

Supporting Information

Patterning of proteins into nanostripes on Si-wafer over large areas: A combination of Langmuir-Blodgett patterning and orthogonal surface chemistry

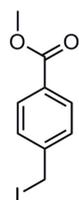
Yong Li, Julia C. Niehaus, Yueyue Chen, Harald Fuchs, Armido Studer, Hans-Joachim Galla and Lifeng Chi

Materials. All reactions were performed under an argon atmosphere using the standard schlenk technique. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker DPX-300 (^1H : 300 MHz; ^{13}C : 75 MHz), a Varian Inova 500 (^1H : 500 MHz; ^{13}C : 125 MHz), or a Varian Unity plus 600 (^1H : 600 MHz; ^{13}C : 150 MHz). Chemical shifts δ in ppm are referenced to the solvent residual peak. Thin layer chromatography was carried out on Merck silica gel 60 F254 plates; detection by UV or dipping into a solution of KMnO_4 (0.75 g), NaHCO_3 (2.5 g) in H_2O (200 mL), followed by heating. Flash chromatography (FC) was carried out on Merck or Fluka silica gel 60 (40 - 63 μm) at about 1.4 bar. ESI-MS (m/z) and HRMS (m/z) were performed using a Bruker MicroTof and a Waters-Micromass Quattro LCZ (ESI-MS).

THF was distilled from K/Na, and CH_2Cl_2 was distilled from P_2O_5 . The following chemicals were purchased and used as received: acetonitrile (Acros, 99.9 % over molecular sieve), sodium iodide (Sigma Aldrich, p.a.), sodium hydride (Acros, 60 % suspended in mineral oil), DIBAL (Acros, 1.1 M in cyclohexane), 2,2-dimethoxy-2-phenylacetophenon (DMPA) (Acros, 99 %), DMF (Acros, 99.8%, extra dry, over molecular sieve), D(+)-biotin (Alfa Aesar, 98%+), lithium acetylide-ethylenediamine complex (Alfa Aesar, 90%), DMSO (Acros, 99.7%, extra dry, over molecular sieve), 2-butanone (Acros, 99%+, extra pure), thio urea (Fluka, p.a.), tetraethyleneglycol monomethyl ether (Acros, 98%), methanesulfonyl chloride (Acros, 99.5%), p-toluenesulfonyl chloride (Acros, 99%+), streptavidin-Oyster® 488 (Luminartis, 1 mg/mL in PBS), histidine-tagged eGFP (BioVision, 1 mg/mL in PBS, purity $\geq 97\%$), *N*-epsilon-carbobenzyloxy-L-lysine (Acros, 98%), bromoacetic acid (Fluka, $\geq 99.0\%$), palladium on activated carbon (Aldrich, 10% Palladium), 7-oct-1-enyltrichlorosilane (ABCR, 95%), *N*-hydroxysuccinimide (Aldrich, 98%), 6-heptynoic acid (Aldrich, 90%), DCC (Acros, 99%).

Azide **1** was introduced by us recently.¹

Methyl 4-(iodomethyl)benzoate

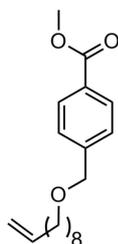


Methyl 4-(hydroxymethyl)benzoate (1.66 g, 0.01 mol, 1.00 eq) and sodium iodide (4.50 g, 30.0 mmol, 3.00 eq) were dissolved in acetonitrile (30 mL). At 0 °C chlorotrimethylsilane (1.36 mL, 0.03 mol, 3.00 eq) was added. The reaction mixture was slowly allowed to warm up to rt and was stirred for 5 h. Afterwards water was added and the phases were separated. The aqueous layer was extracted with MTBE (10 mL). The combined organic layers were washed with sodium bisulfite (10 mL, sat. aq.) and dried over magnesium sulfate. The solvent was removed under reduced pressure. The iodide was obtained as white solid (2.76 g, 10.0 mmol, 99%).

