

Electronic Supplementary Information:

Sequence-controlled molecular layers on surfaces by thiol-ene chemistry: synthesis and multitechnique characterization

1. Materials and methods

a) Materials

All technical solvents and commercially available chemicals were used without further purification. 10-Undecenyltrichlorosilane (95%) was purchased at ABCR, 2,2-dimethoxy-2-phenylacetophenon (99%), 1,4-benzenedimethanethiol (98%), 2,2'-(ethylenedioxy)diethanethiol, diallylmethylamine (97%), chlorohydroquinone (85 %), bromohydroquinone (97 %), (R)-(+)-limonene (97 %) and thioacetic acid (96 %), 1-octanethiol (98.5%) and methyl ethyl ketone (MEK, 99%) were supplied by Sigma Aldrich and allylbromide (98 %) was bought from Fluka. 1H,1H,2H,2H-Perfluorodecyltrichlorosilane (FDTS) (96%) was bought from Alfa Aesar. Poly(methyl methacrylate) (PMMA, $M_w = 9.59$ kg/mol, $D = 1.05$) and polystyrene (PS, $M_w = 96$ kg/mol, $D = 1.04$) were purchased from Polymer Standards Service. Si substrates (single side polished <100> Si, thickness 675 ± 50 μm) were supplied by Siegert Consulting e.K.

b) Characterization of the synthesized marker molecules

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AVANCE DPX spectrometer operating at 300 MHz for ^1H NMR and at 75 MHz for ^{13}C NMR measurements. CDCl_3 was used as solvent and all measurements took place at room temperature.

Infrared spectra (IR) were recorded on a BRUKER Alpha-p instrument in a frequency range from 3997 to 374 cm^{-1} applying ATR-technology.

Fast-atom-bombardement (FAB) and electron ionization (EI) spectra were recorded utilizing a Finnigan MAT 95 mass spectrometer. Molecule fragments were specified as mass / charge ratio m/z .

c) Surface characterization

Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) was carried out using a ToF-SIMS 5 instrument (ION-TOF GmbH, Muenster, Germany). Surface spectroscopy was performed with Bi_3^+ (ion current about 0.5 pA) as primary ion for secondary ion generation. The ion dose density was kept below 10^{11} ions/cm² per polarity, securing that the static SIMS limit of about 10^{12} ions/cm² was not reached performing positive and negative polarity at the same position of the samples. Measurements with high mass resolution were performed on two different positions of each sample obtaining surface images of an area of $2000 \mu\text{m} \times 2000 \mu\text{m}$ using 200 pixels per $1000 \mu\text{m}$. Images were obtained with a so called stage scan where several smaller image scans, here $400 \mu\text{m} \times 400 \mu\text{m}$, were stacked together to gain the large overview scans. Spectra were calibrated on the omnipresent C^- , C_2^- , C_4^- , C_6^- , C_8^- or on the F^+ , CF_2^+ , C_2F_2^+ , C_2F_4^+ , C_3F_4^+ peaks. Spectral data were analyzed and exported with the SurfaceLab 6.6 software of the instrument.

High lateral resolution images were carried out by using the “Delayed Extraction” mode of the instrument. Here, areas of $40 \mu\text{m} \times 40 \mu\text{m}$ with a resolution of 256×256 pixels were analyzed using Bi_3^+ as primary ion for secondary ion generation. The dose density here was above the static SIMS limit, which could be observed in the video image of the instrument were the analyzed area was visible after about 50 to 75 repeated scans. For a good lateral resolution, signal intensity was accumulated over 100 scans per sample area. For positive and negative polarity measurements different sample positions were used and the measurements were repeated five times to obtain a good statistical overview of FDOTS matrix and holes distribution. Data were analyzed using the SurfaceLab 6.6 software of the instrument. Images were normalized to the total ion intensity. Brighter colors indicate higher intensity values. Color scales of specific fragments have always the same values.

X-Ray Photo electron Spectroscopy (XPS) was performed with a K-Alpha+ XPS instrument (Thermo Fisher Scientific, East Grinstead, England). Four random points for each sample were analyzed using a microfocused, monochromated Al K α X-ray source ($400 \mu\text{m}$ spot size). Spectra were fitted with several Voigt profiles (binding energy uncertainty of ± 0.2 eV). Plasmon loss features of the Silicon substrate were additionally fitted to gain the real signals of elements (for example Cl 2p spectra). The analyzer transmission function, Scofield sensitivity factors and effective attenuation lengths (EALs) for photoelectrons were applied for quantification.^[1] EALs were calculated using the standard TPP-2M formalism.^[2] All spectra were referenced

to the C1s peak (C-C, C-H) at 285.0 eV binding energy controlled by the means of the well-known photoelectron peaks of metallic Cu, Ag and Au.

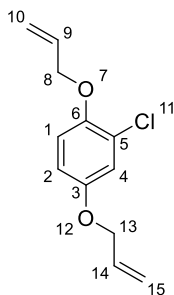
Atomic Force Microscopy (AFM) imaging was carried out in contact mode under liquid using a Bruker Dimension ICON system. A Mikromasch HQ:CSC37/Pt (typical force constant: 0.3 N/m) tip was used.

2. Experimental procedures

a) Synthesis of the marker molecules

1,4-bis(allyloxy)-2-chlorobenzene (molecule 2)

Chlorohydroquinone (14.5 g, 100 mmol, 1.00 eq.) was dissolved in acetone (10.0 mL/mmol). Then, K_2CO_3 (80.0 g, 600 mmol, 6.00 eq.) and allylbromide (36.3 g, 300 mmol, 3.00 eq.) were added and stirred under reflux for 30 h. Finally, the reaction mixture was centrifuged in falcon-tubes and decanted. The liquid part was collected and evaporated. The remaining colorless oily mixture was separated via column chromatography (cyclohexane/dichloromethane: 8:2) resulting in a colorless liquid. Yield: 80 %



1H NMR (300 MHz, $CDCl_3$, δ in ppm): 6.97 (d, $J = 2.9$ Hz, 1H, CH^4), 6.85 (d, $J = 9.0$ Hz, 1H, CH^1), 6.75 (dd, $J = 9.0, 2.9$ Hz, 1H, CH^2), 6.13 – 5.94 (m, 2H, $CH^{9,14}$), 5.48 – 5.24 (m, 4H, $CH_2^{10,15}$), 4.53 (dt, $J = 5.2, 1.4$ Hz, 4H, CH_2^{13}), 4.46 (dt, $J = 5.3, 1.4$ Hz, 4H, CH_2^8).

^{13}C NMR (75 MHz, $DMSO-d_6$, δ in ppm): 153.08 (C^6), 148.66 (C^3), 133.11 ($C^{9,14}$), 123.79 (C^5), 117.77 - 117.73 (2C, $C^{10, 15}$), 117.04 (C^4), 115.40 (C^1), 113.80 (C^2), 70.68 (C^{13}), 69.52 (C^8).

IR (neat): ν = 3081.0, 2863.7, 1647.9, 1604.8, 1573.7, 1491.7, 1453.3, 1422.4, 1382.0, 1361.2, 1273.2, 1203.1, 1155.9, 1102.0, 1049.6, 1018.9, 994.5, 924.2, 860.0, 841.1, 798.5, 679.5, 565.8, 443.3

HRMS (EI): m/z calculated for $C_{12}H_{13}O_2Cl$: 224.0599; found: 224.0597

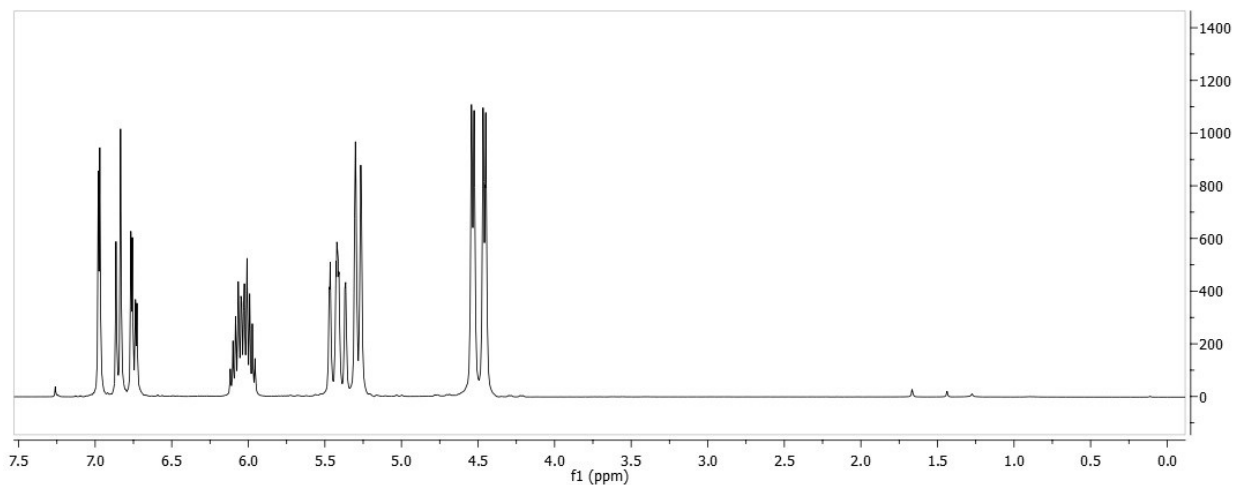


Figure S1. ¹H NMR spectrum of 1,4-*bis*(allyloxy)-2-chlorobenzene (molecule **2**)

