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Supporting Information

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Site-Selective Surface-Initiated Polymerization by Langmuir-Blodgett-Lithography

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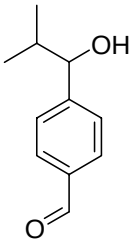
Materials

Styrene and n-butyl acrylate were both distilled under reduced pressure from CaH_2 to remove stabilizer. Et_2O was distilled over K/Na, benzene was distilled from Na, THF was distilled from K and CH_2Cl_2 was distilled from P_2O_5. L-α-dipalmitoyl-phosphatidylcholine (DPPC, grade >99%) was purchased from Fluka and used without further purification. The chloroform used for solutions in the LB-experiments was HPLC grade. Chloroform and isopropanol used for precleaning of substrates were per analysis grade. All other chemicals were used as received.

General

^1H NMR and ^{13}C NMR spectra were recorded on a ARX-300 (300 MHz, Bruker) or AMX-400 (400 MHz, Bruker). Chemical shifts δ in ppm are referenced to $SiMe_4$ as an internal standard. TLC was carried out on Merck silica gel 60 F_{254} plates; detection by UV or dipping into a solution of $KMnO_4$ (1.5 g), $NaHCO_3$ (5.0 g) and H_2O (400 mL) followed by heating. Flash chromatography (FC) was carried out on Merck or Fluka silica gel 60 (40 – 63 μm) at about 0.4 bar. Melting points were determined on a SMP 10 apparatus (Stuart Scientific) and are uncorrected. IR spectra were recorded on a Digilab FTS 4000 equipped with a MKII Golden Gate Single Reflection ATR System or on a Bruker IFS 28. ESI-MS and HRMS were performed using a Bruker MicroTof and a Waters-Micromass Quattro LCZ (only ESI-MS). GC/MS measurements were taken on a GC/MS system Waters-Micromass GCToF [quartz capillary column: HP-U5 (inner diameter: 0.25 mm, film thickness: 0.25 μm, length: 25 m)]. Size exclusion chromatography (SEC) was carried out with degased THF as eluent at a flow rate of 1.0 ml/min at r.t. on a system consisting of a L6200A Intelligent Pump (Merck Hitachi), a set of two PLgel 5 μm MIXED-C columms (300 × 7.5 mm, Polymer Laboratories) and a Knauer RI Differential-Refraktometer detector. Data were analyzed with PSS WinGPC Compact V.7.20 software (Polymer Standards Service) based upon calibration curves built upon polystyrene and poly(methyl-methacrylate) standards (Polymer Laboratories Polystyrene Medium MW Calibration Kit S-M-10 to determine the molecular weight of styrene and Poly(methyl-methacrylate) Medium MW Calibration Kit M-M-10 to determine the molecular weight of n-butyl acrylate) with peak molecular weights ranging from 1660 to 1000000 g/mol. Elemental analyses were performed on a Vario EL III (Elementar-Analysensysteme GmbH) at the University of Münster. All AFM-measurements were done on a commercial AFM (Digital Instruments, Dimension 3000 with a Nanoscope IIIa controler) running in tapping mode under ambient conditions. Si cantilevers (Nanosensors) with eigenfrequencies of 250-350 kHz were used. A self-developed program, written in Visual Basic was utilized to perform the periodicity analysis on the obtained images. Images presented in this work were flattened and then used without further image editing.

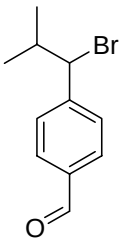
4-(1-Hydroxy-2-methylpropyl)-benzaldehyde (1a)



A solution of terephthaldehyde **1** (20.8 g, 100 mmol, 0.800 eq) in Et_2O (60 mL) was added dropwise to a solution of isopropylmagnesiumchloride [freshly prepared from magnesium (3.04 g, 125 mmol, 1.00 eq) and isopropylchloride (9.82 g, 125 mmol, 1.00 eq)] in Et_2O (60 mL) and the reaction mixture was refluxed for 3 h.
After cooling to r.t. the reaction mixture was hydrolyzed with water (10 mL). The white precipitate formed was dissolved using HCl (ca. 6M, 18 mL). After phase separation and extraction of the aquous phase using Et_2O (2 ×), the combined organic layers were washed with Na_2SO_3 (aq, sat., 50 mL), $NaHCO_3$ (aq, sat., 50 mL) and water (50 mL), were then dried over $MgSO_4$ and the solvent was removed *in vacuo*. Purification by flash chromatography (MTBE/pentane, 1:10→1:5→1:2→1:1) afforded **1a** as a yellow oil (15.2 g, 85.3 mmol, 85%).