¹H-NMR (300 MHz; CDCl₃): δ = 7.96 (*d*, *J* = 8.3, 2H, Ar-*H*); 7.43 (*d*, *J* = 8.2, 2H, Ar-*H*); 4.46 (*s*, 2H, CH₂); 3.91 (*s*, 3H, CH₃).

The spectroscopic data are in agreement with those reported in the literature.²

4-Dec-9-enyloxymethyl-benzoic acid methyl ester

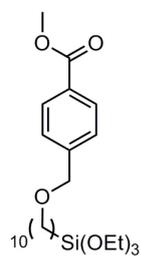


Sodium hydride (60% in mineral oil, 0.36 g, 8.8 mmol, 1.8 eq) was suspended in THF (30 mL). 9-Decen-1-ol (1.45 mL, 8.10 mmol, 1.60 eq) was added. The mixture was stirred for 2 h at rt. Afterwards methyl 4-(iodomethyl)-benzoate (1.15 g, 5.00 mmol, 1.00 eq) was added. The reaction mixture was stirred at rt over night. For working-up ammonium chloride (5 mL, sat. aq.) was added and the phases were separated. The aqueous layer was extracted twice with diethylether (2 × 5 mL). The combined organic layers were washed with brine solution (5 mL, sat. aq.) and dried over magnesium sulfate. The solvent was removed under reduced pressure and the crude product was directly suspended in methanol (20 mL). Sodium methoxide (140 mg, 2.60 mmol, 1.50 eq) was added. The reaction mixture was stirred at rt for 20 h. Afterwards ammonium chloride (2 mL, sat. aq.) and DCM (5 mL) were added, the phases were separated and the aqueous layer was extracted with DCM (2 × 3 mL). The combined organic layers were washed with brine (3 mL, sat. aq.) and dried over magnesium sulfate. The solvent was

removed under reduced pressure and the crude product was purified by FC (MTBE/Pe, 1:20). The ether was obtained as a yellow oil (466 mg, 1.53 mmol, 40%).

IR: 3075_w, 2927_s, 2855_s, 1726_s, 1640_w, 1435_m, 1278_s, 1107_s, 702_m. ¹H-NMR (300 MHz; CDCl₃): δ = 8.01 (*d*, *J* = 8.2, 2H, Ar-*H*); 7.40 (*d*, *J* = 8.2, 2H, Ar-*H*); 5.80 (*ddt*, *J*₁ = 17.0, *J*₂ = 10.2, *J*₃ = 6.7, *J*₄ = 6.7, 1H, CH₂=CH); 4.99 (*ddd*, *J*₁ = 17.0, *J*₂ = 2.2, *J*₃ = 1.4, 1H, CH_AH_BCH); 4.94 (*ddd*, *J*₁ = 10.2, *J*₂ = 2.2, *J*₃ = 1.3, 1H, CH_AH_BCH); 4.55 (*s*, 2H, Ar-CH₂O); 3.91 (*s*, 3H, OCH₃); 3.47 (*t*, *J* = 6.6, 2H, OCH₂CH₂); 2.08 - 1.98 (*m*, 2H, CH₂CHCH₂); 1.67 - 1.55 (*p*, *J* = 6.6, 2H, OCH₂CH₂); 1.40 - 1.22 (*m*, 10H, 5 × CH₂). ¹³C-NMR (75 MHz, CDCl₃): δ = 166.9 (C), 144.1 (C), 139.2 (CH), 129.6 (2 × CH), 129.2 (C), 127.1 (2 × CH), 114.1 (CH₂), 72.2 (CH₂), 70.9 (CH₂), 52.1 (CH₃), 33.8 (CH₂), 29.7 (CH₂), 29.4 (2 × CH₂), 29.1 (CH₂), 28.9 (CH₂), 26.2 (CH₂). ESI-MS: (327 (100, [M+Na]⁺), 631 (30, [2 × M+Na]⁺); HRMS (ESI⁺) calculated for [M+Na]⁺: 327.1931; found: 327.1932; Elem. anal. calculated for C₁₉H₂₈O₃: C 74.96, H 9.27; found: C 74.85, H 9.47.

