# Fluoroalkylphosphonic acid self-assembled monolayer gate dielectrics for threshold-voltage control in low-voltage organic thin-film transistors†

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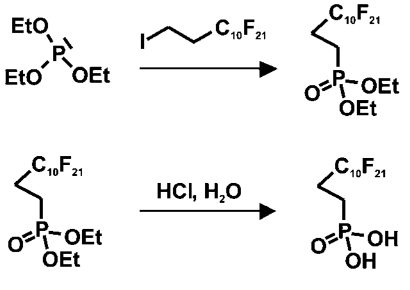
**An important prerequisite for the design of digital integrated circuits is the ability to control the threshold voltage of the individual transistors during manufacturing. To address the problem of controlling the threshold voltage of low-voltage organic transistors we have synthesized a fluoroalkylphosphonic acid that forms self-assembled monolayers on patterned, plasma-oxidized aluminum gate electrodes for use as high-capacitance, low-temperature gate dielectrics in p-channel and n-channel organic transistors. Compared with alkyl phosphonic acid-based monolayers, the strong electron-withdrawing character of the fluoroalkyl monolayers causes a change in the threshold voltage of the transistors by about 1 V, *i.e.* almost half of the supply voltage.**

Many prospective applications of organic thin-film transistors (TFTs) benefit from gate dielectrics that can be processed at low temperature (and thus permit TFT fabrication on flexible polymeric substrates) and provide a large dielectric capacitance per unit area (so that the TFTs can be operated with low voltages). Several approaches to high-capacitance gate dielectrics for organic TFTs have been developed, including ultra-thin polymers,[1–5] vapor-deposited metal oxides,[6–10] self-assembled nanodielectrics,[11–15] electrolytes and ion gels,[16–20] and hybrid dielectrics based on alkylphosphonic acid self-assembled monolayers (SAMs) on plasma-oxidized aluminium gate electrodes.[21–24] For none of these approaches, however, the deterministic control of the threshold voltage of the TFTs during manufacturing has been demonstrated. Threshold-voltage control is a prerequisite for the design of robust and low-power digital circuits.[25] In single-crystalline silicon metal-oxide-semiconductor field-effect transistors (MOSFETs), the threshold voltage is controlled by incorporating small amounts of either electron-donating or electron-accepting impurity atoms (*e.g.*, phosphorus or boron) into the silicon lattice in the channel region of the transistors. In organic TFTs, stable and controlled impurity doping is far more difficult, since the intermolecular interactions in organic semiconductors are due to relatively weak non-covalent forces, rather than strong covalent bonds.

In 2004, Kobayashi *et al.* and Pernstich *et al.* demonstrated that the threshold voltage of organic TFTs fabricated on silicon dioxide gate dielectrics can be controlled by functionalizing the surface of the $SiO_2$ gate dielectric with a silane-based SAM having electron-donating or electron-withdrawing substituents.[26,27] In these experiments, a single-crystalline silicon wafer was employed as the substrate and also served as the gate electrode for all the TFTs on the substrate. The $SiO_2$ gate dielectric was produced by oxidizing the silicon surface at a temperature of about 900 °C, which is incompatible with flexible polymeric substrates. Also, the $SiO_2$ gate dielectrics employed by Kobayashi *et al.* and Pernstich *et al.* were several hundred nanometres thick, so the TFTs required operating voltages of 50 to 100 V.

Here we report on the synthesis of a fluoroalkylphosphonic acid that forms high-quality SAMs on patterned, plasma-oxidized aluminium gate electrodes and thus affords a high-capacitance, low-temperature gate dielectric with strong electron-withdrawing character for the reproducible adjustment of the threshold voltage in organic TFTs that have individual gate electrodes, can be fabricated on flexible polymeric substrates, and can be operated with low voltages (3 V).

