

# SUPPORTING INFORMATION

## Ultrafast layer-by-layer assembly of thin organic films based on triazolinedione click chemistry

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## **General**

### **Instrumentation and Analysis**

#### **NMR**

NMR spectra were recorded at room temperature in deuterated solvents on Bruker AVANCE 300 (300 MHz) FT-NMR spectrometer. Chemical shifts ( $\delta$ ) are reported in units of parts per million relative to tetramethylsilane. All  $^1\text{H}$  spectra were referenced to proton signals of residual undeuterated solvents.

#### **Mass spectrometry**

An Agilent technologies 1100 series LC/MSD system equipped with a diode array detector and single quadMSdetector (VL) with an electrospray source (ESI-MS) was used for MS analysis. ESI accurate masses were measured on a LTQ Orbitap LTQ XL (Thermo-Fisher Scientific, Bremen) with loop injection.

#### **Contact Angle**

Water contact angles were measured by the sessile drop method on a DSA 100 goniometer (Krüss GmbH Wissenschaftliche Laborgeräte, Germany).

#### **X-ray photoelectron spectroscopy (XPS)**

XPS measurements were performed with an Axis Ultra DLD (Kratos Analytical Ltd, UK). A monochromatic Al  $K\alpha$  source ( $h\nu = 1486.6$  eV) at 10 mA filament current and 12 kV filament voltage source energies was used. The pass energy was set to 20 eV for high resolution scans and to 160 eV for survey scans. The charge neutralizer was used to compensate for sample charging. All measurements were carried out in the “hybrid mode”. The data were evaluated with CasaXPS (version 2.3.15, Casa Software Ltd, UK) and the spectra were calibrated to aliphatic carbon ( $\text{C1s} = 285$  eV). High resolution spectra were integrated to determine the atom%.

#### **Ellipsometry**

Ellipsometry measurements were performed using “The Multiskop” build by “Optrel GBR” (Kleinmachnow, Germany). Measurements were performed at an angle of incidence of  $55^\circ$  with a laser of 632.8 nm wavelength. The build in software of the machine was used to analyze the data. The refractive index of the organic materials was assumed to be 1.45. Every sample was measured on 10 different spots. The error bars in the graph represent the standard deviation of these measurements.

#### **Atomic force microscopy (AFM)**

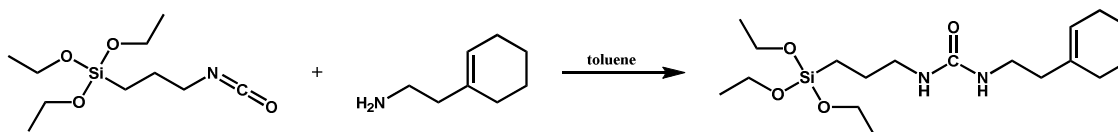
AFM imaging was performed using a Nanowizard 3 from JPK Instruments operated in tapping mode with Veeco RTESP-Tapping Mode Etched Silicon Probes. The AFM was typically operated with a setpoint of 0.900 V and a scan rate of 1.00 Hz with a resolution of 512x512 pixels. Scratching experiments were performed with the same set up operated in contact mode. 10 to 15 images were taken with a setpoint of 2.15 V and a line rate of 10.00 Hz in order to remove the organic material from the silicon wafers. The data was analyzed with Gwyddion (version 2.22). The RMS roughness was measured over an area of  $5 \times 5 \mu\text{m}$ .

## Synthesis

### General Procedures and Materials

Acetone (Sigma-Aldrich, 99.8%); Br<sub>2</sub> (Sigma-Aldrich, 99%); 2-(1-cyclohexenyl)ethylamine (Alfa Aesar, 98%); 1,4-diazabicyclo[2.2.2]octane (DABCO) (Sigma-Aldrich, 99%); dibutyltin dilaurate (TCI); dichloromethane (DCM) (Sigma-Aldrich, 99.8%); ethyl carbazate (Sigma-Aldrich, 97%); trans,trans-2,4-hexadien-1-ol (Sigma-Aldrich, ≥97%); hydrochloric acid (Chem-Lab, 36%); 4,4'-methylenebis(phenyl isocyanate) (Sigma-Aldrich, 98%); potassium hydroxide (Sigma-Aldrich, ≥90%); sulfuric acid (FLUKA, 95-97%); toluene (Sigma-Aldrich, 99.9%) and 3-(triethoxysilyl)propyl isocyanate (Sigma-Aldrich, 95%) were used as received. Tetrahydrofuran (Sigma-Aldrich, analytical grade) was dried over potassium. The isocyanurate-based hexamethylene diisocyanate trimer (HDI<sub>3</sub>, Desmodur N3600) was kindly provided by Bayer MaterialScience and used as received. Silicon wafers were supplied from siltronic AG (Germany).