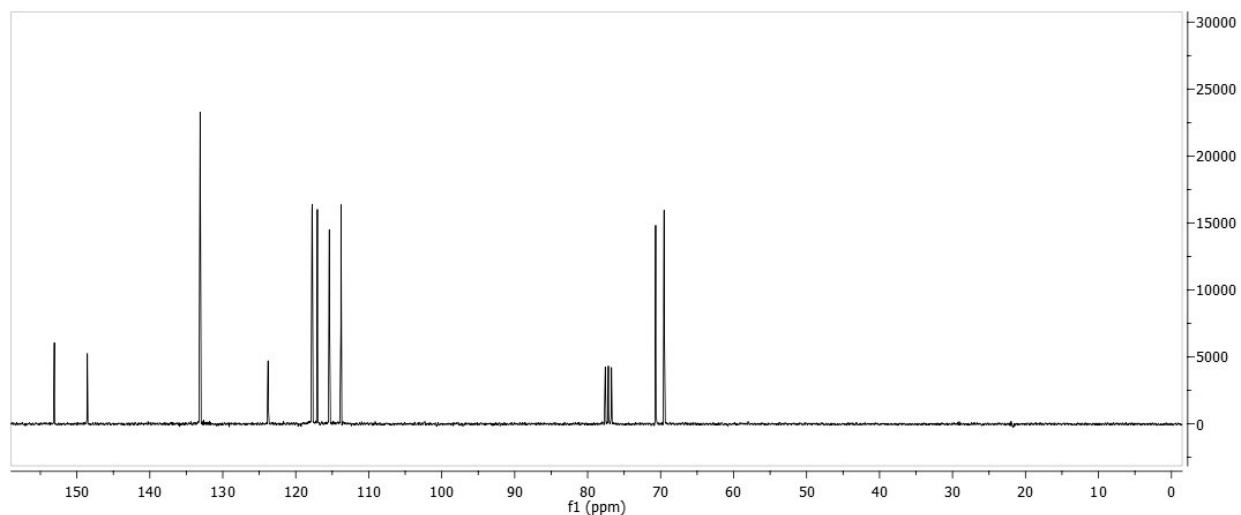
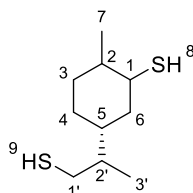


Figure S2. ¹³C NMR spectrum of 1,4-*bis*(allyloxy)-2-chlorobenzene (molecule **2**)

5-((R)-1'-Mercaptopropan-2'-yl)-2-methylcyclohexanethiol (Limonene dithiol **3**)

The synthesis was performed as described by Meier *et al.*^[3] (R)-(+)-Limonene (3.00 g, 22.0 mmol, 1.00 eq.) was slowly dissolved in thioacetic acid (4.19 g, 55.1 mmol, 2.50 eq.) (Caution: exothermic reaction) and stirred overnight (appr. 16 h). Then, the remaining thioacetic acid was evaporated under reduced pressure. Methanol (18.0 mL, 410 mmol, 20.0 eq.) and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (0.306 g, 2.20 mmol, 0.100 eq) were added (color changes from colorless to slight yellow) and stirred under reflux overnight. Afterwards, the methanol was evaporated under reduced pressure and the crude product was purified via column chromatography (cyclohexane/ethylacetate 19:1) resulting in a colorless liquid which is a mixture of several isomers. Yield: 89 %



The NMR attribution was done following the paper of Meier *et al.*^[3] In order to distinguish between the different diastereomers, the descriptors “a, b, c, d” are used. “A” and “B” in the H NMR spectra differentiates between two protons connected to the same carbon. The C NMR assignment is unambiguous. The two major diastereomers are marked with “a” and “b”, and the minor ones with “c” and “d”.

¹H NMR (300 MHz, CDCl₃, δ in ppm): 3.29 (dd, J = 6.8, 3.4 Hz, H^{1a}, H^{1b}), 2.62 – 2.48 (m, H^{1'a}, H^{1'c}, H^{1'd}), 2.44 – 2.28 (m, H^{1c}, H^{1d}, H^{1'b}), 1.95 (dd, J = 12.9, 2.4 Hz, H^{3c}, H^{3d}), 1.86 – 1.71 (m, H^{2a}, H^{2b}, H_A^{3a}, H_A^{3b}), 1.70 – 1.55 (m, H^{5a}, H^{5b}, H_A^{6a}, H_A^{6b}, H^{6c}, H^{6d}), 1.55 – 1.50 (H_B^{3a}, H_B^{3b}), 1.50 - 1.30 (m, H^{2'a}, H^{2'b}, H_A^{4a}, H_A^{4b}), 1.30 – 1.15 (m, SH, H_A^{4c}, H_A^{4d}), 1.15 – 1.00 (H^{2c}, H^{2d}, H_B^{4c}, H_B^{4d}, H^{5c}, H^{5d}, H_B^{6a}, H_B^{6b}), 0.95 (d, J = 6.4 Hz, H^{7c}, H^{7d}), 0.95 – 0.84 (m, H_B^{4a}, H_B^{4d}, H^{7a}, H^{7b}, H^{2'c}, H^{2'd}, H^{3'a}, H^{3'b}, H^{3'c}, H^{3'd})

¹³C NMR (75 MHz, CDCl₃, δ in ppm): 46.25 (C^{1c}), 46.24 (C^{1d}), 44.00 (C^{1a}), 43.89 (C^{1b}), 43.20 (C^{3c}), 42.51 (C_{minor diast}), 42.48 (C_{minor diast}), 41.99 (C_{minor diast}), 41.70 (C^{2'c}), 41.65 (C^{2'd}), 41.33 (C^{5c}, C^{5d}), 41.11 (C_{minor diast}), 41.09 (C_{minor diast}), 40.96 (C^{3d}), 40.94 (C^{2c}), 40.92 (C^{2d}), 40.75 (C^{2'a}), 40.68 (C^{2'b}), 39.35 (C^{3a}), 37.14 (C^{3b}), 36.27 (C^{5a}), 36.24 (C^{5b}), 35.93 (C_{minor diast}), 35.42 (C^{4c}), 35.32 (C^{4d}), 34.43 (C_{minor diast}), 34.41 (C_{minor diast}), 33.93 (C^{2a}), 33.77 (C^{2b}),

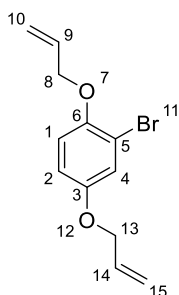
33.06 (C_{minor diast}), 32.98 (C_{minor diast}), 30.46 (C^{6a}), 30.34 (C^{6c}), 29.63 (C^{1'a}), 29.45 (C^{1'b}), 29.40 (C^{1'c}, C^{1'd}), 28.32 (C^{4a}), 28.24 (C^{4b}), 28.10 (C^{6b}), 27.91 (C^{6d}), 20.85 (C^{7c}), 20.82 (C^{7d}), 20.58 (C^{7a}), 20.56 (C^{7b}), 15.44 (C^{3'a}, C^{3'c}), 15.37 (C^{3'd}), 15.34 (C^{3'b})

IR (neat): ν = 2953.4, 2916.1, 2866.5, 2850.3, 2561.2, 1443.9, 1374.3, 1328.1, 1291.1, 1237.0, 1100.7, 978.0, 937.1, 766.0, 717.4, 667.8, 620.7

HRMS (EI): m/z calculated for C₁₀H₁₇S₁: 169.1045; found: 169.1044

1,4-bis(allyloxy)-2-bromobenzene (molecule 4)

Bromohydroquinone (6.62 g, 35.0 mmol, 1.00 eq.) was dissolved in acetone (10.0 mL/mmol). Then, K₂CO₃ (29.0 g, 210 mmol, 6.00 eq.) and allylbromide (12.7 g, 105 mmol, 3.00 eq.) were added and stirred under reflux for 30 h. Finally, the reaction mixture was centrifuged in falcon-tubes and decanted. The liquid part was collected and evaporated. The remaining colorless oily mixture was separated via column chromatography (cyclohexane/dichloromethane 8:2) resulting in a colourless liquid. Yield: 85 %



¹H NMR (300 MHz, DMSO-d₆, δ in ppm): 7.19 (d, J = 2.9 Hz, 1H, CH⁴), 7.01 (d, J = 9.0 Hz, 1H, CH¹) 6.91 (d, J = 9.0, 2.9 Hz, 2H, CH²), 6.07 – 5.95 (m, 2H, CH₂^{9,14}), 5.46 – 5.21 (m, 4H, CH₂^{10,15}), 4.55 (dt, J = 4.9 Hz, 4H, CH₂¹³), 4.51 (dt, J = 4.2 Hz, 4H, CH₂⁸).

¹³C NMR (75 MHz, DMSO-d₆, δ in ppm): 153.28 (C³), 149.52 (C⁶), 133.12 - 133.06 (2C, C^{9,14}), 119.95 (C⁴), 117.83 - 117.68 (2C, C^{10,15}), 115.04 (C¹), 114.61 (C²), 112.88 (C⁵), 70.70 (C¹³), 69.61 (C⁸).