The fluoroalkylphosphonic acid was synthesized in a two-step reaction (see Scheme 1). In the first step, the corresponding fluoroalkyl diethyl ester was obtained by a Michaelis–Arbuzov reaction of 1-iodo-1*H*,1*H*,2*H*,2*H*-perfluorododecane and triethylphosphite,[28] purchased commercially and reacted at 150 °C for 1 d. The main byproduct, ethyl iodide, was distilled off continuously during the reaction in order to avoid side reactions, and excessive triethylphosphite was then eliminated by vacuum distillation. In the second step, the diethyl fluoroalkyl phosphonate was hydrolyzed in hydrochloric acid, yielding 1*H*,1*H*,2*H*,2*H*-perfluorododecylphosphonic acid ($FC_{12}$-PA). The product was purified by recrystallization from methanol and characterized by mass spectrometry, infrared spectroscopy, and $^1$H-NMR (see ESI†).



**Scheme 1** Synthesis of 1*H*,1*H*,2*H*,2*H*-perfluorododecylphosphonic acid ($FC_{12}$-PA) for self-assembled monolayer (SAM) gate dielectrics.

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† Electronic supplementary information (ESI) available: Synthesis and spectroscopic characterization of $FC_{12}$-PA, contact angle analysis, TFT structure, detailed electrical characterization of organic TFTs, atomic force microscopy (AFM) images of organic semiconductor films, and summary of physical and electrical properties of the self-assembled monolayers. See DOI: 10.1039/c0jm01292k

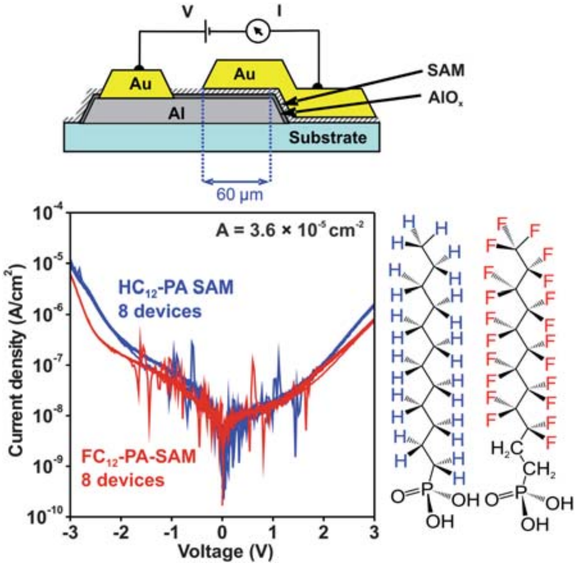

**Fig. 1** Leakage current density through AlO$_x$/SAM gate dielectrics based on SAMs of dodecylphosphonic acid (HC$_{12}$-PA) and 1*H*,1*H*,2*H*,2*H*-perfluorododecylphosphonic acid (FC$_{12}$-PA), measured on metal/insulator/metal (Al/AlO$_x$/SAM/Au) structures with an area of $3.6 \times 10^{-5}$ cm$^2$.

The organic TFTs were fabricated using the inverted staggered (bottom-gate, top-contact) device structure. 30 nm thick aluminium gate electrodes were deposited by thermal evaporation through a shadow mask, followed by a brief oxygen plasma treatment to create a 3.6 nm thick AlO$_x$ layer.[21] The substrate was then immersed in a 2 mM solution of the phosphonic acid in 2-propanol for about 1 h, then rinsed with pure 2-propanol and briefly baked on a hotplate to stabilize the monolayer.[29] Static contact angles measured on the FC$_{12}$-PA SAMs are 121°, confirming the formation of a densely packed monolayer. For comparison, static contact angles on SAMs of dodecylphosphonic acid (HC$_{12}$-PA, purchased from PCI Synthesis, Newburyport, USA) are 110°. The AlO$_x$/SAM gate dielectrics have a thickness of 5.1 nm and a dielectric capacitance per unit area of 650 to 850 nF cm$^{-2}$. Pentacene (for the p-channel TFTs) or hexadecafluorocopperphthalocyanine (F$_{16}$CuPc, for the n-channel TFTs) was then deposited through a shadow mask by sublimation in vacuum, providing a 30 nm thick semiconductor layer on the AlO$_x$/SAM gate dielectric surface. TFTs were completed by evaporating gold source and drain contacts through a shadow mask. All electrical measurements were carried out at room temperature in ambient air.