4-((10-(Triethoxysilyl)decyloxy)methyl)-benzoic acid methyl ester



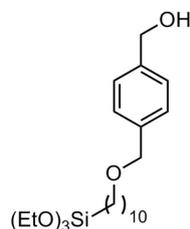
The alkene (302 mg, 1.00 mmol, 1.00 eq) was dissolved in triethoxysilane (370 μL, 2.00 mmol, 2.00 eq) and the resulting solution was heated to 40 °C. At this temperature *Karstedt* catalyst (5 μL, 0.01 mmol, 0.01 eq) was added. The reaction mixture was stirred for 2 h at 40 °C. Afterwards cyclohexane (1.6 mL) und 1,2-propenylcarbonate (1.6 mL) were added. The phases were separated.

The propenylcarbonate phase was extracted with cyclohexane (1 mL). The combined cyclohexane containing phases were concentrated under reduced pressure. The crude product was purified by FC (MTBE/Pe, 1:15 + 1% NEt₃). The product was obtained as a colorless oil (0.27 g, 0.60 mmol, 60%).

IR: 2974_s, 2927_s, 2856_s, 1727_s, 1278_s, 1106_s, 969_m, 793_m. ¹H-NMR (300 MHz; CDCl₃): δ = 8.01 (*d*, *J* = 8.2, 2H, Ar-*H*); 7.40 (*d*, *J* = 8.2, 2H, Ar-*H*); 4.54 (*s*, 2H, ArCH₂O); 3.91 (*s*, 3H, OCH₃); 3.81 (*q*, *J* = 7.0, 6H, 3 × SiOCH₂); 3.47 (*t*, *J* = 6.6, 2H, OCH₂CH₂); 1.67 - 1.55 (*m*, 2H, OCH₂CH₂); 1.40 - 1.22 (*m*, 14H, 7 × CH₂); 1.23 (*t*, *J* = 7.0, 9H, 3 × CH₃), 0.64 - 0.60 (*m*, 2H, CH₂Si). ¹³C-NMR (75 MHz, CDCl₃): δ = 166.9 (C), 144.1 (C), 129.6 (2 × CH), 129.2 (C), 127.0 (2 × CH), 72.2 (CH₂), 70.9 (CH₂), 58.2 (3 × CH₂), 52.0 (CH₃), 33.8 (CH₂), 29.7 (CH₂), 29.5 (2 × CH₂), 29.4 (CH₂), 29.2 (CH₂), 26.2 (CH₂), 22.7 (CH₂), 18.3 (3 × CH₃), 10.4 (CH₂). ESI-MS: 491 (100, [M+Na]⁺), 960 (3, [2 × M+Na]⁺); HRMS (ESI⁺) calculated for [M+Na]⁺:

491.2799; found: 491.2798; Elem. anal. calculated for $C_{25}H_{44}O_6Si$: C 64.06, H 9.46; found: C 64.00, H 9.67.

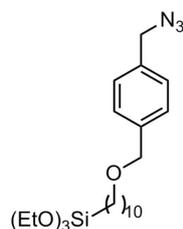
(4-((10-(Triethoxysilyl)decyloxy)methyl)phenyl)methanol



The ester (95 mg, 0.20 mmol, 1.0 eq) was dissolved in DCM (3 mL). The reaction mixture was cooled to $-78\text{ }^{\circ}\text{C}$. At this temperature DIBAL (1.1M in cyclohexane, 0.21 mL, 0.21 mmol, 1.05 eq) was added. The solution was allowed to warm up to rt and was stirred for 3 h at rt. After this time ethanol (1 mL) was added. Solids were removed by filtration over celite and the solvent was removed under reduced pressure. The product (80 mg, 0.18 mmol, 91%) was obtained as colorless oil.