IR (neat): ν = 3079.8, 3017.5, 2982.1, 2914.1, 2866.0, 1648.2, 1601.5, 1574.6, 1486.8, 1452.8, 1421.6, 1382.0, 1360.7, 1271.5, 1202.1, 1155.4, 1100.2, 1016.6, 994.04, 923.24, 860.93, 841.11, 797.21, 678.27, 638.62, 570.65, 440.38

HRMS (EI): m/z calculated for $C_{12}H_{13}O_2Br_1$: 268.0093; found: 268.0095

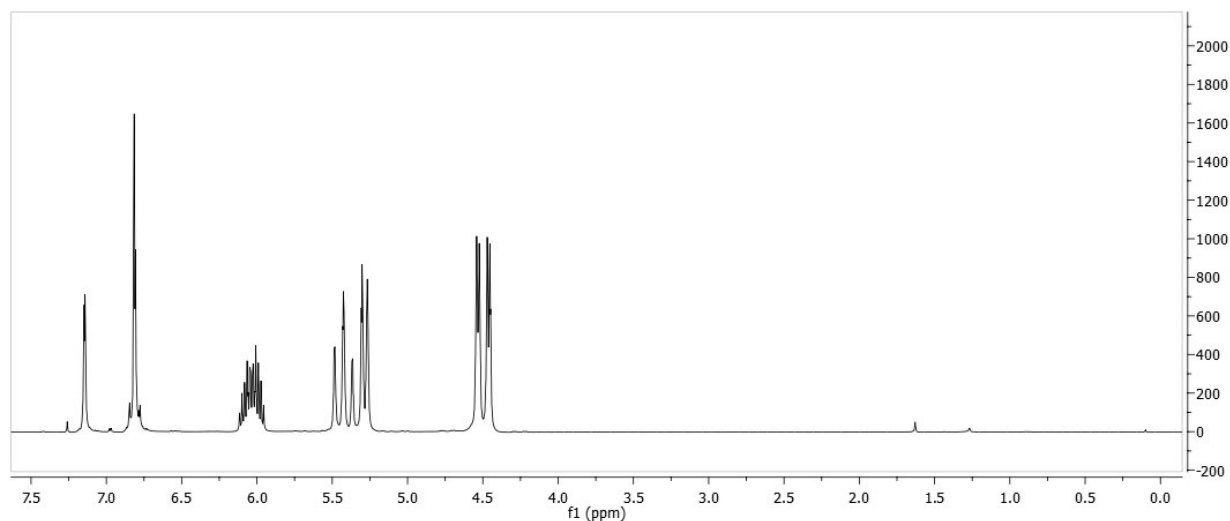


Figure S3. 1H NMR spectrum of 1,4-*bis*(allyloxy)-2-bromobenzene (molecule 4)

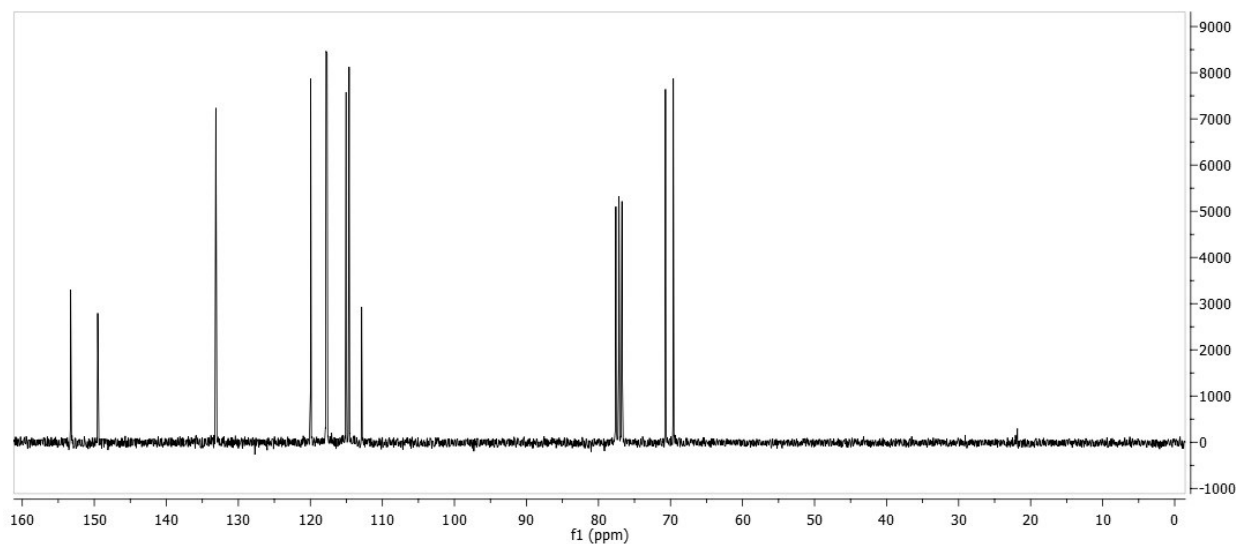


Figure S4. ^{13}C NMR spectrum of 1,4-*bis*(allyloxy)-2-bromobenzene (molecule 4)

b) Polymer blend lithography

Based on the procedure reported by Schimmel *et al.*, polymer blend lithography (PBL) was applied for the creation of a monolayer island pattern.^[4] A PS:PMMA 3:7 solution in MEK with a solution concentration of 15 mg polymer/mL was used. 35 μ L of this solution was spin cast on a Si substrate freshly cleaned by CO₂ snowjet (K4-05, Tectra, Germany) at a rate of 1500 rpm and at a humidity level of 40% RH. The subsequent polymer pattern of PS islands against a PMMA

background was washed in acetic acid to selectively remove the PMMA, leaving the PS cylinders against a bare Si background. Gas phase self-assembly of FTDS followed by placing the samples overnight in a desiccator containing a few drops of liquid FDTD, evacuated to a pressure of 50 mbar, was performed. After the FDTD monolayer had been formed, the PS islands were removed by tetrahydrofuran and the surface was cleaned by snowjet.

c) Silanization with 10-undecenyltrichlorosilane

The wafer pieces were immersed in a 8.4 mM solution of 10-undecenyltrichlorosilane in dry toluene for 1.5 h under a controlled humidity of 28-33%. Subsequently, the wafer pieces were washed with CHCl_3 , sonicated for 5 min in CHCl_3 and soaked in cyclohexane at 60 °C for 10 min. Finally, the wafers were dried under a stream of argon.^[5]

d) Thiol-ene reaction

2,2-Dimethoxy-2-phenylacetophenone (DMPA) (5 mg) was dissolved in 10 μL of dimethylformamide (DMF) and mixed with 1.5 mL of diene or dithiol. A silicon wafer previously functionalized with 10-undecenyltrichlorosilane was immersed in this solution in an open 3 mm diameter petri dish. Then, the samples was placed under a UV-lamp (VL-115.L, 15 W, Vilber Lourmat GmbH, Eberhardzell/ Germany) and irradiated for 120 min with light with the wavelength 365 nm. Finally, the samples were washed with toluene, sonicated for 2 min in toluene, washed with acetone, sonicated for 2 min in acetone and dried under a stream of argon. When diallylmethylamine **6** was used, the samples were additionally washed with water in order to remove some salt formed.

3. Charaterization of the silanization

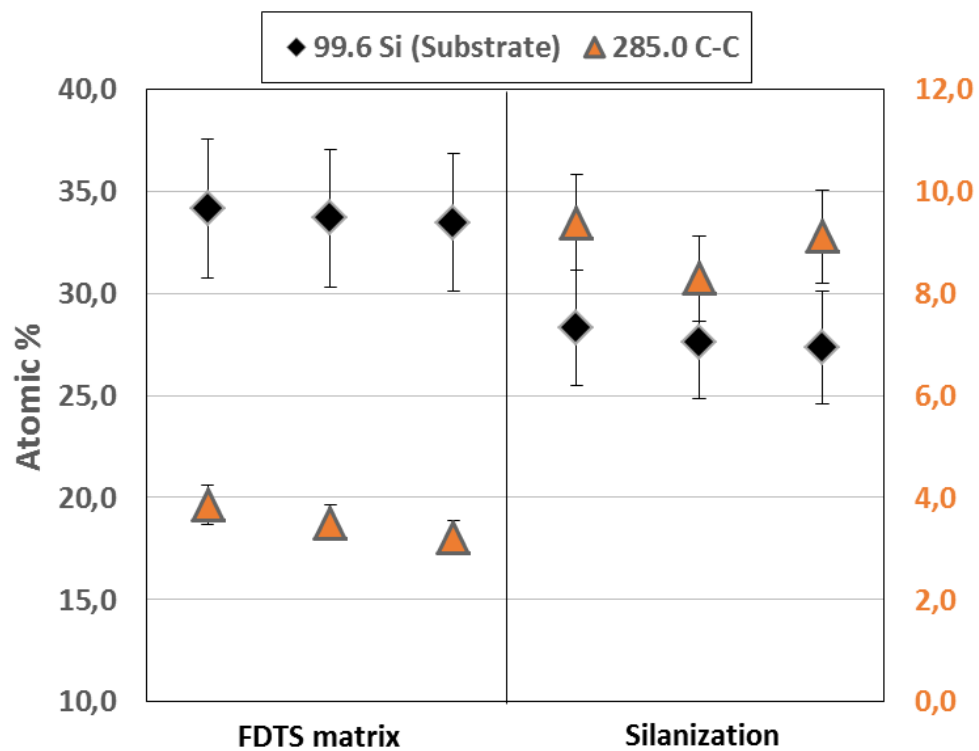


Figure S5. XPS measurements: atomic concentrations of Si 2p (substrate) and C-C (C 1s feature) in the silicon substrate cover with the FDTD matrix and after silanization.