IR: 3453*w,br*, 2962*w*, 2872*w*, 2738*w*, 1691*s*, 1606*m*, 1577*w*, 1467*w*, 1421*w*, 1386*m*, 1305*m*, 1210*m*, 1168*m*, 1011*m*, 817*s*, 781*m*. ^{1}H-NMR (400 MHz; $CDCl_3$): δ = 9.99 (*s*, 1 H, CHO); 7.85 (*m*, 2 H, Ar-H); 7.48 (*d*, *J* = 8.0 Hz, 2 H, Ar-H); 4.50 (*d*, *J* = 6.2 Hz, 1 H, C*H*OH); 2.09 (*s, br*, 1 H, OH); 2.04-1.92 (*m*, 1 H, C*H*$(CH_3)_2$); 0.96 (*d*, *J* = 6.7 Hz, 3 H, CH_3); 0.85 (*d*, *J* = 6.8 Hz, 3 H, CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 191.9 (CH), 150.6 (C), 135.7 (C), 129.6 (2 × CH), 127.1 (2 × CH), 79.2 (CH), 35.4 (CH), 18.9 (CH_3), 17.6 (CH_3). GC-MS: 178 (2, $[M]^+$), 160 (81, $[M\text{-}H_2O]^+$), 159 (81, $[M\text{-}H_2O\text{-}H]^+$), 145 (30, $[M\text{-}H_2O\text{-}CH_3]^+$), 135 (100, $[M^+\text{-}C_3H_7]$), 131 (60, $[M\text{-}CO\text{-}H_2O\text{-}H]^+$), 117 (62, $[M\text{-}C_3H_9O]^+$), 115 (88, $[M\text{-}C_3H_9O\text{-}H_2]^+$), 105 (14, $[M\text{-}C_4H_9O]^+$), 91 (80, $[C_7H_7]^+$), 79 (52, $[C_6H_7]^+$), 77 (67, $[C_6H_5]^+$), 51 (33, $[C_4H_3]^+$). Anal. calculated for $C_{11}H_{14}O_2$: C: 74.13, H: 7.92. Found: C: 74.05, H: 7.99.

4-(1-Bromo-2-methylpropyl)-benzaldehyde (2)

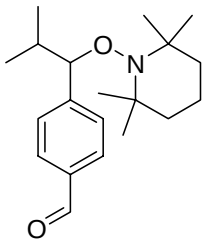


The alcohol **1a** (3.24 g, 18.2 mmol, 1.00 eq) was dissolved in CH_2Cl_2 (22 mL) and HBr (in AcOH, 33%, 5.8 mL, 23.6 mmol, 1.30 eq) was added at 0 °C. The reaction mixture was allowed to warm up to r.t. during 4.5 h. After addition of water, the phases were separated and the organic layer was washed with water, $NaHCO_3$ (aq, sat., 2 ×), NaCl (aq, sat.), and water. The organic layer was dried with $MgSO_4$ and the solvent. Purification of the crude product by flash chromatography (MTBE/pentane, 1:30) afforded the benzylic bromide **2** as a yellow oil (3.77 g, 15.6 mmol, 85%).

IR: 2966*w*, 1696*s*, 1605*m*, 1577*w*, 1466*w*, 1387*w*, 1305*w*, 1210*m*, 1169*m*, 819*m*, 783*s*, 730*w*, 673*m*. ^{1}H-NMR (300 MHz; $CDCl_3$): δ = 10.01 (*s*, 1 H, CHO); 7.87-7.83 (*m*, 2 H, Ar-H); 7.53 (*d*, *J* = 8.2 Hz, 2 H, Ar-H); 4.73 (*d*, *J* = 8.4 Hz, 1 H, CHBr); 2.39-2.26 (*m*, 1 H, C*H*$(CH_3)_2$); 1.20 (*d*, *J* = 6.5 Hz, 3 H, CH_3); 0.88 (*d*, *J* = 8.4 Hz, 3 H, CH_3). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 191.4 (CH), 148.1 (C), 136.0 (C), 129.9 (2 × CH), 128.6 (2 × CH),

62.3 (CH), 36.3 (CH), 21.3 (CH_3), 20.4 (CH_3). ESI-MS: 519 (64, $[2M+Na]^+$), 381 (41), 295 (13, $[M+MeOH+Na]^+$), 263 (39, $[M+Na]^+$), 215 (100, $[ArC(OMe)iPr+Na]^+$), 193 (15, $[ArC(OMe)iPr+H]^+$), 183 (41). Anal. calculated for $C_{11}H_{13}BrO$: C: 54.79, H: 5.43. Found: C: 54.82, H: 5.46.