### Synthesis of triethoxysilane precursor 1 for monolayer formation



3-(Triethoxysilyl)propyl isocyanate (2 g, 8.09 mmol, 1 eq) was dissolved in toluene (10 mL) in a dry two neck flask under inert atmosphere. Then 2-(1-cyclohexenyl)ethylamine (1.013 g, 8.09 mmol, 1 eq) was added dropwise and the mixture was allowed to stir at room temperature overnight. The solvent was removed, the flask heated to 60 °C and evacuated with an oil pump for several hours.

**Yield:** 2.52 g white powder (6.76 mmol, 84%).

**Bruto formula:** C<sub>18</sub>H<sub>36</sub>N<sub>2</sub>O<sub>4</sub>Si.

**MW.:** 372.58 g/mol.

**ESI-MS (m/z):** 153.13855 (100%) [C<sub>9</sub>H<sub>17</sub>N<sub>2</sub>]<sup>+</sup>, 373.25171 (10%) [M+H]<sup>+</sup>, 767.47809 (25%) [2M+H]<sup>+</sup>.

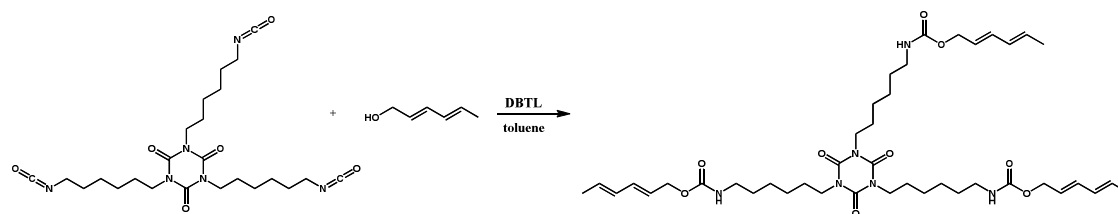
**<sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>):** δ (ppm) = 0.64 (t, 2, Si-CH<sub>2</sub>), 1.23 (t, 9, O-CH<sub>2</sub>-CH<sub>3</sub> x 3), 1.49-1.69 (band, 6, CH<sub>2</sub>(C<sub>6</sub>) x 2 + Si-CH<sub>2</sub>-CH<sub>2</sub>), 1.92 (broad, 2, CH=C-CH<sub>2</sub>), 1.99 (broad, 2, C=CH-CH<sub>2</sub>), 2.13 (t, 2, CH=C-CH<sub>2</sub>-CH<sub>2</sub>-NH), 3.16 (q, 2, NH-CH<sub>2</sub>), 3.23 (q, 2, NH-CH<sub>2</sub>), 3.82 (q, 6, O-CH<sub>2</sub>-CH<sub>3</sub> x 3), 4.28 (br. t, 1, NH), 4.51 (br. t, 1, NH), 5.47 (s, 1, C=CH).

**<sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>):** δ (ppm) = 158.31, 134.90, 123.63, 58.56, 43.06, 38.32, 38.29, 27.96, 25.36, 23.67, 22.94, 22.49, 18.42, 7.74.

### Synthesis of bis triazolinedione 2

4,4'-(4,4'-diphenylmethylene)-bis-(1,2,4-triazoline-3,5-dione) **2** was synthesized in three steps as described elsewhere.<sup>1</sup>

### Synthesis of isocyanurate derivative 3



In a 250 mL flask, HDI<sub>3</sub> (10.0 g, 19.8 mmol, 1 eq) was dissolved in 100 mL toluene under inert atmosphere. To this solution, 2,4-hexadiene-1-ol (5.84 g, 59.5 mmol, 3 eq) and dibutyltin dilaurate (100  $\mu$ L) were sequentially added. The reaction mixture was stirred at room temperature for two hours. An exothermic reaction can be observed. After evaporation of the solvent *in vacuo*, the resulting oil solidified overnight in a vacuum oven at 40°C.