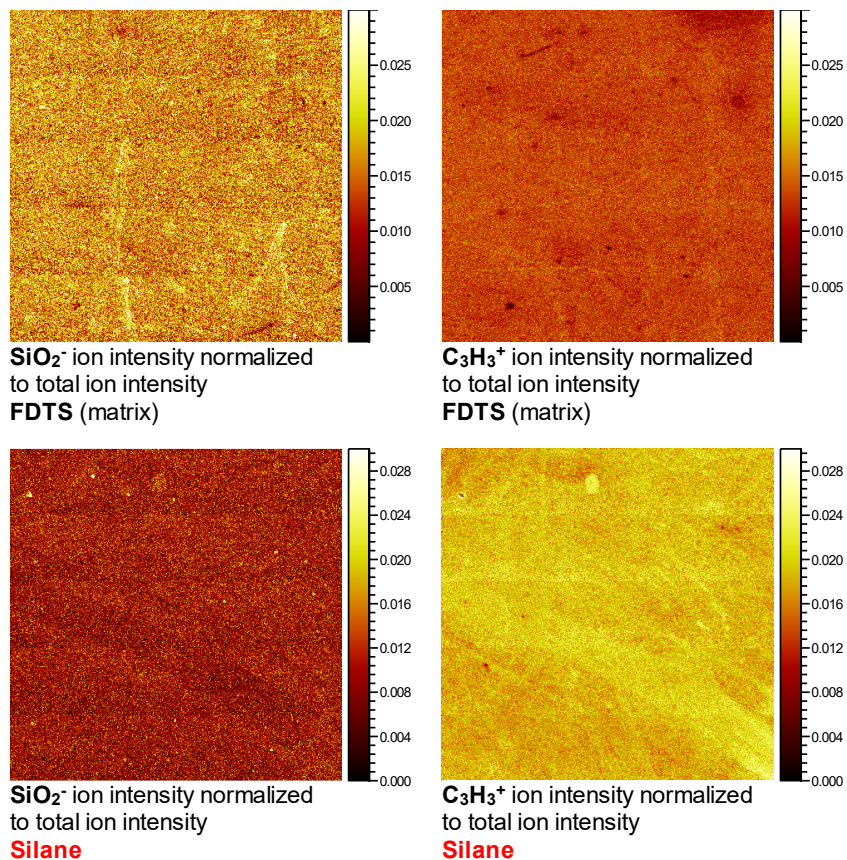
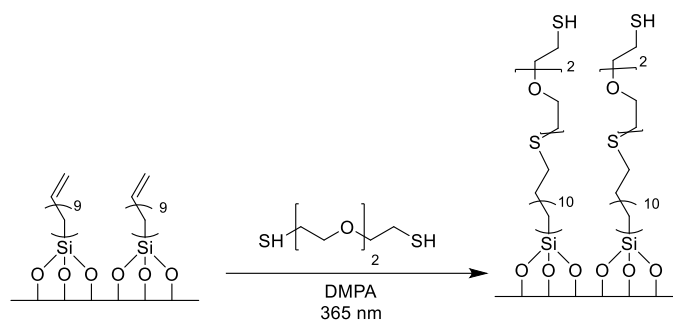


Figure S6. ToF-SIMS images obtained with delayed extraction mode showing the SiO_2^- and C_3H_3^+ ion distributions (included in the FDTS matrix) before (top) and after (bottom) silanization.

4. Thiol-ene reaction optimization

The experimental conditions for thiol-ene reactions were screened for the first reaction employing 2,2'-(ethylenedioxy)diethanethiol **1**. First, the influence of the amount of DMPA was investigated. Three experiments with 0, 5 and 10 mg of DMPA per 1.5 mL of dithiol were performed. The AFM pictures revealed that a higher amount of DMPA led to inhomogeneous functionalization (Figure S5).



Scheme S1. Reaction of the surface functionalized with 10-undecenyltrichlorosilane with 2,2'-(ethylenedioxy)diethanethiol **1**.

Table S1. Influence of the reaction time and mass of DMPA (per 1.5 mL of dithiol) on the thiol-ene reaction of the surface functionalized with 10-undecenyltrichlorosilane with 2,2'-(ethylenedioxy)diethanethiol **1**.

Entry	Reaction time (min)	Mass of DMPA (mg)	AFM height (nm)
1	30	10	0.3
2	60	10	0.4
3	120	10	1.0 + polymerized particles
4	90	10	0.5
5	120	5	0.7
6	120	0	0.4

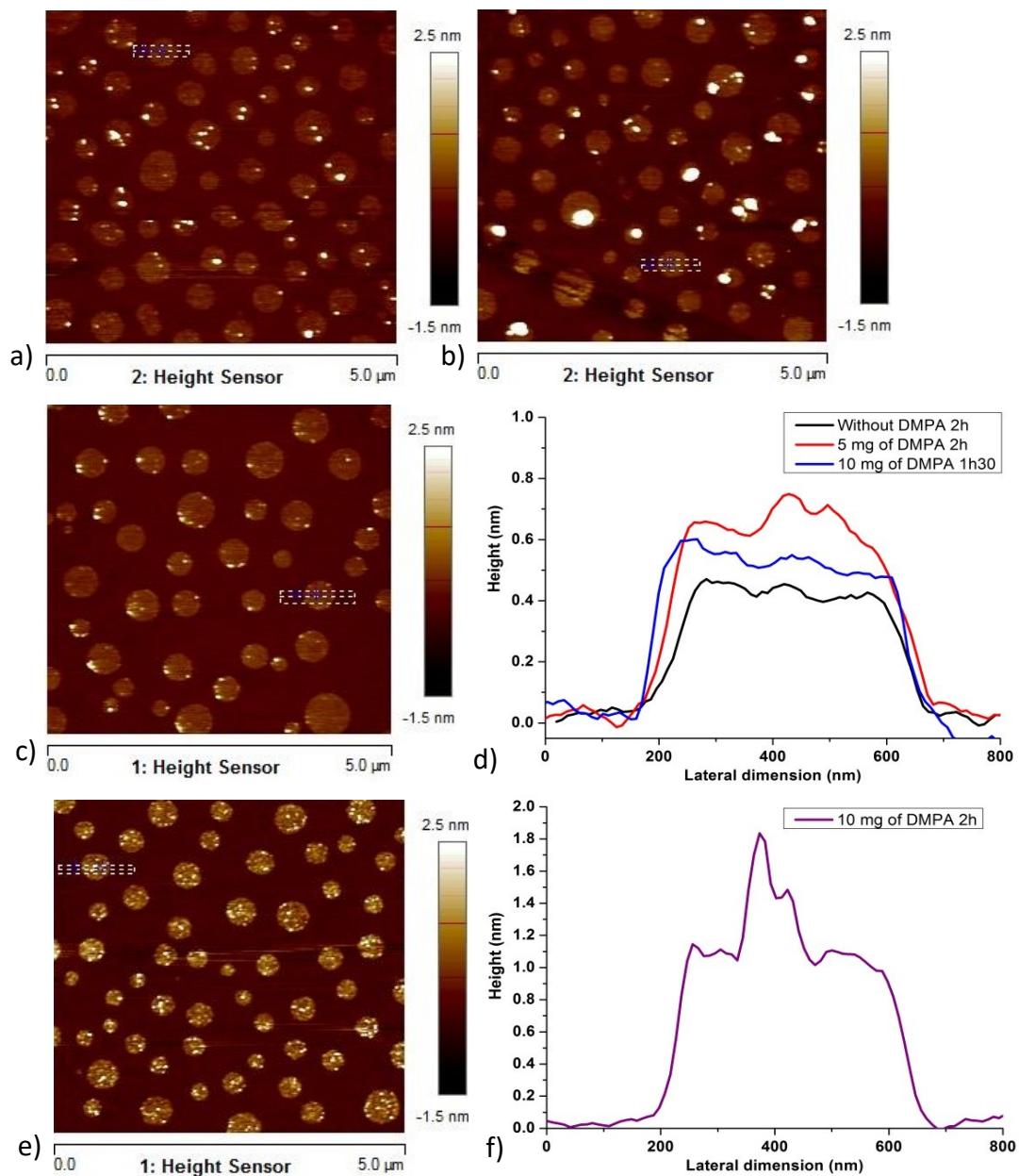


Figure S7. a) AFM image of the sample produced without DMPA for 2 h, b) AFM image of the sample produced with 5 mg DMPA for 2 h, c) AFM image of the sample produced with 10 mg of DMPA for 1 h 30 min, d) Representative profile of one matrix hole after thiol-ene reaction performed under different conditions, e) AFM image of the sample produced with 10 mg of DMPA for 2 h, f) Representative profile of one matrix hole after thiol-ene reaction performed produced with 10 mg of DMPA for 2 h.