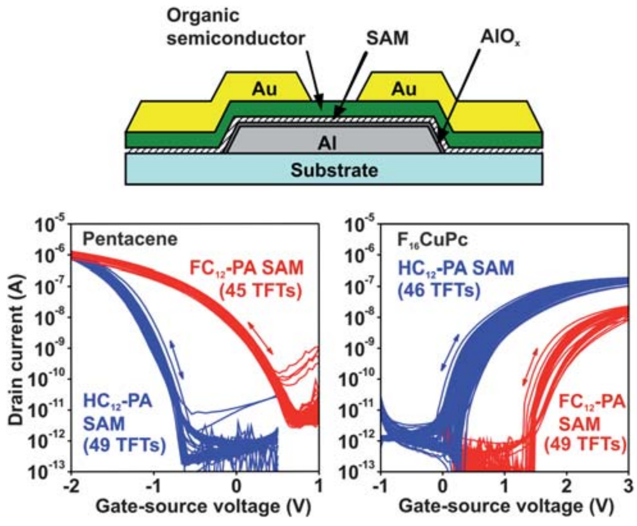

**Fig. 2** Electrical transfer characteristics of organic p-channel TFTs (left graph) and organic n-channel TFTs (right graph) with gate dielectrics based on SAMs of dodecylphosphonic acid (HC$_{12}$-PA) and 1*H*,1*H*,2*H*,2*H*-perfluorododecylphosphonic acid (FC$_{12}$-PA).

The leakage current density through the FC$_{12}$-PA SAM-based dielectric, measured on metal/insulator/metal (Al/AlO$_x$/SAM/Au) structures with an area of $3.6 \times 10^{-5}$ cm$^2$, is about 5 µA cm$^{-2}$ at an applied voltage of 3 V (which corresponds to an electric field of about 6 MV cm$^{-1}$). This is about a factor of two smaller than the leakage current through the HC$_{12}$-PA SAM-based dielectric (see Fig. 1), which further confirms the high quality of the fluoroalkyl SAM.

Fig. 2 shows the transfer characteristics of pentacene p-channel and F$_{16}$CuPc n-channel TFTs with HC$_{12}$-PA and FC$_{12}$-PA SAM-based gate dielectrics. Owing to the large capacitance of the thin dielectrics, the TFTs operate with low voltages of 2 to 3 V. For both semiconductors, the TFTs with the FC$_{12}$-PA SAM have a threshold voltage that is 1.0 to 1.2 V more positive than the threshold voltage of the TFTs with the HC$_{12}$-PA SAM. This means that replacing the H-terminated SAM with an F-terminated SAM provides a change in threshold voltage by almost half the supply voltage of the TFTs. A detailed statistical analysis of more than 40 pentacene p-channel TFTs and more than 40 F$_{16}$CuPc n-channel TFTs with HC$_{12}$-PA SAM and with FC$_{12}$-PA SAM gate dielectrics is provided in the ESI†.

The pentacene p-channel TFTs have hole mobilities of 1 cm$^2$ V$^{-1}$ s$^{-1}$ when using the HC$_{12}$-PA SAM and 0.2 cm$^2$ V$^{-1}$ s$^{-1}$ when using the FC$_{12}$-PA SAM. These mobilities are similar to those reported by Pernstich *et al.* for pentacene TFTs with SiO$_2$ gate dielectrics functionalized with octadecyltrichlorosilane (1 cm$^2$ V$^{-1}$ s$^{-1}$) and perfluorooctyltrichlorosilane (0.15 cm$^2$ V$^{-1}$ s$^{-1}$).[27] On the other hand, Kobayashi *et al.* reported hole mobilities of 0.15 cm$^2$ V$^{-1}$ s$^{-1}$ and 0.2 cm$^2$ V$^{-1}$ s$^{-1}$ for pentacene TFTs with SiO$_2$ gate dielectrics functionalized with octyltrichlorosilane and perfluorodecyltrichlorosilane,[26] indicating that there is no simple relationship between SAM termination and hole mobility. Our F$_{16}$CuPc n-channel TFTs have electron mobilities of 0.03 cm$^2$ V$^{-1}$ s$^{-1}$ when using the HC$_{12}$-PA SAM and 0.006 cm$^2$ V$^{-1}$ s$^{-1}$ when using the FC$_{12}$-PA SAM, similar to the electron mobilities reported by Kobayashi *et al.* for C$_{60}$ n-channel TFTs with SiO$_2$ functionalized with octyltrichlorosilane (0.07 cm$^2$ V$^{-1}$ s$^{-1}$) and perfluorodecyltrichlorosilane (0.005 cm$^2$ V$^{-1}$ s$^{-1}$).[26]