**Yield:** 15.7 g off-white solid (19.7 mmol, 99 %).

**Bruto formula:** C<sub>42</sub>H<sub>66</sub>N<sub>6</sub>O<sub>9</sub>.

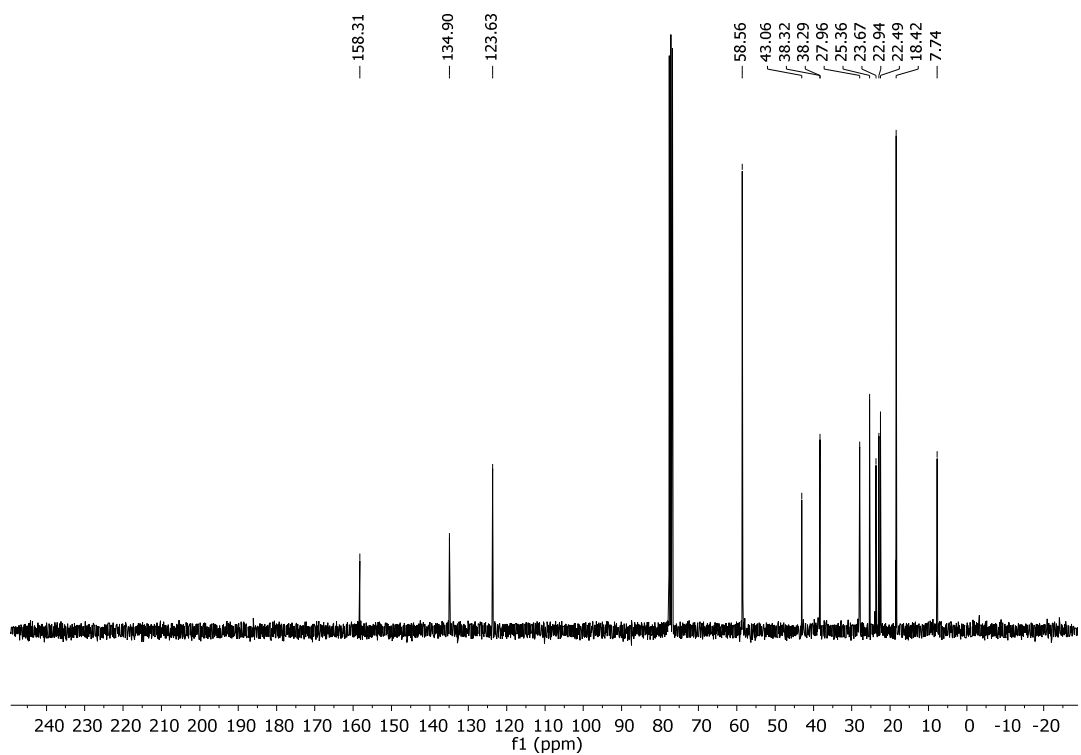
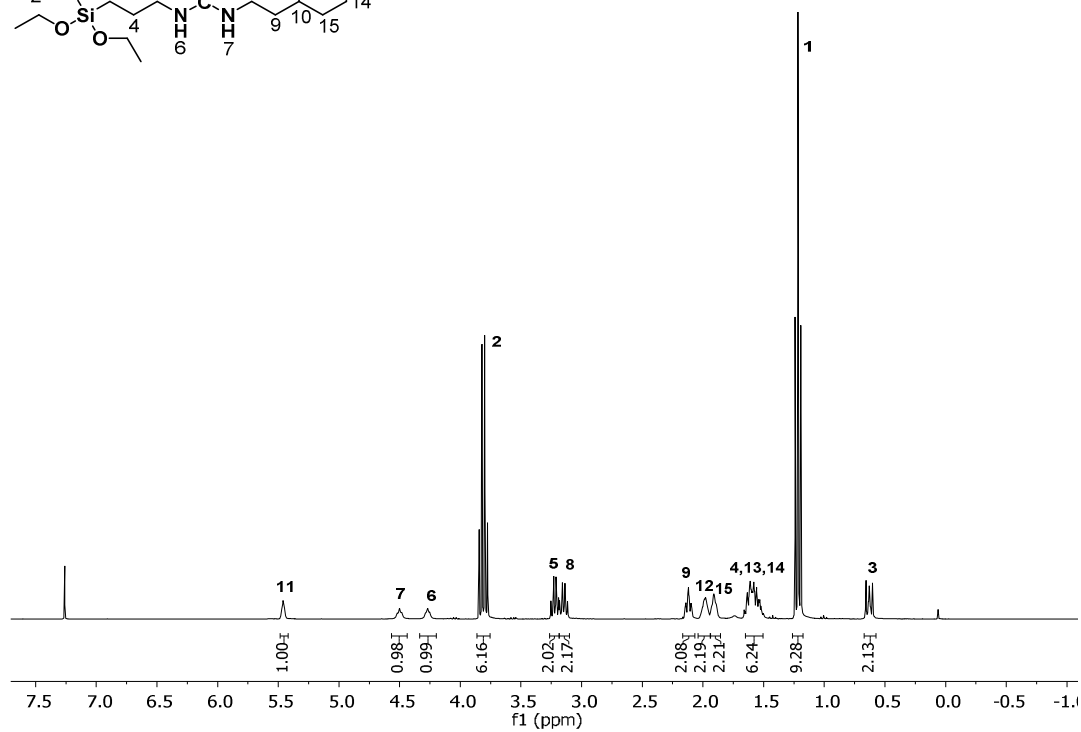
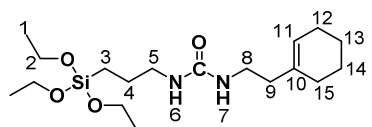
**MW.:** 799.02 g/mol.