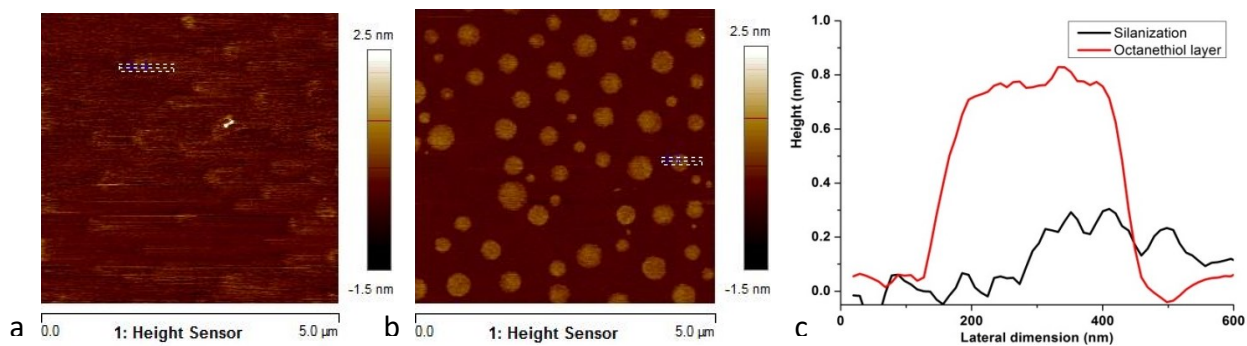
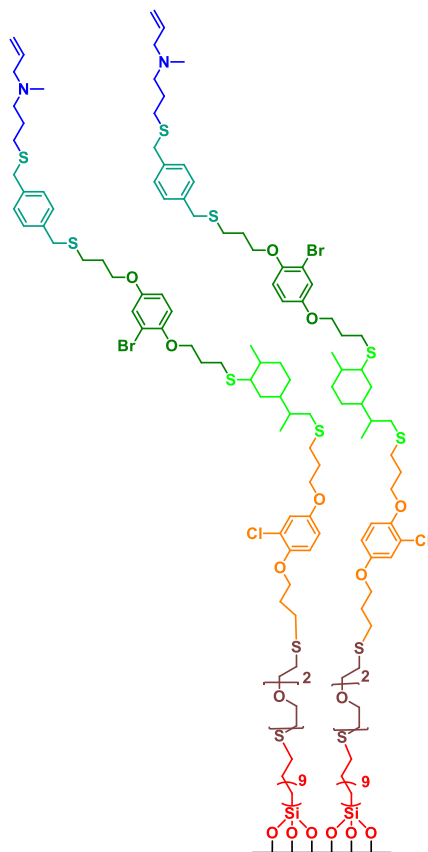


Figure S8. a) AFM image of the sample after silanization, b) AFM image of the sample after reaction with 1-octanethiol, c) Representative profile of one matrix hole before and after reaction with octanethiol.

5. Molecular structure of the sequence



Scheme S2. Structure of the sequence-controlled surface functionalization: silanization of silicon wafer with 10-Undecenyltrichlorosilane and thiol-ene reactions successively employing 2,2'-(Ethyleneedioxy)diethanethiol **1**, 1,4-*bis*(allyloxy)-2-chlorobenzene **2**, limonene dithiol **3**, 1,4-*bis*(allyloxy)-2-bromobenzene **4**, 1,4-benzenedimethanethiol **5**, diallyldimethylamine **6**.

6. Complementary analyses: surface characterization

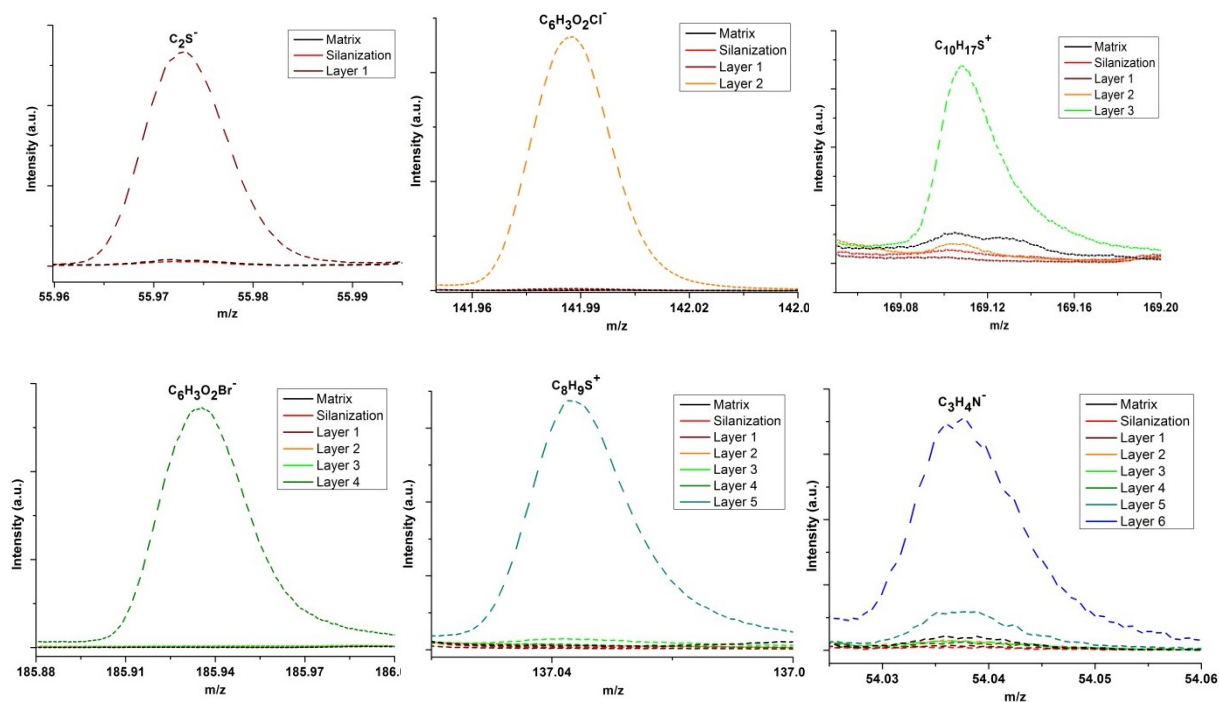


Figure S9. ToF-SIMS data, high mass resolution, spectra cutoff of specific fragments characteristic of each layer.

Table S2. List of some characteristic fragments detected after reaction of the different molecules.

Molecules	Fragments (m/z)
1	$C_2H_5S^+$ (61.01), $C_2H_4S^+$ (60.00), $C_2H_5O^+$ (45.03)
2	$C_9H_9O_2Cl^+$ (184.03), $C_{12}H_{15}O_2Cl^+$ (226.06), $C_6H_3O_2^{37}Cl^-$ (143.99), Cl_2^- (69.94)
3	$C_{10}H_{17}S_2^+$ (201.08), $C_7H_7S^+$ (123.03), $C_6H_9S^+$ (113.04), $C_{10}H_{17}S_2^-$ (201.08), $C_{10}H_{17}S$ (169.11)
4	$C_9H_9O_2Br^+$ (227.98), $C_{12}H_{15}O_2Br^+$ (270.01), $C_6H_3O_2^{81}Br^-$ (187.93), Br_2^- (157.84)
5	$C_8H_7S^+$ (135.03), $C_8H_7S_2^+$ (167.00)
6	$C_7H_{12}N^+$ (110.10), $C_4H_6N^+$ (68.05), $C_2H_5N^+$ (43.04), CH_2NO^- (44.01), $C_6H_3N^-$ (89.03)