In summary, we have synthesized a fluoroalkylphosphonic acid and prepared high-quality self-assembled monolayers on patterned, plasma-oxidized aluminium gate electrodes for use as high-capacitance, low-temperature gate dielectrics in low-voltage organic p-channel and n-channel thin-film transistors. The strong electron-withdrawing character of the fluoroalkyl SAM causes a change in threshold voltage by about 1 V, *i.e.* almost half of the transistors' supply voltage. These monolayers therefore provide a powerful method to reproducibly control the threshold voltage of low-voltage organic TFTs.

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*SUPPLEMENTARY INFORMATION*

# Fluoroalkylphosphonic acid self-assembled monolayer gate dielectrics for threshold-voltage control in low-voltage organic thin-film transistors

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## Diethyl 1H,1H,2H,2H-perfluorododecylphosphonate

3.0 g (3.7 mmol) of 1-iodo-1H,1H,2H,2H-perfluorododecane were suspended in 10 ml (57.4 mmol) triethylphosphite. The mixture was stirred for 40 h at 150°C while ethyl iodide was distilled off continuously during the reaction. Then the excessive triethylphosphite was eliminated by vacuum distillation to give a white waxlike solid (2.1 g, 69 %)
$^1$**H-NMR** (300 MHz, $CD_3OD$, ppm): $\delta = 4.0 - 4{,}1$ (m, 4H, $\mathbf{CH_2}CH_3$) ; 2.2 - 2.4 (m, 2 H, $C_2F_2\mathbf{CH_2}$); 1,8 - 1,9 (m, 2 H, $C\mathbf{H_2}P$); 1,3 (t, 6 H, $CH_2C\mathbf{H_3}$)**; MS** (LD-TOF MS) calculated for $[F_{21}C_{12}PO_3H_4(C_2H_5)]^-$ 655.00, found 655.02

## 1H,1H,2H,2H-perfluorododecylphosphonic acid

2.0 g (0.92 mmol) of diethyl 1H,1H,2H,2H-perfluorododecylphosphonate were suspended in 20 ml hydrochloric acid (37%) and stirred over night under reflux at 100°C. After cooling to room temperature the volatile components were eliminated by rotary evaporation and the product was purified by recrystallization from methanol yielding 1H,1H,2H,2H-perfluorododecylphosphonic acid as a white solid (0.85 g, .Yield: 49 %)
$^1$**H-NMR** (300 MHz, $CD_3OD$, ppm): $\delta = 2.3\text{-}2.6$ (m, 2H, $C_2F_2\mathbf{CH_2}$); 1.8-2.0 (m, 2H, $C\mathbf{H_2}P$); **IR** (KBr, $cm^{-1}$): 2323, 1210, 1151, 1013, 955, 901, 818, 665, 647, 558; **MS** (LD-TOF MS) calculated for $[F_{21}C_{12}PO_3H_5]^-$ 626.96, found 626.98.

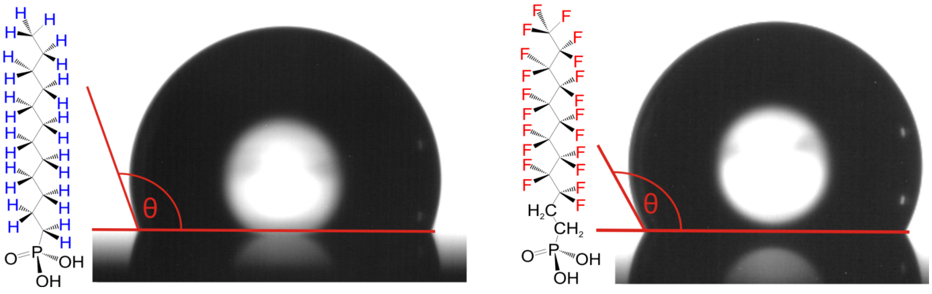

**Figure S1:** Static water contact angles on self-assembled monolayers (SAMs) of dodecylphosphonic acid ($HC_{12}$-PA; left; 110°) and 1H,1H,2H,2H-perfluorododecylphosphonic acid ($FC_{12}$-PA; right; 121°) on plasma-oxidized aluminum oxide.