**ESI-MS (m/z):** 857.5 [M+OAc].

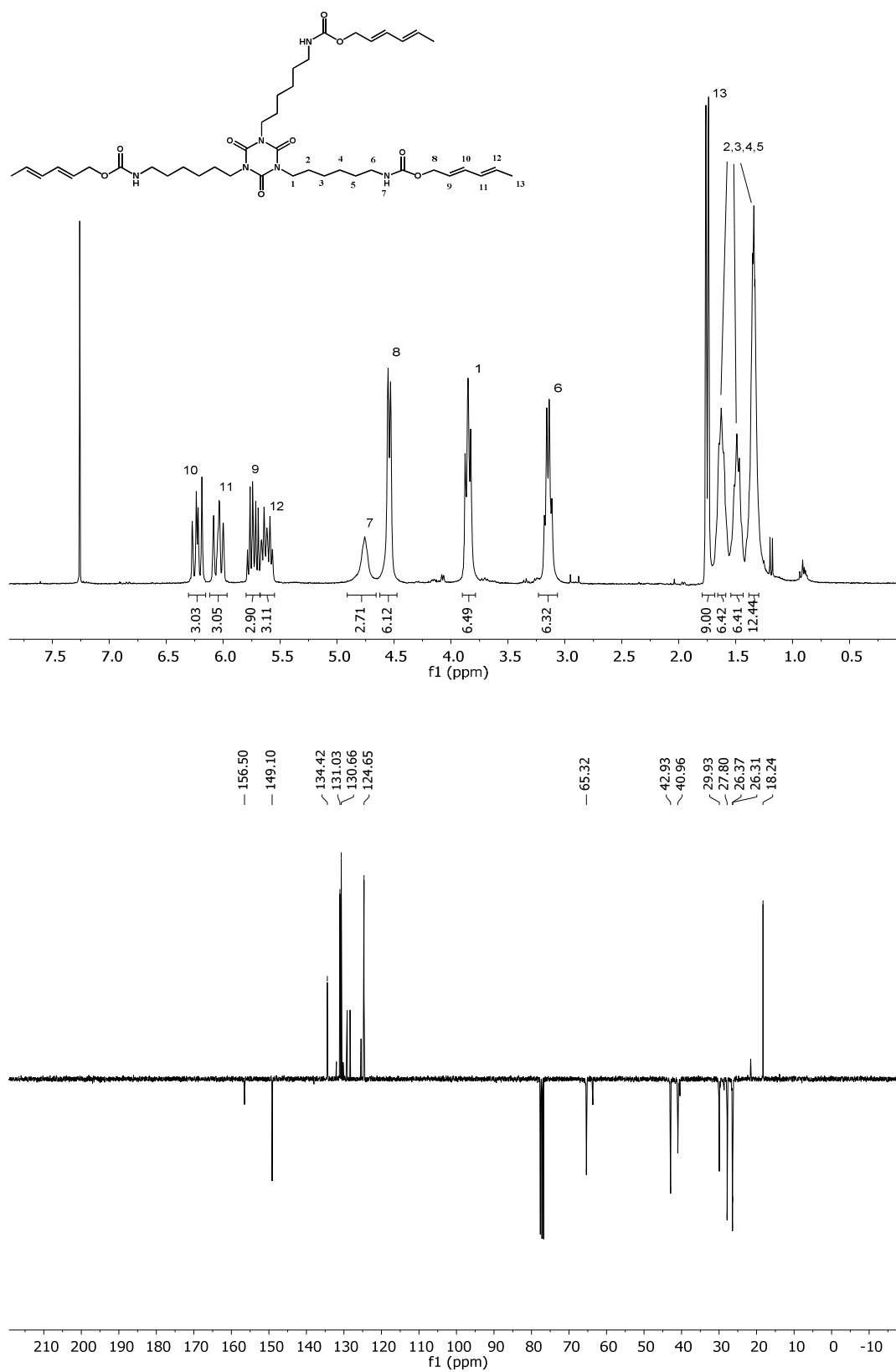
**<sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>):**  $\delta$  (ppm) = 1.35 (broad, 12, CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>), 1.50 (broad, 6, CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>), 1.64 (broad, 6, CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>), 1.76 (d, 9, CH=CH-CH<sub>3</sub>), 3.16 (q, 6, NH-CH<sub>2</sub>), 3.86 (t, 6, N-CH<sub>2</sub>), 4.55 (d, 6, O-CH<sub>2</sub>), 4.77 (br. s, 3, NH), 5.62 (m, 3, CH=CH-CH<sub>3</sub>), 5.75 (m, 3, O-CH<sub>2</sub>-CH), 6.05 (dd, 3, CH=CH-CH<sub>3</sub>), 6.24 (dd, 3, CH<sub>2</sub>-CH=CH).