IR: 3449 w , 2973 s , 2926 s , 2855 s , 1460 w , 1103 s . $^1\text{H-NMR}$ (300 MHz; CDCl_3): δ = 7.33 - 7.35 (m , 4H, Ar- H); 4.67 (s , 2H, Ar CH_2OH); 4.49 (s , 2H, Ar CH_2O); 3.81 (q , J = 7.0, 6H, 3 \times SiO CH_2); 3.44 (t , J = 4.4, 2H, O CH_2); 1.79 ($br\ s$, 1H, OH); 1.61 (p , J = 4.2, 2H, O CH_2CH_2); 1.30 - 1.24 (m , 14H, 7 \times CH_2); 1.23 (t , J = 7.0, 9H, 3 \times CH_3); 0.68 - 0.60 (m , 2H, CH_2Si). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): δ = 139.9 (C), 130.3 (C), 129.6 (2 \times CH), 127.8 (2 \times CH), 72.5 (CH_2), 70.5 (CH_2), 65.1 (CH_2), 58.3 (3 \times CH_2), 33.2 (CH_2), 29.7 (CH_2), 29.6 (CH_2), 29.5 (2 \times CH_2), 29.2 (CH_2), 26.2 (CH_2), 22.7 (CH_2), 18.3 (3 \times CH_3), 10.3 (CH_2). ESI-MS: 463 (100, $[\text{M}+\text{Na}]^+$); HRMS (ESI $^+$) calculated for $[\text{M}+\text{Na}]^+$: 463.2850; found: 463.2827; Elem. anal. calculated for $C_{24}H_{44}O_5Si$: C 65.41, H 10.06; found: C 65.29, H 10.18.

(10-(4-(Azidomethyl)benzoyloxy)decyl)triethoxysilane

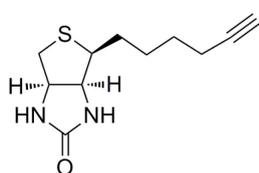


The alcohol (0.22 g, 0.50 mmol, 1.0 eq) and triphenylphosphine (144 mg, 550 μmol , 1.10 eq) were dissolved in DCM (3 mL). At $0\text{ }^{\circ}\text{C}$ a toluene solution of HN_3 (prepared after an instruction in „Org. Reactions“^{cx2}) (10 % in toluene, 6 mL, 0.55 mmol, 1.1 eq) and diethyl azodicarboxylate (87 μL , 0.55 mmol, 1.1 eq) were added. The reaction mixture was stirred at $0\text{ }^{\circ}\text{C}$ for 30 min and afterwards at rt for 6 h. After this time the solvent was removed under reduced pressure and the crude product was purified by FC (MTBE/Pe, 1:15 + 1% NEt_3). Azide **1** (0.14 g, 0.30 mmol, 60%) was obtained as a colorless oil.

IR: 2974 s , 2926 s , 2855 s , 2361 w , 2098 s , 1458 w , 1390 w , 1103 s , 1098 s , 958 m , 792 m . $^1\text{H-NMR}$ (300 MHz; CDCl_3): δ = 7.36 (d , J = 8.2, 2H, Ar- H); 7.29 (d , J = 8.2, 2H, Ar- H); 4.50 (s , 2H, Ar CH_2O); 4.32 (s , 2H, Ar CH_2N_3); 3.81 (q , J = 7.0, 6H, 3 \times SiO CH_2); 3.48 (t , J = 6.6, 2H,

OCH₂); 1.62 (*p*, *J* = 6.6, 2H, OCH₂CH₂); 1.45 - 1.25 (*m*, 14H, 7 × CH₂); 1.23 (*t*, *J* = 7.0, 9H, 3 × CH₃); 0.65 - 0.59 (*m*, 2H, CH₂Si). ¹³C-NMR (75 MHz, CDCl₃): δ = 139.1 (C), 134.5 (C), 128.2 (2 × CH), 127.9 (2 × CH), 72.4 (CH₂), 70.7 (CH₂), 58.3 (3 × CH₂), 54.6 (CH₂), 33.2 (CH₂), 29.8 (CH₂), 29.6 (2 × CH₂), 29.5 (CH₂), 29.2 (CH₂), 26.2 (CH₂), 22.8 (CH₂), 18.3 (3 × CH₃), 10.4 (CH₂); ESI-MS: 488 (100, [M+Na]⁺); HRMS (ESI⁺) calculated for [M+Na]⁺: 488.2915; found: 488.2916; Elem. anal. calculated for C₂₄H₄₃O₄Si: C 61.90, H 9.31, N 9.02; found: C 61.89, H 9.33, N 9.35.