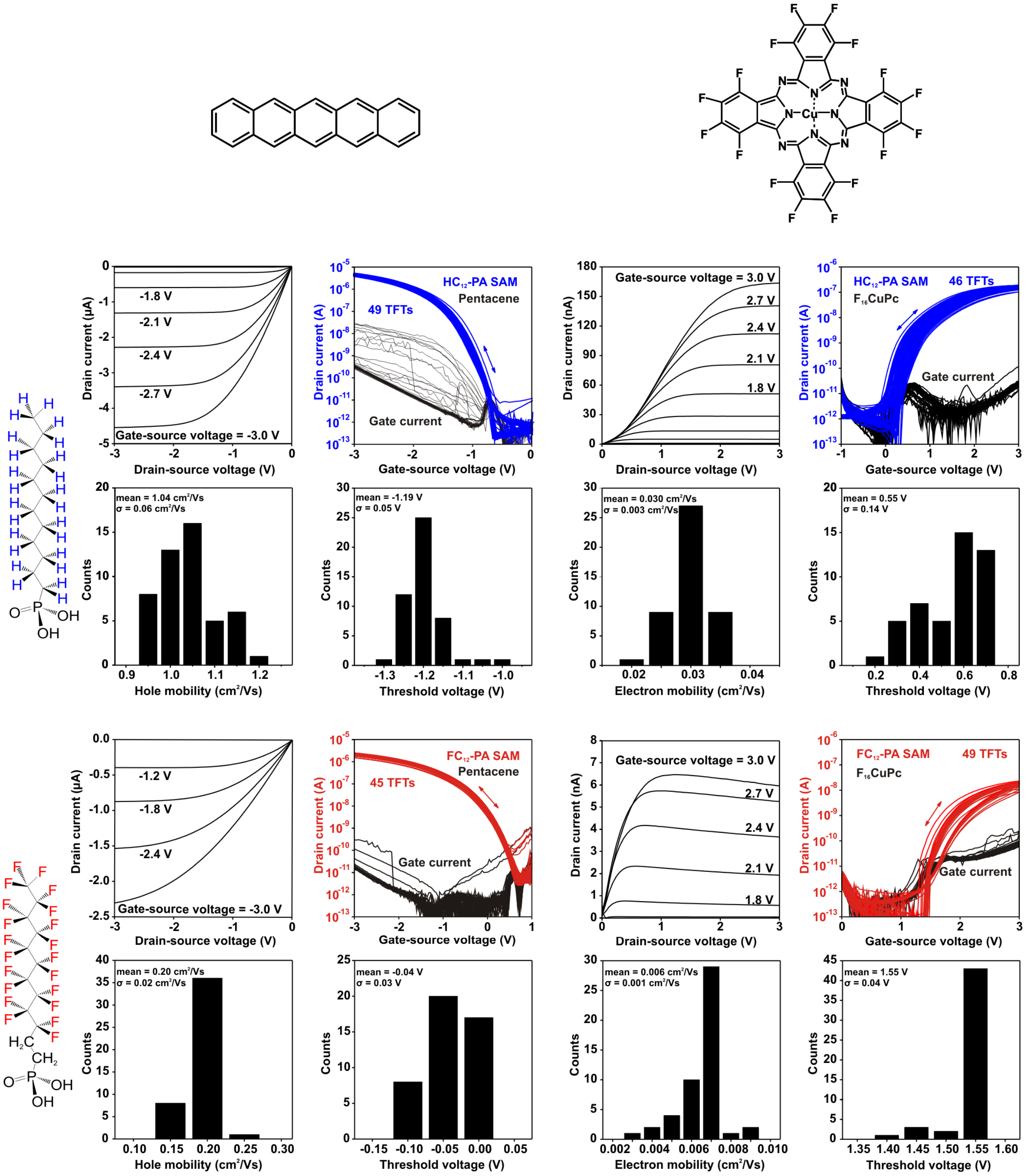

**Figure S2:** Electrical characteristics of pentacene p-channel transistors (left graphs) and $F_{16}CuPc$ n-channel transistors (right graphs) with gate dielectrics based on SAMs of dodecylphosphonic acid ($HC_{12}$-PA; blue) and 1H,1H,2H,2H-perfluorododecylphosphonic acid ($FC_{12}$-PA; red). All TFTs have a channel length of 30 µm and a channel width of 100 µm.