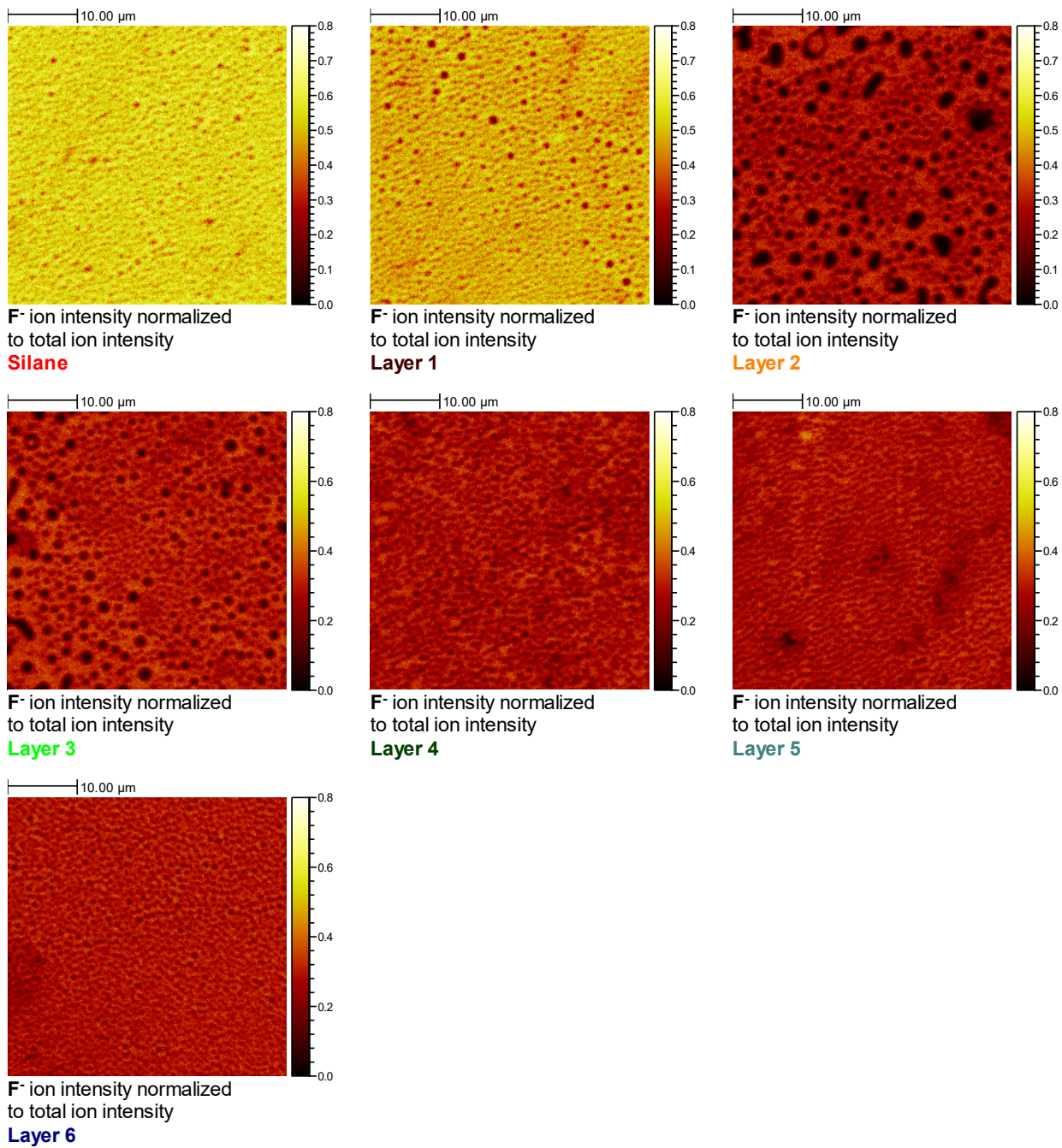


Figure S10. ToF-SIMS images obtained with delayed extraction mode showing the F^- ion distribution (included in the FDTS matrix) after the synthesis of each layer.

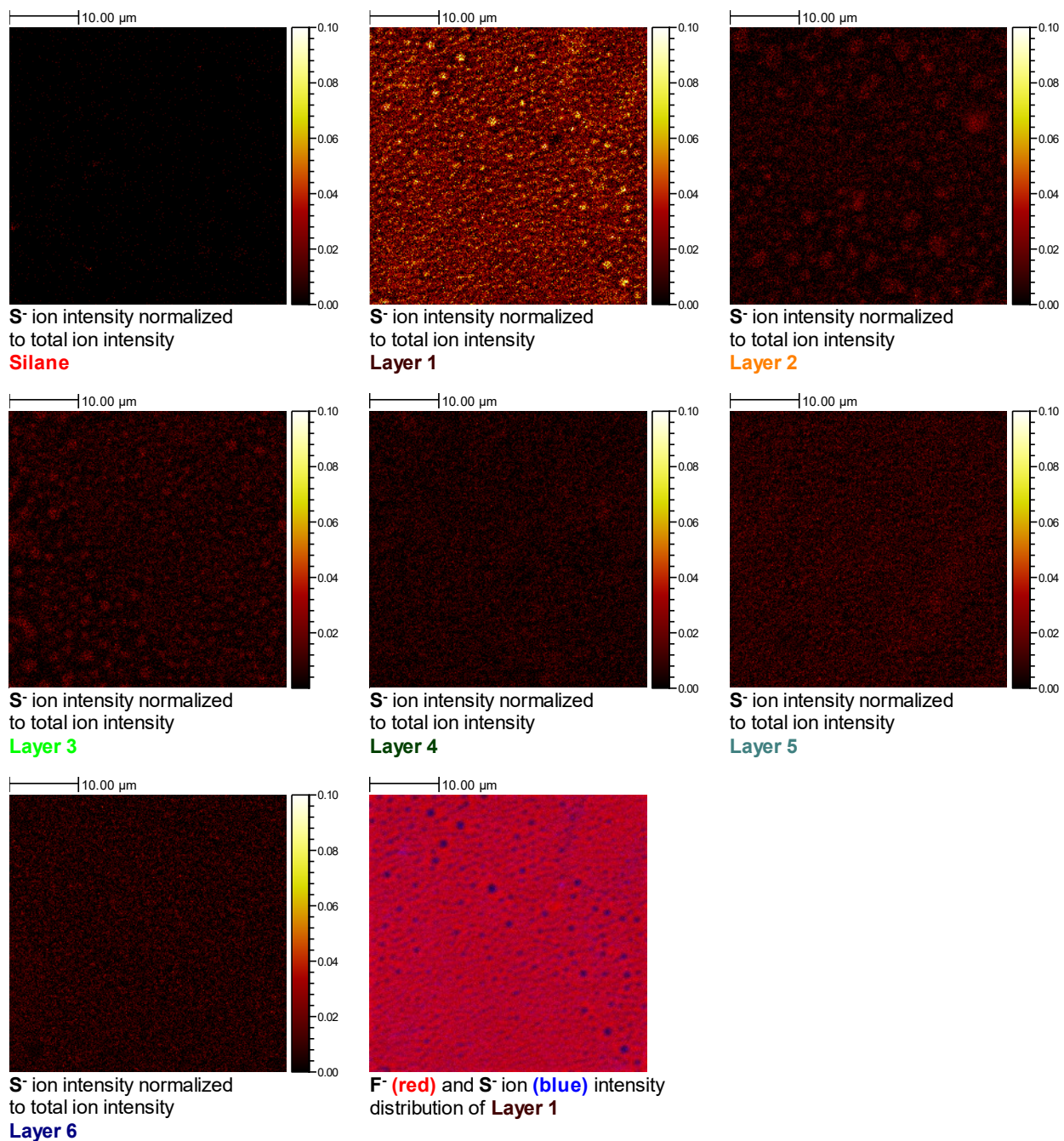


Figure S11. ToF-SIMS images obtained with delayed extraction mode showing the S⁻ ion distribution after the synthesis of each layer. Bottom right: superposition of the F⁻ and S⁻ signal of the layer 1 (first layer exhibiting this marker).