(3aR,6S,6aS)-6-Hept-6-ynyl-tetrahydro-thieno[3,4-*d*]imidazol-2-one 3

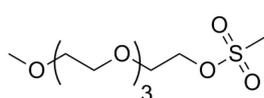


Biotin alkyne **3** was synthesized after an experimental procedure published by *Corona et al.*³

¹H-NMR (300 MHz; CDCl₃): δ = 4.54 (*m*, 1H, CHNH); 4.33 (*dd*, *J*₁ = 7.7, *J*₂ = 4.7, 1H, CHNH); 3.18 (*ddd*, *J*₁ = 7.9, *J*₂ = 6.6, *J*₃ = 4.8, 1H, SCH); 2.94 (*dd*, *J*₁ = 12.9, *J*₂ = 5.0, 1H, CH_AH_BS); 2.76 (*d*, *J* = 12.8; 1H, CH_AH_BS); 2.20 (*dt*, *J*₁ = 6.7, *J*₂ = 6.7, *J*₃ = 2.6, 2H, CH₂CCH); 1.94 (*t*, *J* = 2.6, 1H, CCH); 1.74 – 1.63 (*m*, 2H; CH₂); 1.59 – 1.35 (*m*, 6H, 3 × CH₂).

The spectroscopic data are in agreement with those reported in the literature.³

Methanesulfonic acid 2-{2-[2-(2-methoxy-ethoxy)-ethoxy]-ethoxy}-ethyl ester

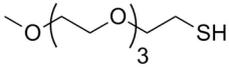


Tetraethylen glycol monomethylether (2.1 mL, 10 mmol, 1.0 eq) and sodium hydride (60% in mineral oil, 0.44 g, 11.0 mmol, 1.10 eq) were added to THF (50 mL). Mesyl chloride (0.85 mL, 11.0 mmol, 1.10 eq) was added slowly to this suspension. The reaction mixture was refluxed for 6 h. After cooling to rt the solvent was removed under reduced pressure and the crude product was purified by flash chromatography at SiO₂ with EtOAc as eluent. The product was obtained as a colorless oil (1.9 g, 6.6 mmol, 66%).

¹H (270 MHz, CDCl₃): δ = 4.38 – 4.33 (*m*, 2H, CH₂OMs); 3.77 – 3.72 (*m*, 2H, CH₂); 3.67 – 3.57 (*m*, 10H, 5 × CH₂); 3.55 – 3.50 (*m*, 2H, CH₂); 3.35 (*s*, 3H, CH₃); 3.06 (*s*, 3H, CH₃).

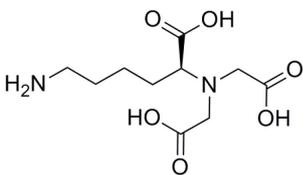
The spectroscopic data are in agreement with those reported in the literature.⁴

2-{2-[2-(2-Methoxy-ethoxy)-ethoxy]-ethoxy}-ethanethiol **4**

 Mesylate (1.9 g, 6.6 mmol, 1.0 eq) and thio urea (0.63 g, 8.32 mmol, 1.26 eq) were dissolved in ethanol (40 mL). The reaction mixture was refluxed for 12 h. Sodium hydroxide (1M, 13.2 mL, 13.2 mmol, 2.0 eq) was added and refluxing was continued for 2 h. After cooling to rt aqueous HCl (1M) was added until a neutral pH was reached. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography at SiO₂ with EtOAc as eluent. The product **4** was isolated as a colorless oil (331 mg, 1.48 mmol, 22.0%). ¹H (270 MHz, CDCl₃): δ = 3.66 – 3.54 (*m*, 10H, 5 × CH₂); 3.54 – 3.38 (*m*, 2H, CH₂); 3.34 (*s*, 3H, CH₃); 2.70 – 2.60 (*m*, 2H, CH₂); 1.55 (*t*, *J* = 8.2, 1H, SH).