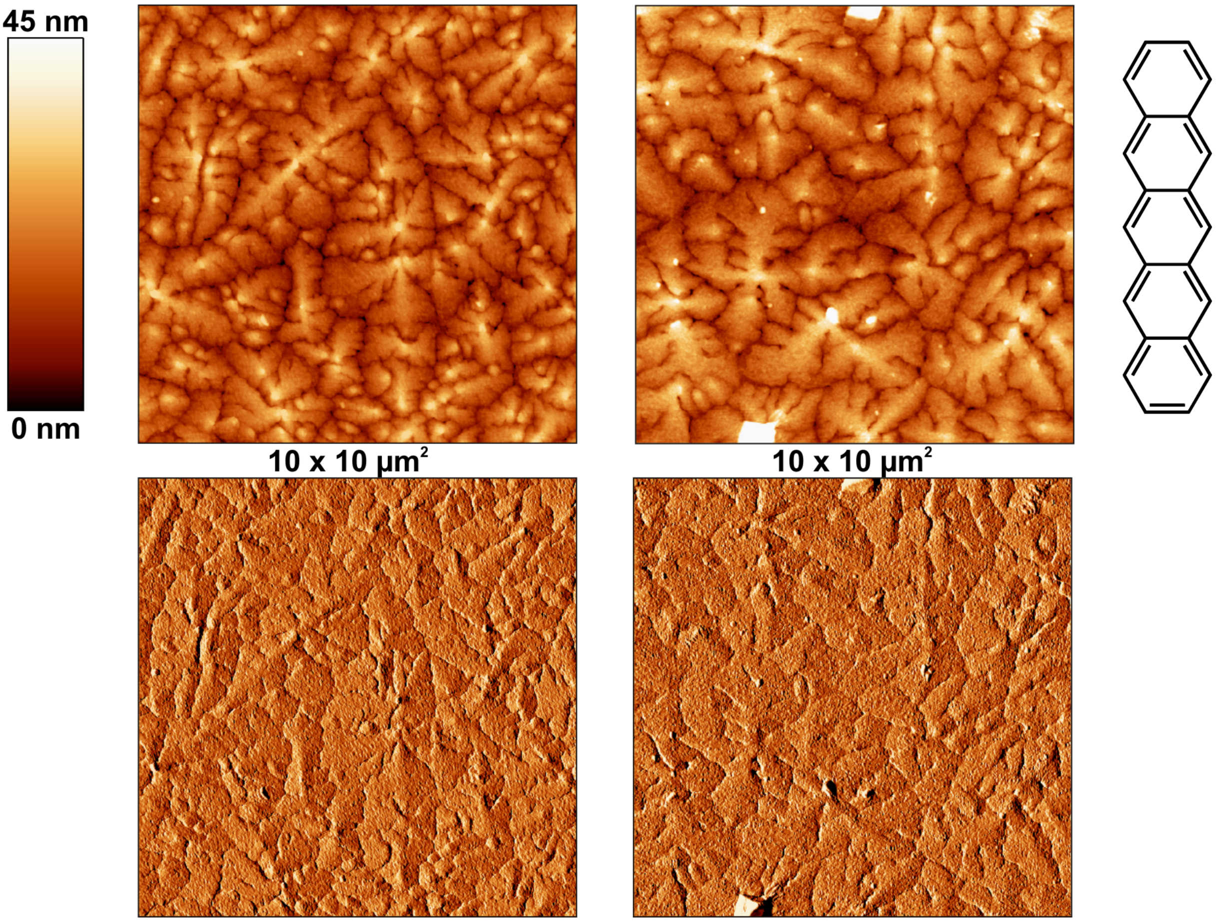

**Figure S3:** Atomic force microscopy (AFM) images (top: topography; bottom: amplitude) of 30 nm thick pentacene films deposited onto gate dielectrics based on SAMs of dodecylphosphonic acid ($HC_{12}$-PA; left) and 1H,1H,2H,2H-perfluorododecylphosphonic acid ($FC_{12}$-PA; right).