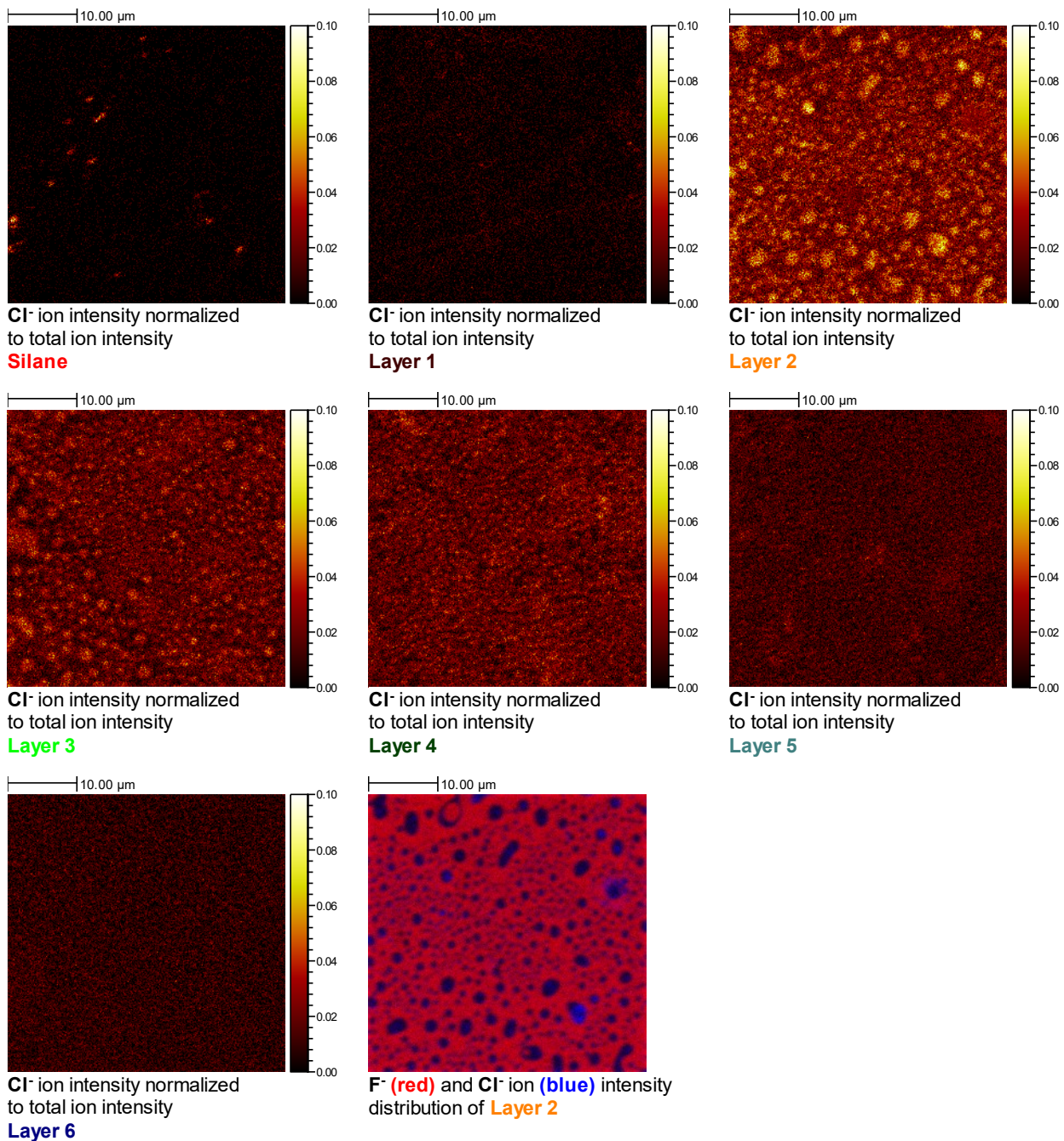


Figure S12. ToF-SIMS images obtained with delayed extraction mode showing the Cl⁻ ion distribution after the synthesis of each layer. Bottom right: superposition of the F⁻ and Cl⁻ signal of the layer 2 (first layer exhibiting this marker).

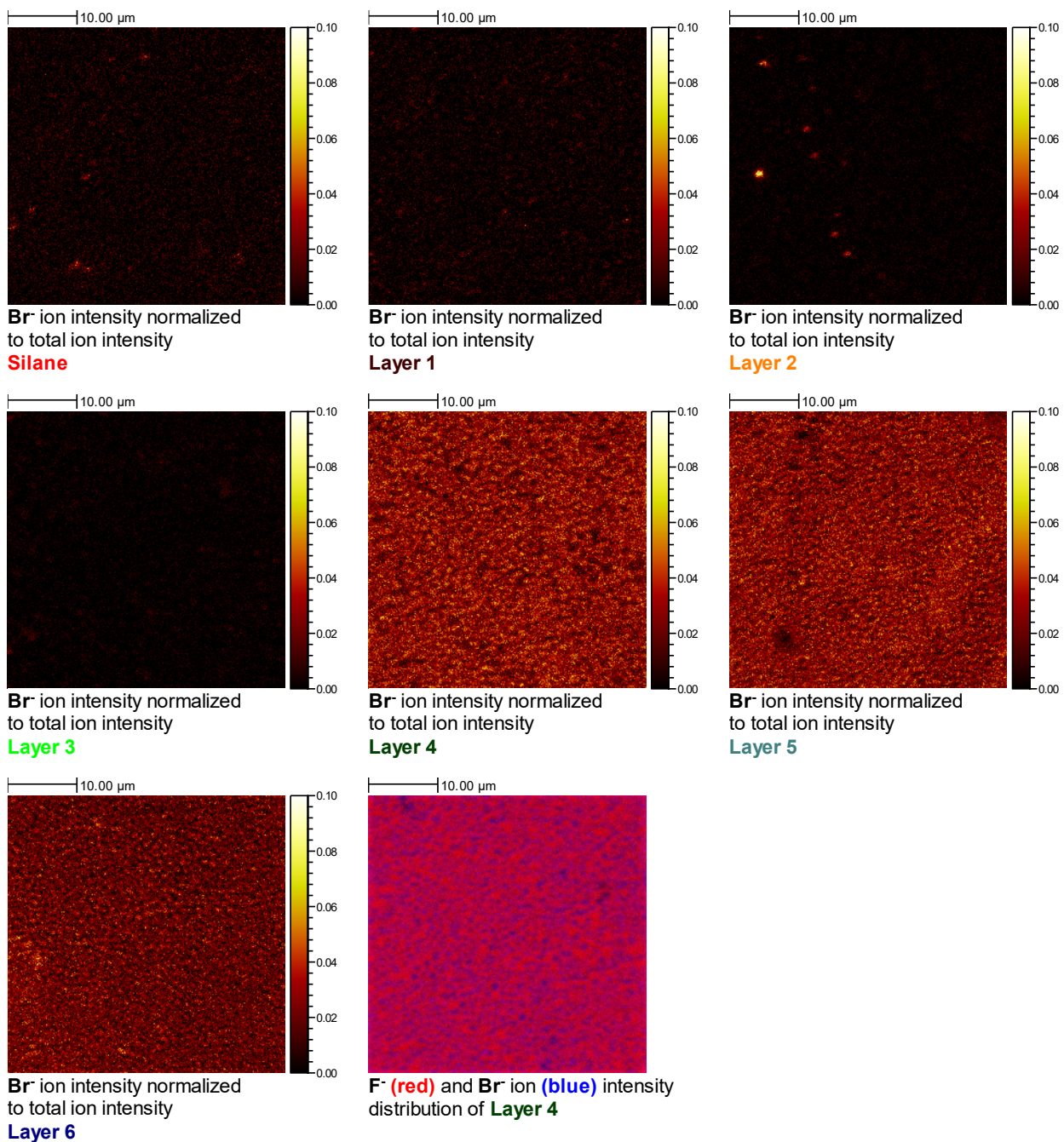


Figure S13. ToF-SIMS images obtained with delayed extraction mode showing the Br⁻ ion distribution after the synthesis of each layer. Bottom right: superposition of the F⁻ and Br⁻ signal of the layer 4 (first layer exhibiting this marker).

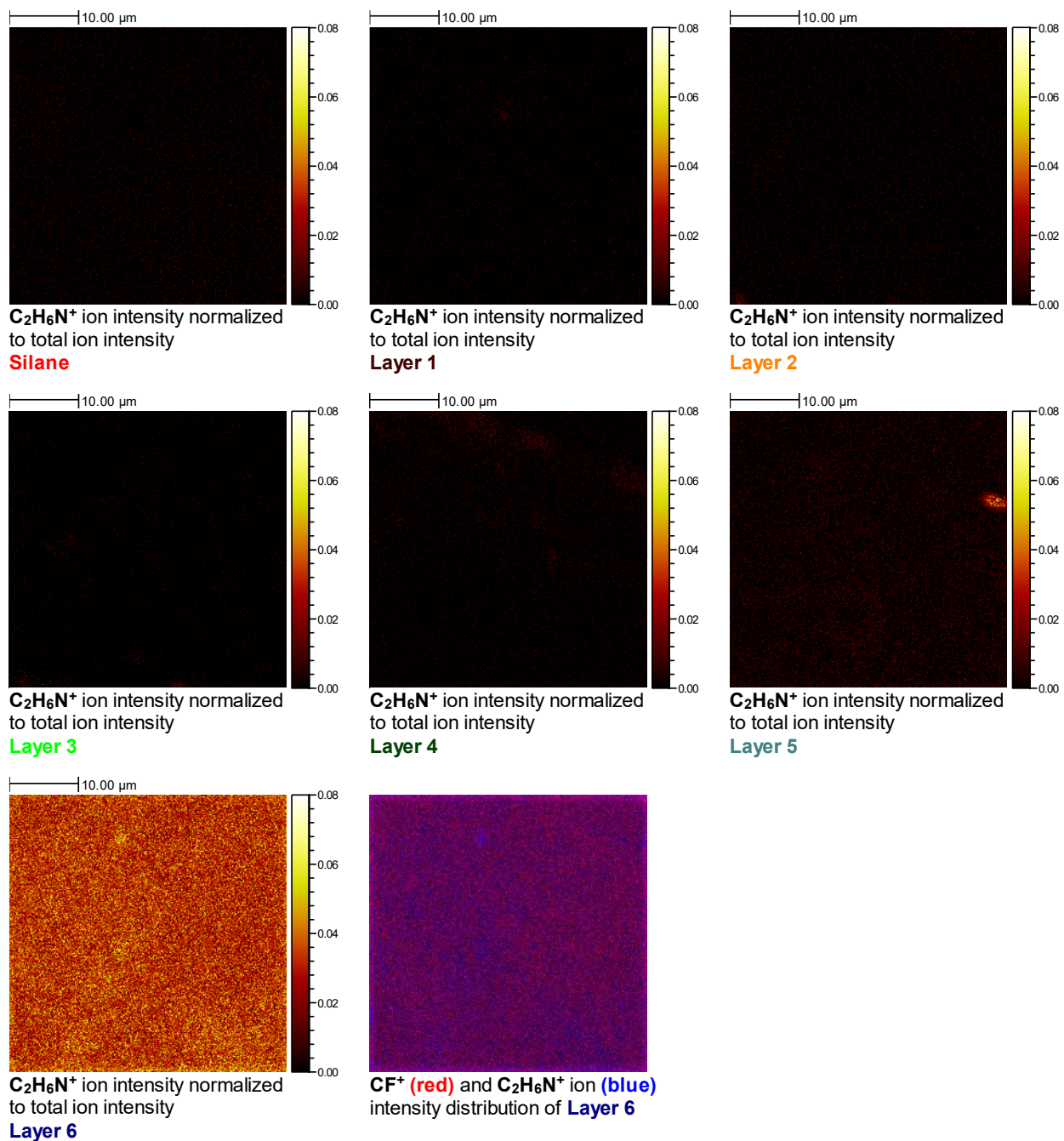


Figure S14. ToF-SIMS images obtained with delayed extraction mode showing the $C_2H_6N^+$ ion distribution after the synthesis of each layer. Bottom right: superposition of the CF^+ and $C_2H_6N^+$ signal of the layer 6 (first layer exhibiting this marker).