**<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):**  $\delta$  (ppm) = 156.50, 149.10, 134.42, 131.03, 130.66, 124.65, 65.32, 42.93, 40.96, 29.93, 27.80, 26.37, 26.31, 18.24.

<sup>1</sup>H-NMR and <sup>13</sup>C-NMR of triethoxysilane precursor 1



$^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR (attached proton test) of isocyanurate derivative 3



### Preparation of self-assembled monolayers

Silicon wafers were first cleaned by sonication for 3 min in pentane, acetone and water. Next, they were activated in piranha solution ( $\text{H}_2\text{SO}_4(\text{conc.}): \text{H}_2\text{O}_2(30\%) = 2:1$ ) for 30 min (Danger!), rinsed with copious amounts of water, dried in a stream of argon and transferred into a solution of silane **1** (10 mM in toluene (analytical grade)) under a blanket of argon. After stirring the solution for 18 h at room temperature, the samples were taken out and rinsed with dichloromethane, ethanol and water and dried in a stream of argon.

### Layer-by-layer assembly of triazolinedione **2** and isocyanurate derivative **3**

Two solutions were prepared for the layer-by-layer assembly of the active layer and kept in Schlenk flasks under an atmosphere of argon:

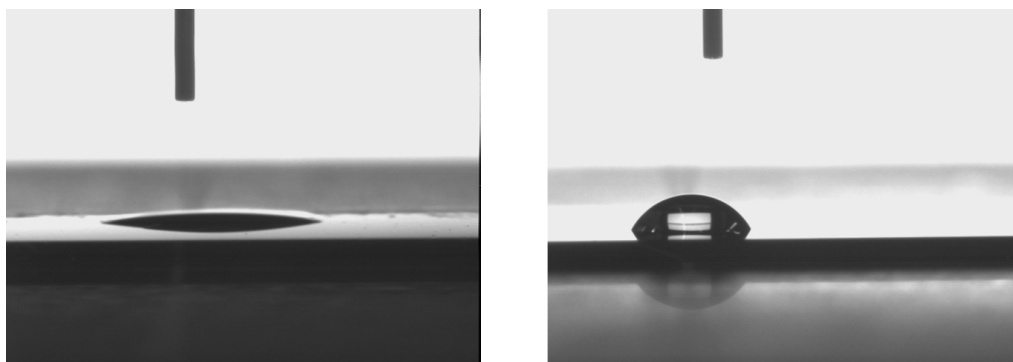
A: 150 mM triazolinedione **2** in dry THF.

