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): δ = 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): δ = 2.3-2.6 (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.

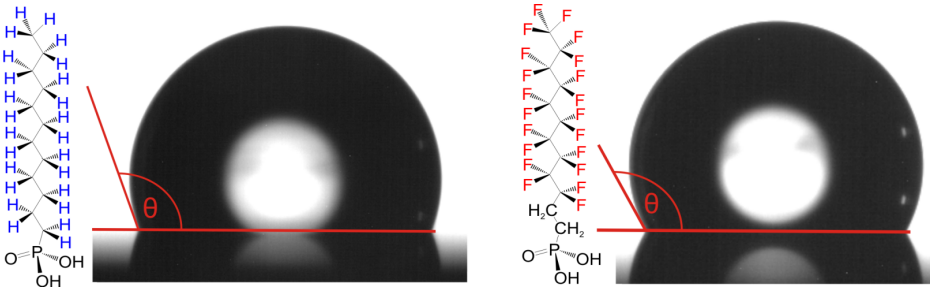

Figure S1: Static water contact angles on self-assembled monolayers (SAMs) of dodecylphosphonic acid (HC_{12}-PA; left; 110°) and 1H,1H,2H,2H-perfluorododecylphosphonic acid (FC_{12}-PA; right; 121°) on plasma-oxidized aluminum oxide.

