Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C

Supporting Information

For *"Growth of Rylene Diimide Crystalline Layers on Aminoalkyltriethoxysilane-Monolayers for Organic Field Effect Transistor Applications"*

Table S1: Averaged contact angles of modified wafers

Material	Si (ozone cleaned)	OTS	APTES	AUDTES
Contact Angle [°]	~ 0	111 ± 1	62 ± 3	69 ± 10

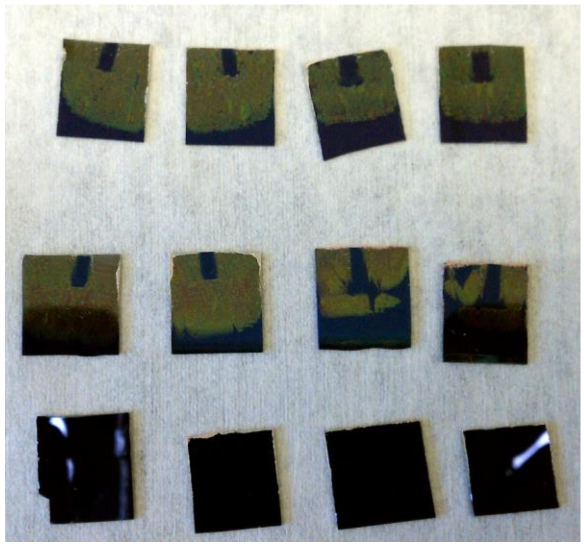

Figure S1: NDI-crystal layers grown on differently modified substrates. Top row: APTES modification, center: AUDTES modification, bottom: OTS modification – no crystal can adhere. The missing part in the top part of each crystal layer is inflicted by the tweezers holding the substrate.

Crystal Growth

*Growth of NDI **1** films on aminoalkyl triethoxysilane modified substrates:*

A monolayer-modified substrate is fixed on clean tweezers and centered in a 20 mL glass vial so that it does not touch the bottom or sides of the vial. The tweezers are fixed on a support structure. It is made sure, that the substrate surface is positioned perpendicular to the ground. A 0.3 mg/ml solution of NDI **1** in DCM is prepared and filtered through a 0.2 µm syringe filter. The vial, with the substrate in it, is filled with the solution so that the meniscus lies slightly higher than the highest part of the sample. While the solution is allowed to evaporate overnight, an oriented crystal film is grown on the surface of aminoalkyl triethoxysilane modified surfaces.

*Growth of PDI **2** films on aminoalkyl triethoxysilane modified substrates:*

A monolayer-modified substrate is fixed on clean tweezers and centered in a 20 mL glass vial so that it does not touch the bottom or sides of the vial. The tweezers are fixed on a support structure. It is made sure, that the substrate surface is positioned perpendicular to the ground. A 0.3 mg/mL solution of PDI **2** in a 2:2:1 mixture of chlorobenzene/1,2-dichloroethane/DCM is prepared at 50 ℃ and filtered through a 0.2 μm syringe filter. The vial, with the substrate in it, is positioned on a heating plate to keep the temperature at 50 ℃ and filled with the warmed solution so that the meniscus lies slightly higher than the highest part of the sample. While the solution is allowed to evaporate for several hours, an oriented film of single crystalline PDI-needles is grown on the surface of aminoalkyl triethoxysilane modified surfaces.

Table S2 and Figure S2 show morphological details of the films measured by a surface profiler. The surface was profiled at 5 positions that are evenly spaced in the 1 to 9 mm distance from the top edge of the grown NDI crystal layers on both APTES and AUDTES. The displayed thicknesses were averaged over a distance of 500 μm. The average as well as the root mean square (rms) roughness was calculated for each position in profiles parallel and perpendicular to the evaporation direction. A decrease in film thickness can be observed while moving along the substrate. The roughness of profiles parallel to the evaporation / crystal growth direction significantly decreases upon the first 3 mm of the film, while the roughness perpendicular to the film is evenly distributed over the whole substrate.

APTES	average thickness [nm]	average roughness [nm]		rms*** roughness [nm]	
position* [mm]		parallel**	perpendicular**	parallel	perpendicular
1	197.5	60.5	6.5	71.40	7.90
3	142.7	10.6	6.03	15.4	6.95
5	107.0	4.19	7.05	5.64	8.66
7	94.0	6.67	6.07	8.13	7.42
9	92.8	6.69	7.93	8.53	10.51
AUDTES	**average thickness [nm]**	**average roughness [nm]**		**rms roughness [nm]**	
position [mm]		**parallel**	**perpendicular**	**parallel**	**perpendicular**
1	133.1	33.1	7.64	37.5	9.82
3	104.7	10.9	6.72	13.60	8.14
5	93.9	8.79	7.63	10.30	9.10
7	78.7	9.15	6.13	11.71	8.37
9	70.9	9.06	7.28	12.30	9.01

* position from the starting point of the crystallization
** parallel and perpendicular towards the growing / evaporation-direction
*** root mean square

Drop cast control samples showed an average film thickness of 260.1 nm (APTES) and 242.3 nm (AUDTES) with corresponding average roughness of 128.8 nm (APTES) and 153.9 nm (AUDTES) and rms roughness of 177.7 nm (APTES) and 207.9 nm (AUDTES).