B: 75 mM isocyanurate derivative **3** in dry THF.

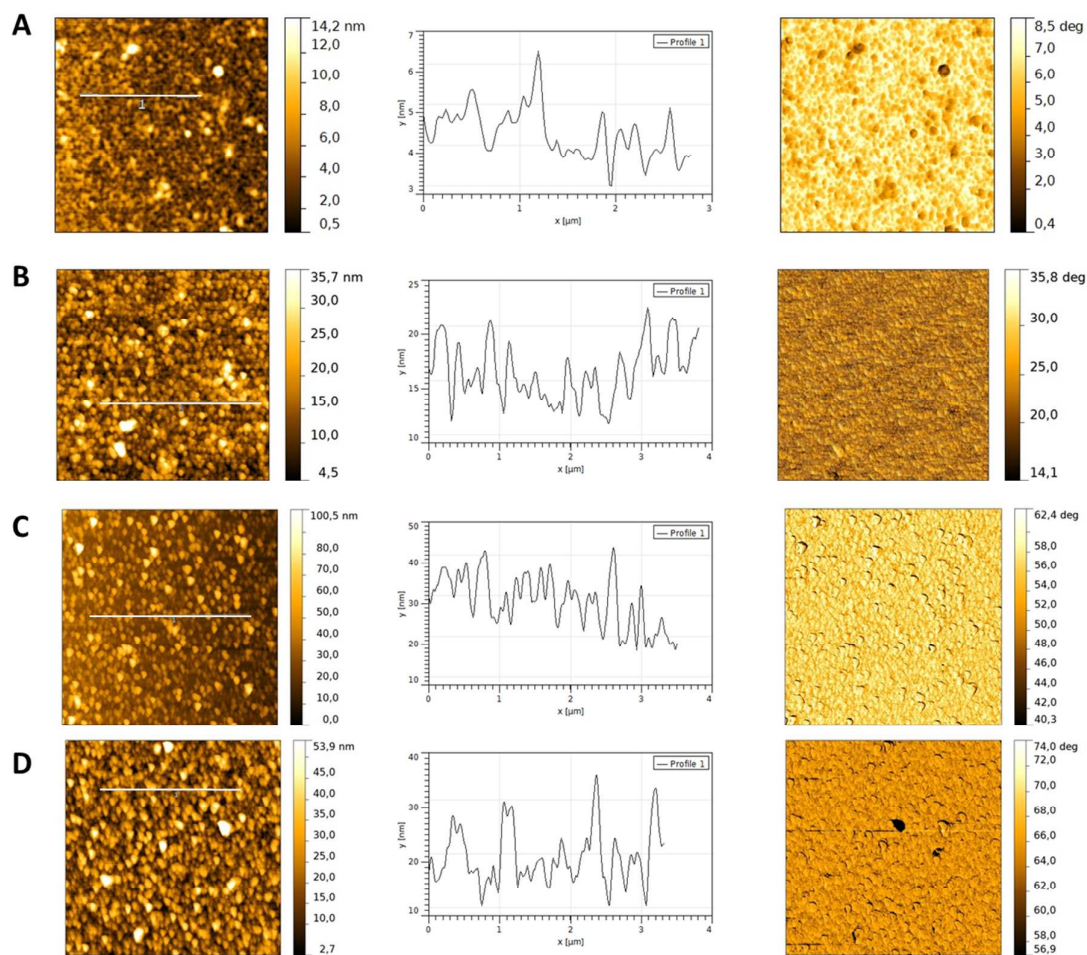
The samples were initially placed in the solution A for 1 min, rinsed with acetone, dried in a stream of argon and then left alternatingly in the solutions A and B for 10 s. The samples were washed between each deposition step by rinsing with acetone and drying in an argon stream. The samples were typically rinsed for 5-10 s with 20-40 mL of acetone. Reaction times were the same for the last multilayer batch, but the rinsing and drying steps were omitted. Instead, the samples were simply dipped into beakers with acetone (300 mL) and THF (300 mL) for about 3 s each.