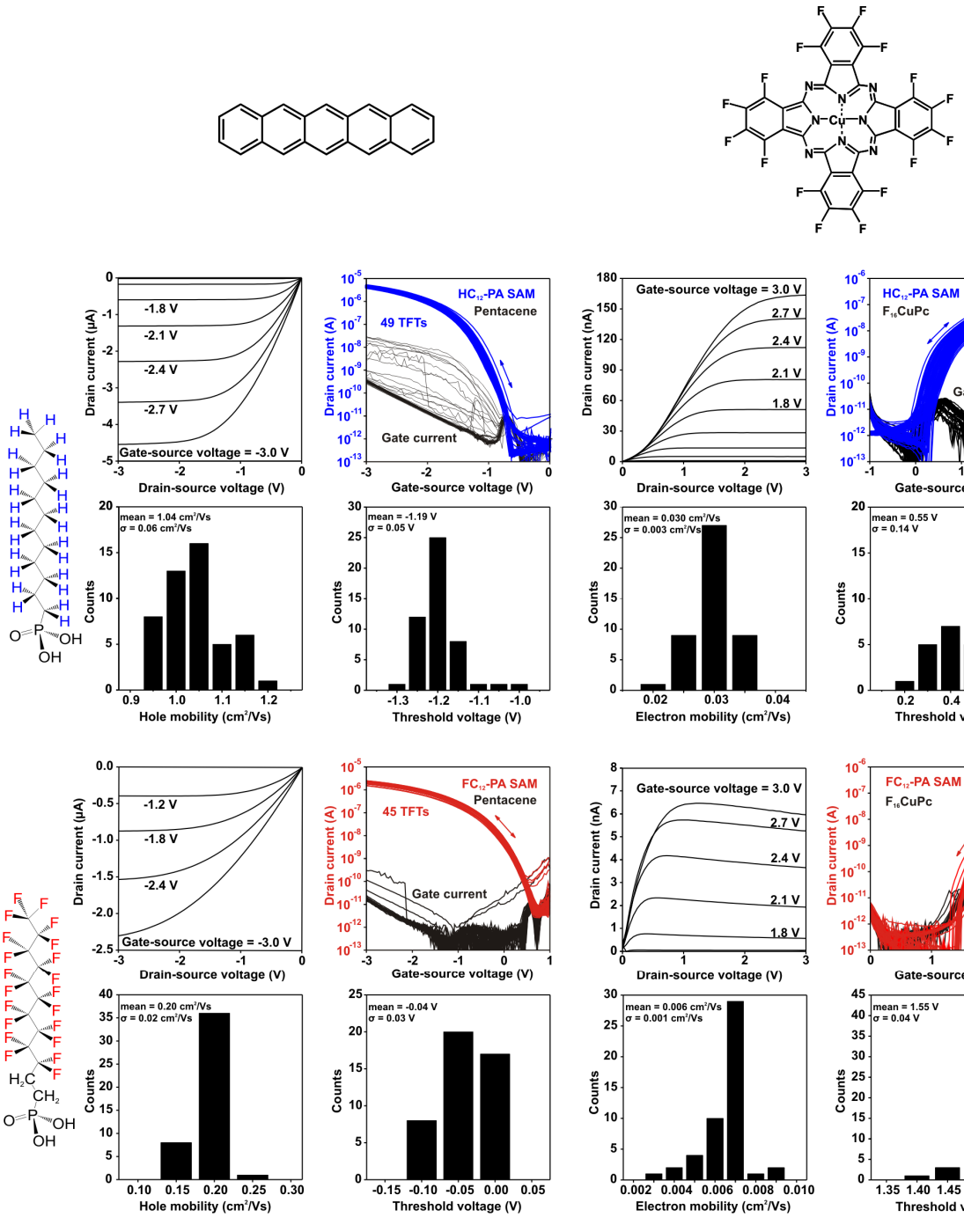

Figure S2: Electrical characteristics of pentacene p-channel transistors (left graphs) and $F_{16}CuPc$ n-channel transistors (right graphs) with gate dielectrics based on SAMs of dodecylphosphonic acid (HC_{12}-PA; blue) and 1H,1H,2H,2H-perfluorododecylphosphonic acid (FC_{12}-PA; red). All TFTs have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