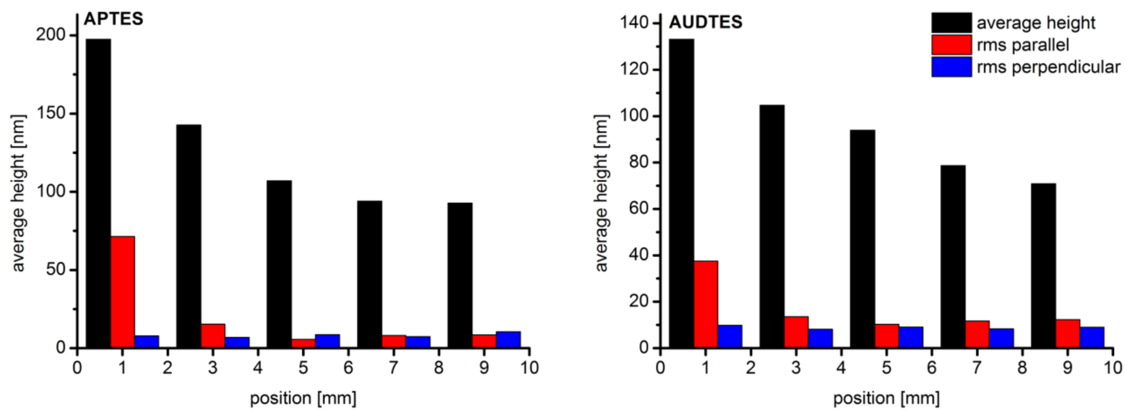

Figure S2: Film thickness and root mean square roughness of NDI films on APTES (left) and AUDTES (right) depending on their position on the film.

Methodology for Estimation of Surface Coverage of PDI-films

To estimate the fraction of surface covered by PDI-needles, images from the PDI-transistors taken with cross polarizers were converted into grey scale images. This converts all color channels to just one, representing the sum of all intensities. Under cross-polarizers, only crystals are colored, the background is ideally dark. “Black” is represented with an intensity value of “0”. To consider noise, a threshold of 16 was defined (all values below or equal 16 were defined as “black” and set to “0”). All values above this threshold were set to 255, “white”. Using this function, the number of “white” pixels divided by the number of pixels in the image represents the surface coverage of PDI needles on the substrate. It can be considered a maximum value, as the needles may not touch the surface on their full diameter as seen on the micrographs. Using this method, coverage of the channels of the fully functional PDI-transistors were calculated. They varied between 26 and 62 percent of surface coverage, with an average coverage of 45 percent.

Device Fabrication and Analysis. The OSC coated samples are placed in an inverted mask with the transistor-pattern so that the coated side faces down. The mask with the samples is placed in the respective holder in the thermal evaporator and 500 Å of gold are evaporated onto the crystal layers. The substrates were transferred in a probe station and transfer and output curves were measured at 10^{-3} Torr.

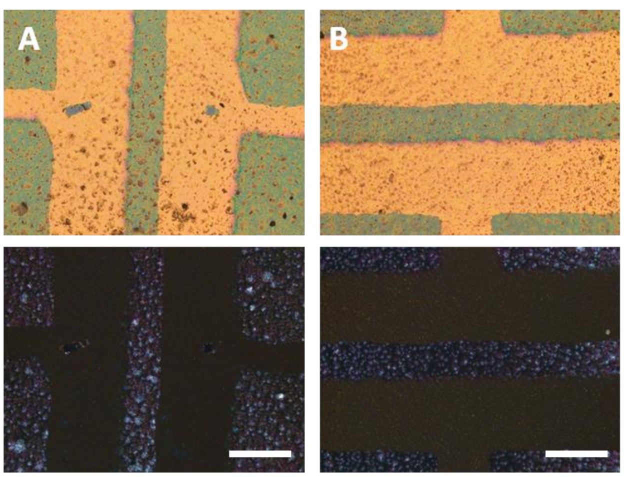

Figure S3: True color (top row) and cross polarized (bottom row) images showing the morphology of drop cast NDI films on APTES **(A)** and AUDTES **(B)** in OFETs.