The spectroscopic data are in agreement with those in the literature.⁵

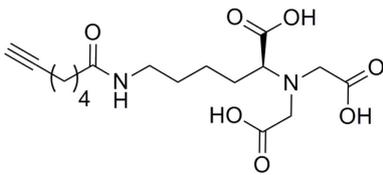
(1*S*)-*N*-(5-Amino-1-carboxypentyl)iminodiacetic acid

 NTA amine was synthesized after an experimental procedure published by *Du Roure et al.*⁶

¹H-NMR (300 MHz; D₂O): δ = 4.05 – 3.82 (*m*, 5H, 2 × CH₂, 1 × CH); 3.04 (*t*, *J* = 6.9, 2H, NCH₂); 2.08 – 1.82 (*m*, 2H, CH₂); 1.81 – 1.44 (*m*, 4H, 2 × CH₂).

The spectroscopic data are in agreement with those reported in the literature.⁶

(*S*)-2-(Bis-carboxymethyl-amino)-6-hept-6-ynoylamino-hexanoic acid **3**

 6-Heptynoic acid (0.63 mL, 5.00 mmol, 1.00 eq) and N-hydroxysuccinimide (853 mg, 5.50 mmol, 1.10 eq) were dissolved in DMF (50 ml). DCC (1.14 g, 6.00 mmol, 1.20 eq) was added slowly. The reaction mixture was stirred at rt for 24 h. The precipitation was removed by filtration and the solvent was removed under reduced pressure. The resulting solid was washed with methanol and dried. The resulting NHS ester was used without further purification.

NHS ester (1.25 g, 5.00 mmol, 1.00 eq) was dissolved in acetone (5 mL) and ethanol (50 mL). A solution of NTA amine (1.58 g, 6.00 mmol, 1.20 eq) and sodium bicarbonate (1.68 g, 20 mmol, 4.00 eq) in water (25 mL) was dropwise added to the NHS ester solution. The reaction mixture was stirred for 43 h at rt. The solvent was removed under reduced pressure. Water (25 mL) and sodium bicarbonate (aq. 0.25 M, 10 mL) were added and the precipitation was removed by filtration. The solution was acidified to pH 3 using hydrochloric acid (aq. 1 M). The solvent was removed under reduced pressure and the crude product was purified by flash chromatography at SiO₂ with DCM/Methanol/water (3:1:0.1) as eluent. The product **3** was obtained as a white solid (1.67 g, 4.50 mmol, 91%).

IR: 3289 m , 2944 m , 2871 w , 2363 m , 2334 m , 1734 s , 1718 s , 1623 s , 1559 s , 1437 m , 1374 m , 1242 s , 1895 w . ¹H-NMR (300 MHz; D₂O): δ = 4.11 – 3.88 (m , 5H, 2 \times CH₂, 1 \times CH); 3.37 (s , 2H, CH₂N); 3.30 – 3.18 (m , 2H, CH₂); 2.40 – 2.35 (m , 1H, CCH); 2.33 – 2.21 (m , 4H, 2 \times CH₂); 2.10 – 1.83 (m , 2H, CH₂); 1.80 – 1.46 (m , 8H, 4 \times CH₂). ¹³C-NMR (75 MHz, CD₃OD): δ = 176.8 (4 \times C), 85.5 (CH), 70.6 (CH), 67.5 (CH), 56.2 (2 \times CH₂), 40.9 (CH₂), 37.4 (CH₂), 31.6 (CH₂), 30.8 (CH₂), 30.1 (CH₂), 25.6 (CH₂), 19.6 (2 \times CH₂). ESI-MS: 371 (100 [M+H]⁺), 393 (11 [M+Na]⁺); HRMS (ESI⁺) calculated for [M+H]⁺: 371.1813; found: 371.1808.

CuAAC on silicon wafers

The bifunctional silicon wafer was placed into a 0.5 M solution of the alkyne **2** or **3** in EtOH/H₂O (1:2, 1 mL). Copper(II) sulfate (8.0 mg, 50 μ mol, 0.1 eq) and sodium ascorbate (20 mg, 0.1 mmol, 0.2 eq) were added. The system was allowed to stand for 12 h at rt. After removal of the wafer from the reaction mixture, the wafer was sonicated in following solvents: DCM, acetone, ethanol and water (each 5 min) and dried under an argon flow.