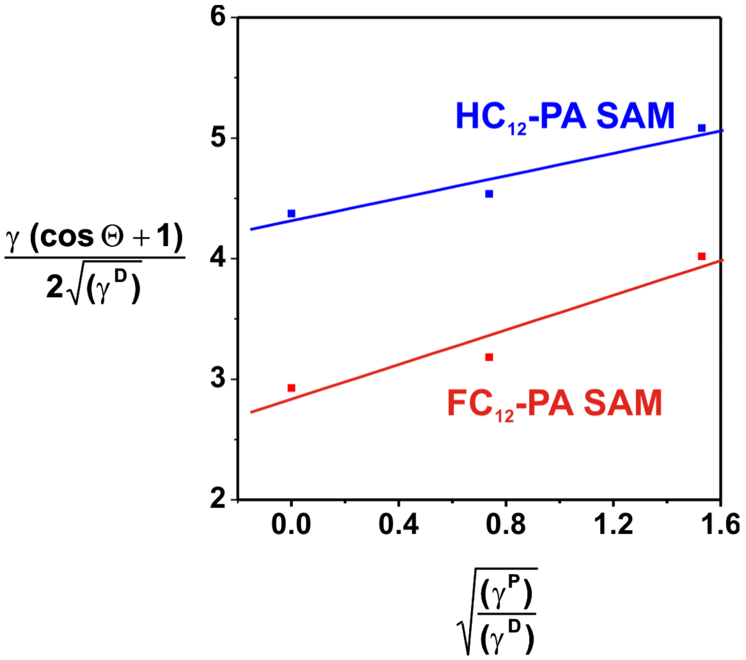

**Figure S4:** Owens-Wendth plot for SAMs of dodecylphosphonic acid ($HC_{12}$-PA; blue) and 1H,1H,2H,2H-perfluorododecylphosphonic acid ($FC_{12}$-PA; red). The data were obtained from contact-angle measurements performed with deionized water (data points on the right; $\gamma^D = 21.8$ mN/m, $\gamma^P = 51$ mN/m), with ethylene glycole (data points in the center; $\gamma^D = 30.9$ mN/m, $\gamma^P = 16.8$ mN/m) with diiodomethane (data points on the left; $\gamma^D = 50.8$ mN/m, $\gamma^P = 0$ mN/m). The linear fits produce the following results for the polar and dispersive components of the surface energy of the SAMs:

$HC_{12}$-PA SAM: $\gamma^D = 18.8$ mN/m, $\gamma^P = 0.2$ mN/m;

$FC_{12}$-PA SAM: $\gamma^D = 8.5$ mN/m, $\gamma^P = 0.5$ mN/m.

**Table S1:** Summary of the physical and electrical properties of SAMs of dodecylphosphonic acid ($HC_{12}$-PA) and 1H,1H,2H,2H-perfluorododecylphosphonic acid ($FC_{12}$-PA).

| | **$HC_{12}$-PA SAM** | **$FC_{12}$-PA SAM** |
|---|---|---|
| **molecular structure** | $CH_3(CH_2)_{11}PO(OH)_2$ | $CF_3(CF_2)_9(CH_2)_2PO(OH)_2$ |
| **SAM thickness** | 5.1 nm | 5.1 nm |
| **static water contact angle** | 110° | 121° |
| **surface energy** | 19 mN/m | 9 mN/m |
| **capacitance** | ~750 ± 100 nF/cm$^2$ | ~750 ± 100 nF/cm$^2$ |
| **leakage current density (@3 V)** | ~10 µA/cm$^2$ | ~5 µA/cm$^2$ |
| **threshold voltage of pentacene TFTs** | -1.19 V ± 0.05 V | 0.55 V ± 0.14 V |
| **threshold voltage of $F_{16}$CuPc TFTs** | -0.04 V ± 0.03 V | 1.55 V ± 0.04 V |