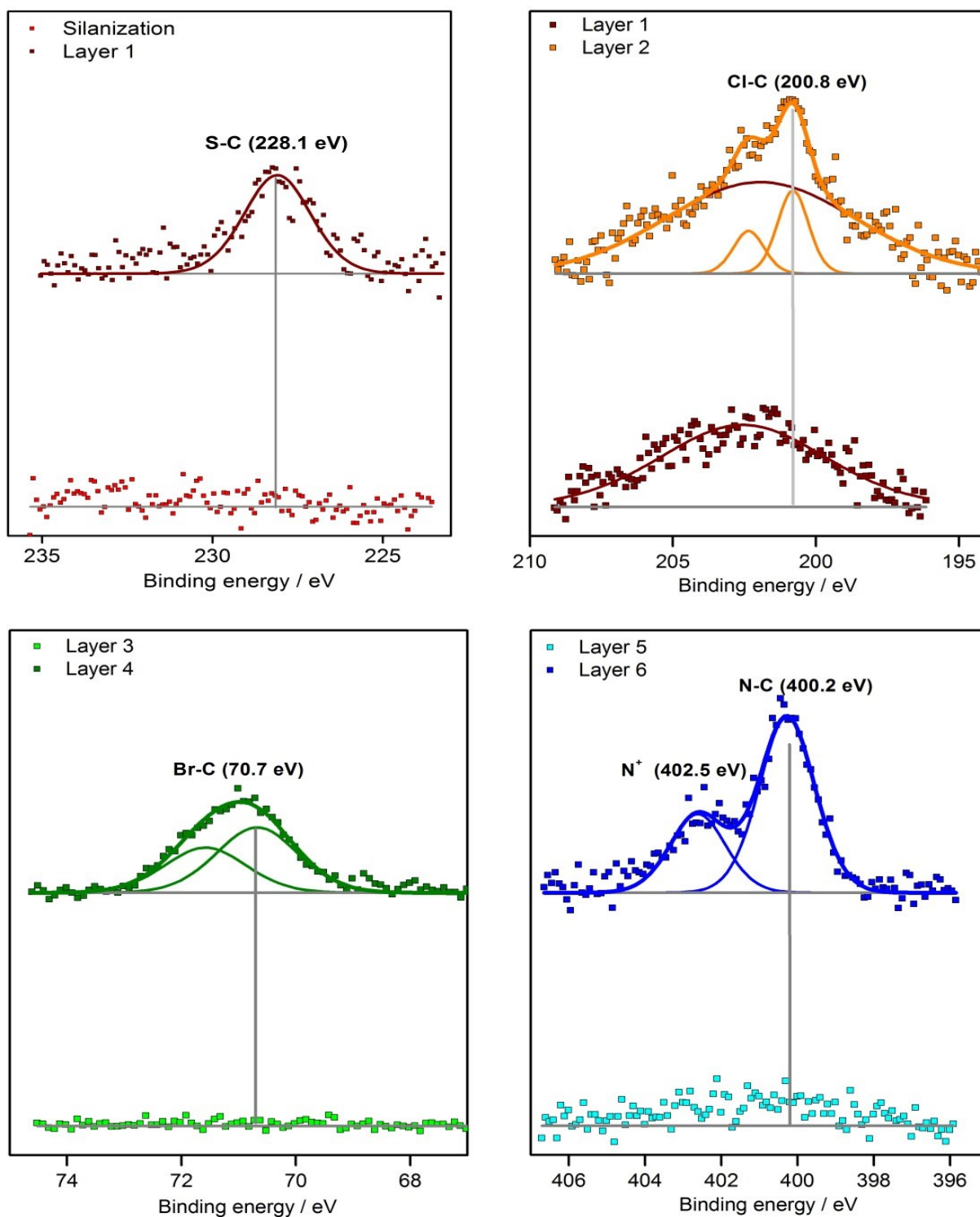
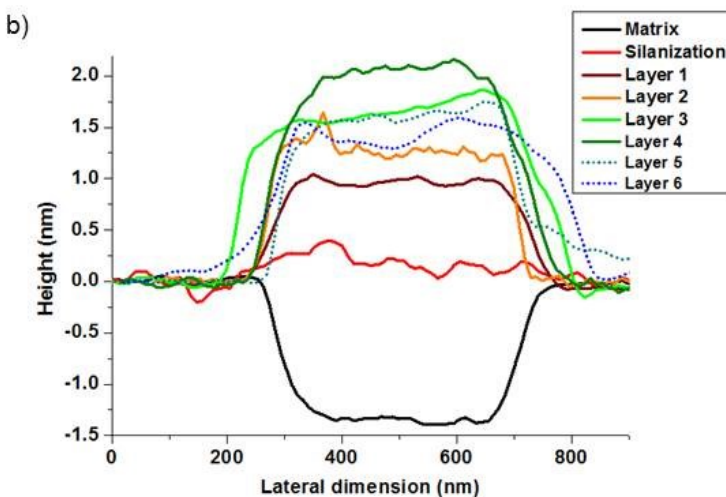
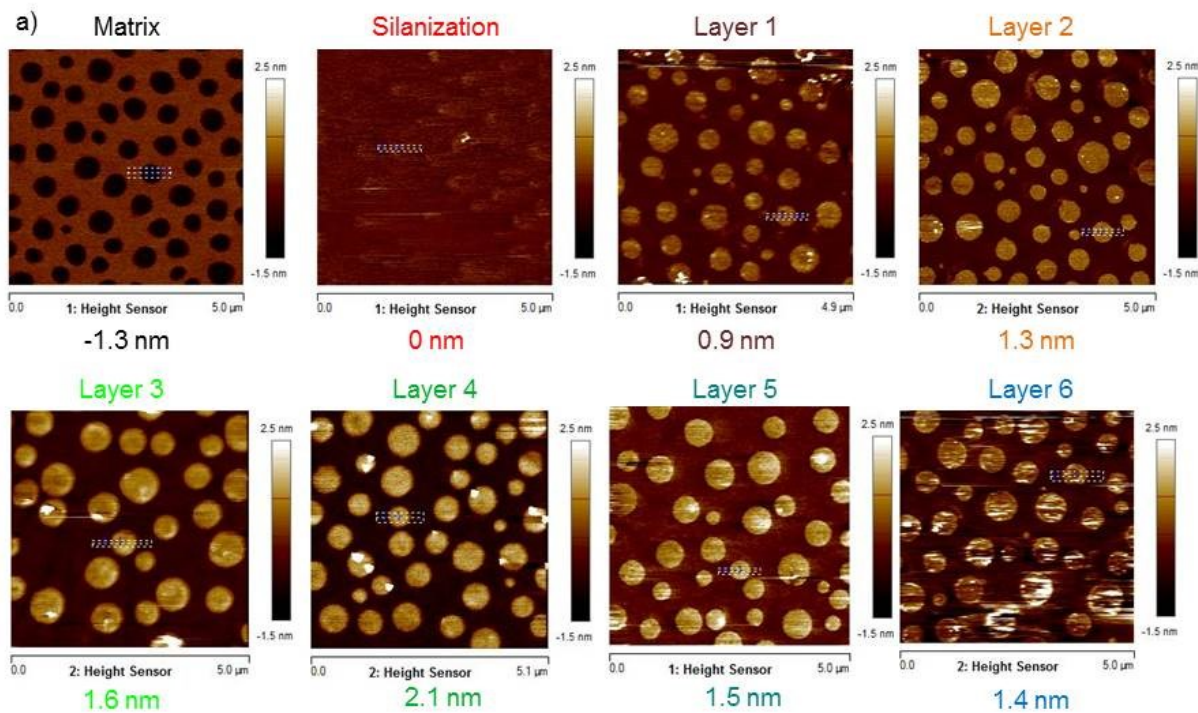


Figure S15. Recorded XPS S 2s spectra, Cl 2p spectra, Br 3d spectra and N 1s spectra of the layers where the corresponding marker molecule is introduced (top graph) and the previous layer (bottom graph). Obtained binding energies are shown in the graphs with the bond assignment. For the sulfur, the Silicon plasmon free area of the S 2s signal was chosen for analysis. In the case of chlorine, the silicon plasmon feature visible in the Cl 2p was additionally fitted to get the correct attribution of the Cl-C bond.



c)

Molecule	Theoretical height (nm)
Silane	1.4
Molecule 1	1.3
Molecule 2	1.2
Molecule 3	0.8
Molecule 4	1.2
Molecule 5	0.8
Molecule 6	0.6

Figure S16. a) AFM images of the samples after the deposition of each layer, b) Representative profile of one matrix hole after the deposition of each layer, c) Theoretical height of the molecules.

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