Thiol ene reaction on silicon wafers

The bifunctional silicon wafer was placed in a 0.5 M solution of EG4 thiol **4** in DMF (1 mL). 2,2-dimethoxy-2-phenylacetophenon (DMPA) (2 mg) was added and the reaction was irradiated with a tungsten lamp for 5 h (distance lamp/reaction vessel around 10 cm). After removal of the wafer from the reaction mixture, the wafer was sonicated in following solvents: DCM, acetone, ethanol and water (each 5 min) and dried under an argon flow.

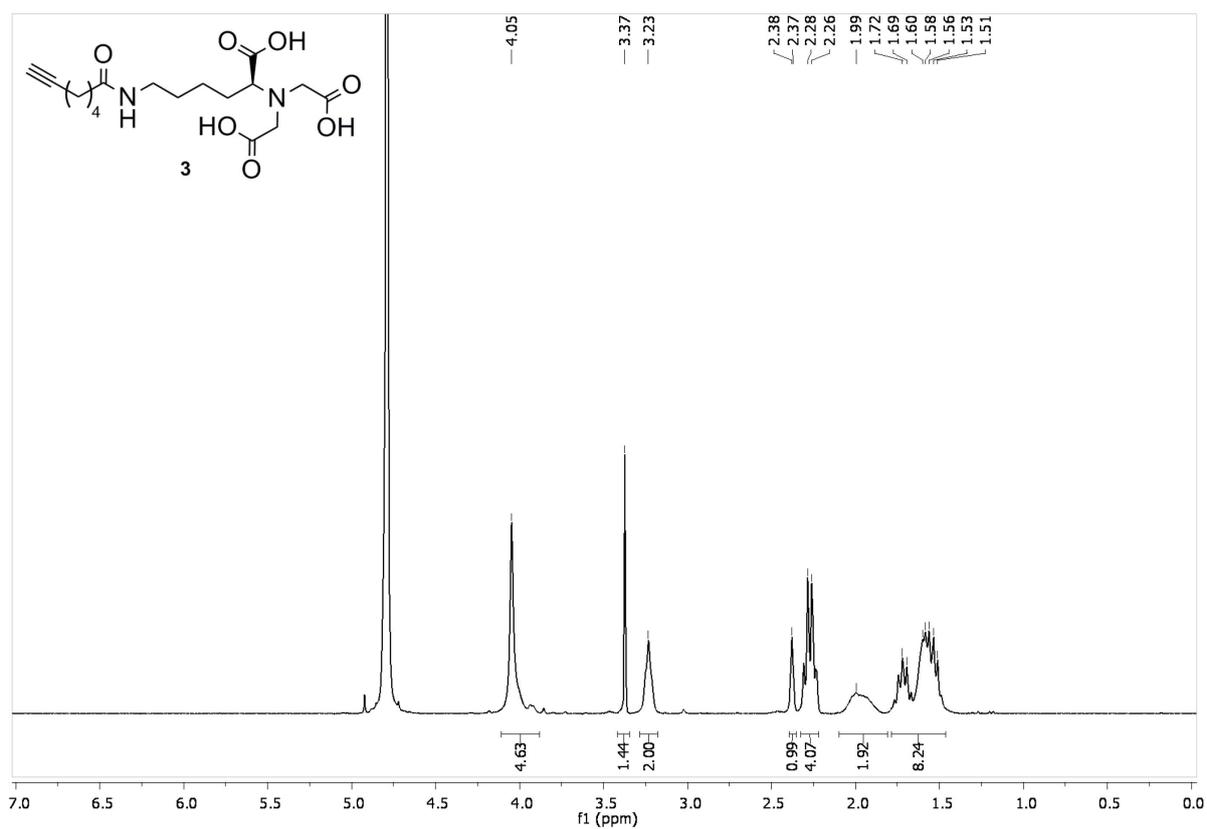
Immobilisation of Streptavidin

A solution of streptavidin modified with fluorescent dye in PBS buffer was spread onto the silicon wafer. The system was allowed to stand for 4 h at 4 °C. Afterwards the wafer was washed several times with MilliQ water and dried under an argon flow.

