70 \ \mu$ F/cm² (Fig. 2B), $V_G = -1.5 \ \text{V}$, and $V_T = 0 \ \text{V}$ is the threshold voltage. This gives $\mu = 2.7 \cdot 10^{-3} \ \text{cm}^2 \ \text{V}^{-1} \ \text{s}^{-1}$. The higher mobility in Regime II, as compared to Regime I, can be attributed to higher charge carrier density (27). In conclusion, charge carriers in Regime II are confined to a few monolayers close to the polyelectrolyte/semiconductor interface, giving rise to a high current density (10³ A/cm²).

A question arises as to the origin of the electrochemical Regimes II and III. Electrochemical doping of a semiconductor in an electrolyte-gated transistor typically involves migration of small ions from the electrolyte into the semiconductor bulk (7). In the present OTFTs, however, the anions of the P(VPA-AA) are immobile due to the covalent binding to the polymer backbone, which is expected to significantly suppress electrochemical bulk doping. Indeed, all the results presented here indicate that electrochemical bulk doping does not occur in the P3HT-based OTFTs under the studied voltage range. However, each repeat unit of the P3CPT bears an additional carboxyl side group. Impedance spectroscopy showed evidence that the protons of the carboxyl groups of P3CPT start to dissociate and migrate toward the bulk of P(VPA-AA) when the gate voltage is high enough $(|V_G| > 0.9 \text{ V})$. The remaining carboxylate anions are suggested to balance the positive polarons in the P3CPT backbone. This self-doping of the conjugated P3CPT backbone by the anionic carboxylate side groups is proposed to serve as the driving force for the electrochemical doping in Regimes II and III under high gate voltage. The protons in the first monolayers of P3CPT have only a little energy barrier to migrate to the P(VPA-AA) layer, whereas in the bulk of P3CPT, the alkyl side chains of P3CPT create a higher energy barrier to the passage of protons. Therefore, Regime II is assigned to a fast process associated with the transport of protons from a few monolayers of P3CPT to the P(VPA-AA), whereas Regime III is assigned to a slow process associated with the transport of protons in the P3CPT bulk.

What remains to be identified is the type of the process at the gate electrode/polyelectrolyte interface. There are two options (28): The electrochemical doping of P3CPT is balanced by charging of an ionic double layer at the gate electrode and/or by an electrochemical half-reaction that takes place at the gate via, e.g., reduction of protons to dihydrogen gas. We believe that the former option is more probable based on the high capacitance of the electric double layer at the gate (Fig. 2) and the reversibility in the electrical characteristics (see *Process at the Gate Electrode* in *SI Text*).

Conclusions. We have fabricated polyelectrolyte-gated organic thin-film transistors (OTFTs) comprising a semiconducting layer of carboxyl-functionalized polyalkylthiophenes, and we have shown that the OTFTs can be operated in three different regimes. At low gate bias, the OTFTs operate similar to a conventional field-effect transistor (Regime I). At high gate bias, electrochemical doping dominates, and the extent of doping can be controlled by the duration of the applied gate bias; a fast intermediate regime is characterized by charge transport through a few monolayers (Regime II) and a slow regime by 3D charge transport through the bulk of the semiconductor (Regime III). Regime II is especially interesting because of the low operating voltage, high current density (10^3 A/cm^2) , and fast switching speed (10^{-2} s). Furthermore, we have proposed a design methodology to build digital circuits comprising P3CPT-based transistors that operate only in Regime II (SI Text). These circuits can

find applications in printed electronic systems where, e.g., control of a display cell is done using OTFTs that operate in Regime II. The superior wettability of the conjugated polyelectrolyte surface toward aqueous solutions could pave the way for printing of the polyelectrolyte-gated OTFTs. Finally, the carboxyl group of the conjugated polyelectrolyte can be used to immobilize various biomolecules, which could allow construction of various biosensors where the covalent linkage between the biomolecule and the carboxyl groups of the sensor would trigger a significant change in the conductivity of the transistor (29). Finally, the results presented here provide guidelines for designing enhancementmode electrochemical transistors that not only carry high current densities but can also switch fast.