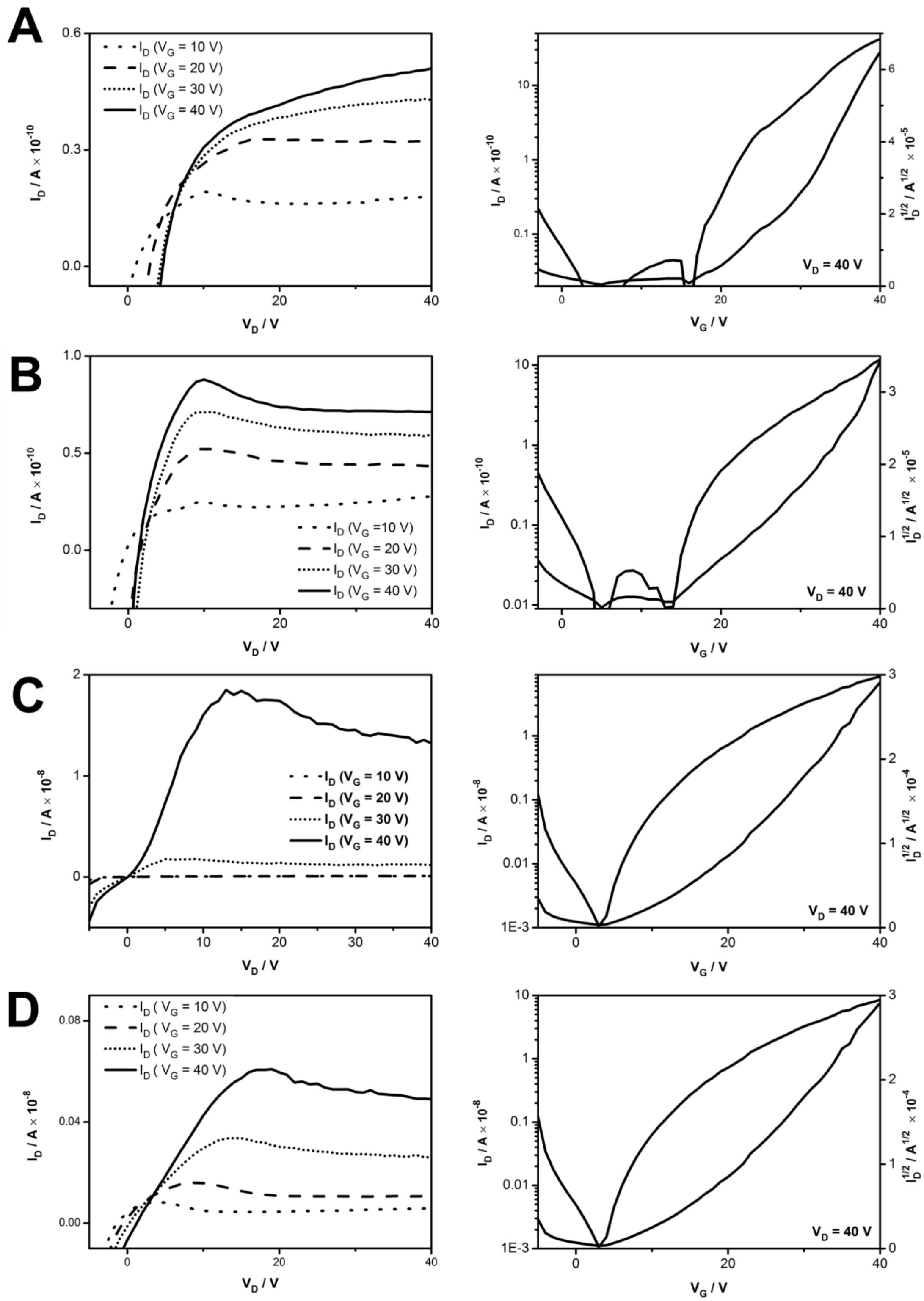

Figure S4: Output (left) and transfer characteristics (right) of representative transistors. **A:** NDI **1** on APTES-modified surface. **B:** NDI **1** on AUDTES-modified surface. **C:** PDI **2** on APTES-modified surface. **D:** PDI **2** on AUDTES-modified surface.

Calculation of Mobilities:

Field effect mobilities were calculated using equation 1:

$$I_d = \frac{W}{2L}\mu C(V_g - V_t)^2 \text{ (eq 1)}$$

For the extraction of the channel mobility μ and the threshold voltage V_t, straight lines were fitted in the $I_D^{1/2}$-V_G curves. To ensure a statistically valid interpretation of the measurements, a minimum of N = 7 data points was included in the analysis. To evaluate the quality of fit, regression factors (R^2) were calculated for all fits. R^2 was usually ca. 0.95 (very good fit), devices with R^2 below 0.85 were defined as non-functional.

For the calculation of device parameters, the following constants were used: Capatitance per unit area of the insulating layer C = 11.5 nF/cm², channel width W = 3 mm, channel length L= 100 μm.