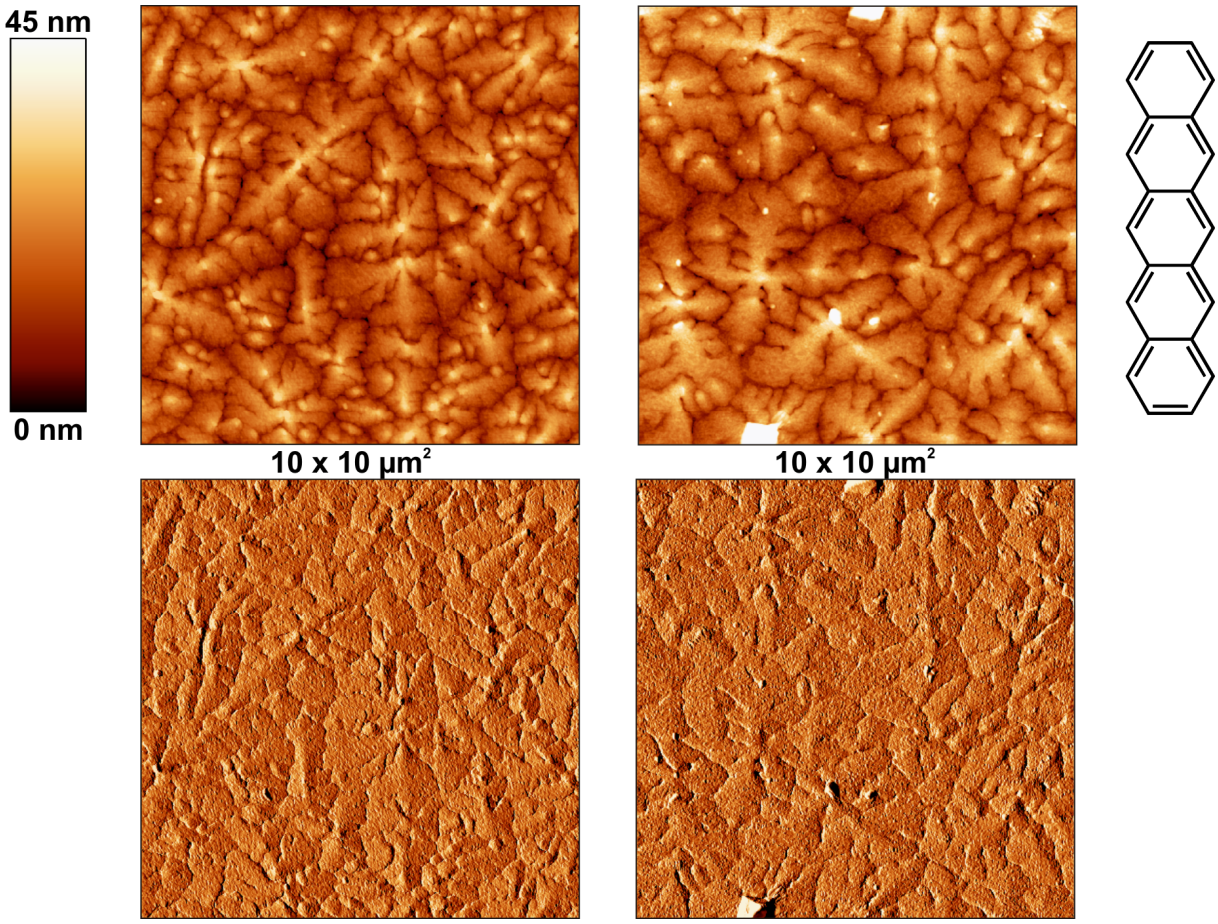

Figure S3: Atomic force microscopy (AFM) images (top: topography; bottom: amplitude) of 30 nm thick pentacene films deposited onto gate dielectrics based on SAMs of dodecylphosphonic acid (HC_{12}-PA; left) and 1H,1H,2H,2H-perfluorododecylphosphonic acid (FC_{12}-PA; right).

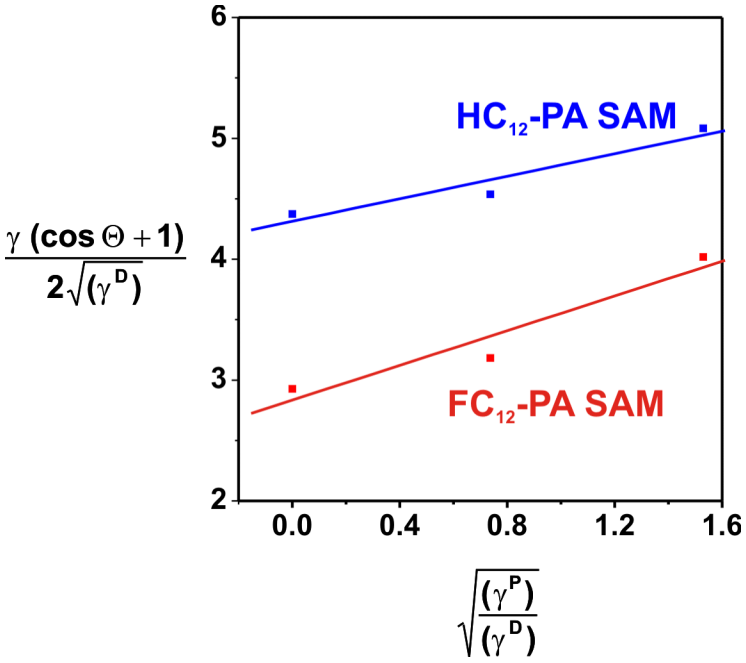

Figure S4: Owens-Wendth plot for SAMs of dodecylphosphonic acid (HC_{12}-PA; blue) and 1H,1H,2H,2H-perfluorododecylphosphonic acid (FC_{12}-PA; red). The data were obtained from contact-angle measurements performed with deionized water (data points on the right; γ^D = 21.8 mN/m, γ^P = 51 mN/m), with ethylene glycole (data points in the center; γ^D = 30.9 mN/m, γ^P = 16.8 mN/m) with diiodomethane (data points on the left; γ^D = 50.8 mN/m, γ^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: γ^D = 18.8 mN/m, γ^P = 0.2 mN/m;
FC_{12}-PA SAM: γ^D = 8.5 mN/m, γ^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