Materials and Methods

Materials. Regioregular poly(3-hexylthiophene) (P3HT) and poly(3-carboxypentylthiophene) (P3CPT) were purchased from Sigma-Aldrich and Rieke Metals Inc., respectively, and were used without further purification. Poly (vinylphosphonic acid-co-acrylic acid) (P(VPA-AA)) was obtained from Rhodia.

Device Fabrication. Top-gate/bottom-contact OTFTs were fabricated as follows. First, an adhesive 5-nm-thick chromium layer and a 50-nm-thick gold layer were thermally evaporated onto borosilicate glass substrates. Standard photolithography and wet-etching were used to pattern interdigitated source and drain electrodes onto the glass substrates. P3CPT and P3HT were dissolved in analytical grade dimethyl sulfoxide (5-20 mg/mL) and 1,2-dichlorobenzene (10 mg/mL), respectively, sonicated at 60 °C for 10 min and finally passed through 0.2 μm Nylon and PTFE filters, respectively. The warm solutions (60 °C) were spin coated on preheated substrates (105-110 °C), and the resulting semiconductor thin films were dried in a vacuum oven at 110 °C for 2 min. The thickness of the P3CPT film (12 to 63 nm) was controlled by varying the concentration of P3CPT in dimethyl sulfoxide (5 and 20 mg/mL) and the spin-coating speed (1,500 to 4,000 rpm). The thickness of the semiconductor film was 30 nm if not otherwise stated. P(VPA-AA) polyelectrolyte was dissolved (20 mg/mL) in a mixture of 1-propanol and deionized water (4:1 vol:vol), passed through a 0.2 µm Nylon filter, spin coated onto the semiconductor film at 3,000 rpm for 60 s, and finally dried in a vacuum oven at 110 °C for 2 min. Typical film thickness of the polyelectrolyte was 53–57 nm. Devices were completed by thermally evaporating Ti gate electrodes through

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a nickel shadow mask. All the transistors had the same channel length (L = 3 $\mu m)$ and width (W = 1,000 $\mu m).$

Characterization. Contact angle measurements were carried out on a CAM 200 contact angle meter (KSV Instruments), and the photographs of the water droplets (7 μ L) were analyzed by Attension Theta software (Biolin Scientific). Film thicknesses were measured by using an ellipsometer (Sentech SE400) and a surface profilometer (Veeco, Dektak 3 ST). The impedance data were collected with an alpha high-resolution dielectric analyzer (Novocontrol GmbH) by scanning from 1 MHz to 0.1 Hz while applying an rms amplitude of 0.1 V and a constant DC voltage to a Ti-electrolyte-semiconductor-Au capacitor (100 $\mu\text{m}\,{\times}\,100$ $\mu\text{m}).$ Output and transfer characteristics were measured with a Keithley semiconductor characterization system (4200-SCS) at a scan rate of 0.2 V/s. The switching transients were obtained with an oscilloscope (Agilent 54832D Infiniium) by measuring a voltage drop across a resistor connecting the source electrode to ground while applying a square-wave voltage to the gate electrode (Agilent 33120A waveform generator) and a DC voltage to the drain electrode (Agilent E3631A power supply). A parasitic current that arises from charging of the gate capacitor was removed from the transients by subtracting a response measured at $V_D = 0$ V from the response measured at $V_D \neq 0$ V (4). Current versus film thickness measurements were carried out on the same systems as the switching transients and the output/transfer characteristics. The current values at low gate voltage (at $V_G = V_D = -0.5$ V) were extracted from the transfer characteristics, whereas at higher gate voltage ($V_G = V_D = -1.5$), the transistors were biased until the saturation of the drain current. In both cases, the off current (at $V_G = 0$ V and $V_D = -0.5$ or -1.5 V) was subtracted from the on current to eliminate effects arising from a leakage current between source and drain. All measurements were carried out in ambient conditions at room temperature (40% relative humidity).

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