The 2,4-hexadien-1-ol blocking layer was assembled by soaking the sample for 5 min in a 500 mM solution in dry THF.

### Supplementary figures

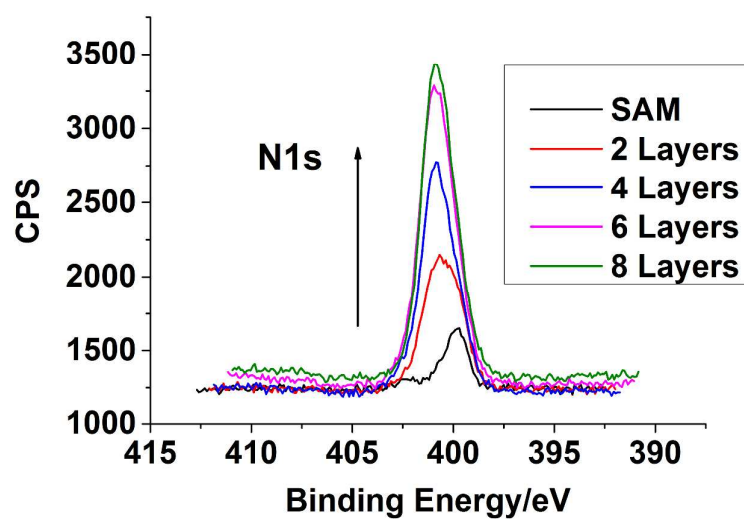


**Figure S1.** Static contact angles for the activated silicon wafer (left,  $<10^\circ$ ) and the cyclohexene monolayer (right,  $67^\circ$ ).

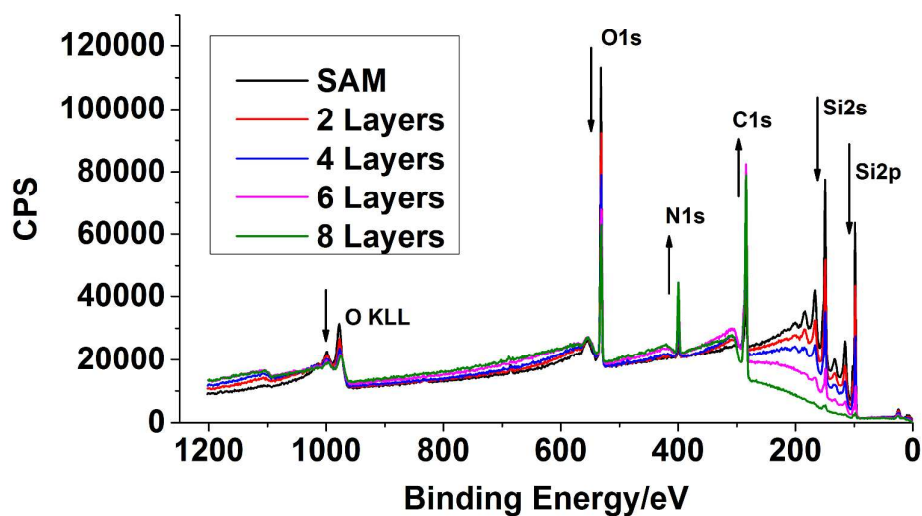


**Figure S2.** AFM height images (left), height profiles (middle, thickness of the line 30 px,) and phase images (right) (5x5 μm): (A) 5 layer sample and (B) 15 layer sample by traditional washing method and (C) 5 layer sample and (D) 15 layer sample by dip washing method.





**Figure S3.** High-resolution x-ray photoelectron spectrum of the N 1s signal.



**Figure S4.** XPS survey spectra of samples with up to eight layers.

## References

- (1) Billiet, S.; De Bruycker, K.; Driessen, F.; Goossens, H.; Van Speybroeck, V.; Winne, J. M.; Du Prez, F. E. *Nat. Chem.* **2014**, *6*, 815–821.