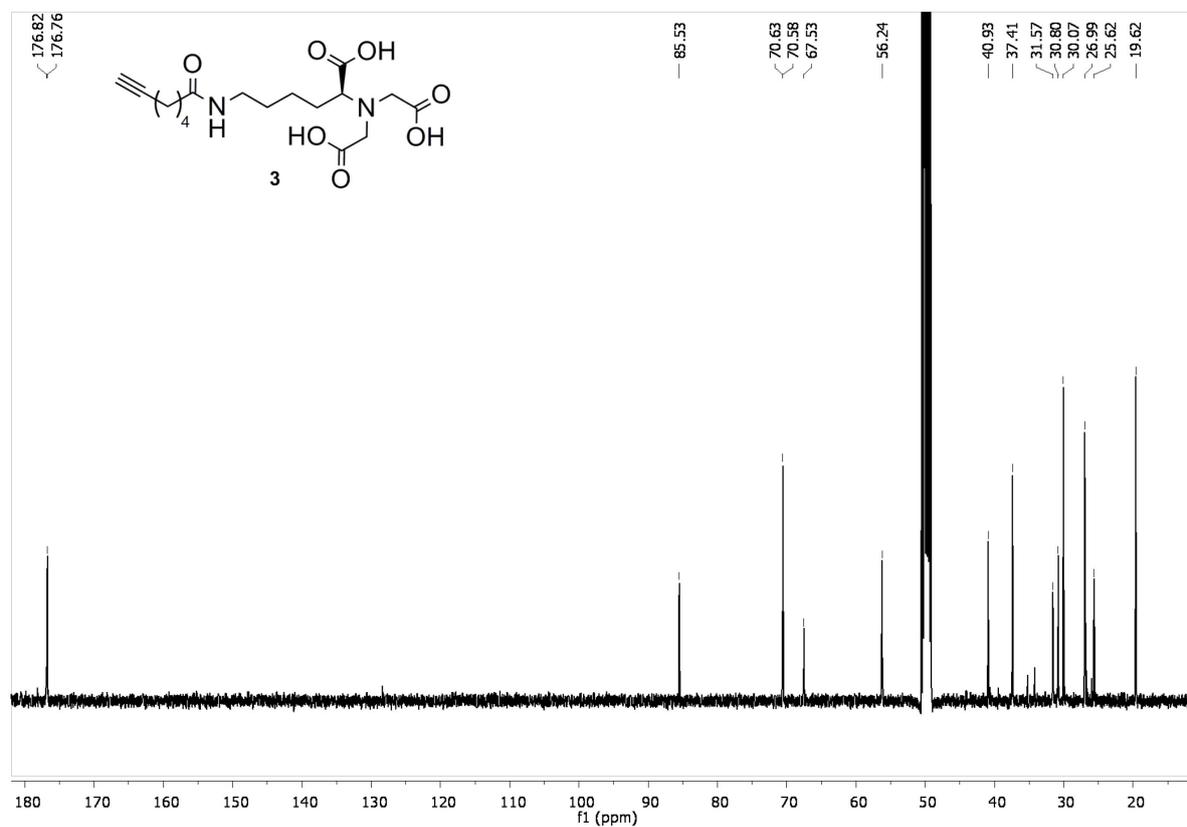
Immobilisation of eGFP

The wafer was put into a solution of EDTA (aq. 100 mM) and left standing for 1 h. Then the wafer was sonicated using MilliQ water (2×5 min) and put into a solution of Nickel(II)-sulfate (aq. 100 mM) for 1 h. The wafer were washed with MilliQ water several times and dried under an Argon flow. A solution of histag modified eGFP in PBS buffer was spread onto the silicon wafer. The system was allowed to stand for 4 h at 4 °C. Afterwards the wafer was washed several times with MilliQ water and dried under an argon flow.

¹H-NMR spectra of 3



¹³C-NMR spectra of 3



References

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