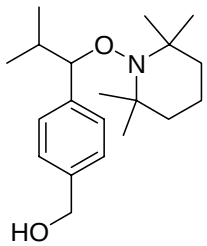
4-[2-Methyl-1-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-propyl]-benzaldehyde (2a)



Bromide **2** (1.57 g, 6.50 mmol, 1.00 eq), 2,2,6,6-tetramethyl-piperidin-1-oxyl (1.12 g, 7.15 mmol, 1.1 eq), Cu powder (434 mg, 6.83 mmol, 1.05 eq), $Cu(OTf)_2$ (24 mg, 66 µmol, 1 mol-%) and 4,4'-di-*tert*-butyl-2,2'-bipyridyl (70 mg, 0.26 mmol, 4 mol-%) were suspended under an argon atmosphere in benzene (9.0 mL). In a sealed tube the reaction mixture was stirred under an argon atmosphere at 75 °C for 3 d. The solids were removed by filtration over silica gel (washing with CH_2Cl_2). Purification by flash chromatography (MTBE/pentane, 1:20) afforded the alkoxyamine **2a** as a colorless solid (2.04 g, 6.43 mmol, 99%).

mp = 82 °C. IR: 2966*w*, 2932*m*, 2873*w*, 1699*s*, 1605*m*, 1574*w*, 1461*w*, 1376*w*, 1363*w*, 1303*w*, 1260*w*, 1207*m*, 1164*w*, 1132*w*, 1016*m*, 991*m*, 954*w*, 911*w*, 842*w*, 811*s*, 699*w*. ^{1}H-NMR (300 MHz; $CDCl_3$): δ= 10.00 (*s*, 1 H, CHO); 7.81 (*d*, *J* = 8.2 Hz, 2 H, Ar-H); 7.39 (*d*, *J* = 8.1 Hz, 2 H, Ar-H); 4.63 (*d*, *J* = 5.4 Hz, 1 H, C*H*CH$(CH_3)_2$); 2.61-2.56 (*m*, 1 H, C*H*$(CH_3)_2$); 1.54-0.59 (*m*, 24 H, 6 × CH_3, 3 × CH_2). ^{13}C-NMR (75 MHz, $CDCl_3$): δ= 192.1 (CH), 147.7 (C), 135.1 (C), 129.3 (2 × CH), 128.7 (2 × CH), 91.0 (CH), 60.0 (2 × C), 40.6 (2 × CH_2), 31.2 (CH, 2 × CH_3), 20.1 (2 × CH_3), 17.2 (CH_2), 15.9 (2 × CH_3). ESI-MS: 372 (17, $[M+MeOH+Na]^+$), 340 (100, $[M+Na]^+$), 318 (26, $[M+H]^+$), 184 (21, $[M-TEMPO+Na]^+$), 179 (57, $[M-TEMPO+NH_4]^+$). Anal. calculated for $C_{20}H_{31}NO_2$: C: 75.67, H: 9.84, N: 4.41. Found: C: 75.51, H: 9.71, N: 4.33.

{4-[2-Methyl-1-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-propyl]-phenyl}-methanol (2b)

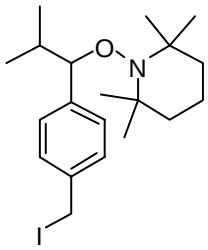


Alkoxyamine **2a** (500 mg, 1.57 mmol, 1.00 eq.) was dissolved in THF (27.5 mL). $LiAlH_4$ (59 mg, 1.6 mmol, 1.00 eq) was added to the solution at r.t. and the reaction mixture was stirred for 1.5 h. The reaction was stopped by addition of water (74 µL). After 5 min NaOH (aq, 15%, 74 µL) and after further 5 min water (148 µL) was added. After 20 min stirring, the colorless precipitate was filtered and washed with CH_2Cl_2. The filtrate was dried over $MgSO_4$ and the solvent was removed under reduced pressure. After purification of the crude product by flash chromatography (MTBE/pentane, 1:2), the alcohol **2b** was isolated as a colorless solid (471 mg, 1.47 mmol, 94%).

mp = 114 °C. IR: 3271*w*,*br*, 2969*w*, 2928*m*, 2872*w*, 1463*w*, 1421*w*, 1361*m*, 1212*w*, 1134*w*, 1012*s*, 955*m*, 912*w*, 823*m*, 800*m*, 766*m*, 696*w*. ^{1}H-NMR (300 MHz; $CDCl_3$): δ=

7.27 (*m*, 2 H, Ar-H); 7.20 (*m*, 2 H, Ar-H); 4.68 (*d*, $J = 5.8$ Hz, 2 H, CH_2OH); 4.54 (*d*, $J = 5.3$ Hz, 1 H, C*H*CH(CH_3)$_2$); 2.60-2.49 (*m*, 1 H, C*H*(CH_3)$_2$); 1.69-1.65 (*m*, 1 H, OH); 1.42-0.58 (*m*, 24 H, $3 \times CH_2$, $1 \times$ CH(CH_3)$_2$, $2 \times$ C(CH_3)$_2$). ^{13}C-NMR (75 MHz, $CDCl_3$): $\delta = 139.9$ (C), 139.0 (C), 129.0 ($2 \times$ CH), 125.8 ($2 \times$ CH), 91.0 (CH), 65.4 (CH_2), 59.9 ($2 \times$ C), 40.6 ($2 \times CH_2$), 31.1 (CH, $2 \times CH_3$), 20.2 ($2 \times CH_3$), 17.2 (CH_2), 16.1 ($2 \times CH_3$). ESI-MS: 662 (5, $[2M+Na]^+$), 358 (9, $[M+K]^+$), 342 (12, $[M+Na]^+$), 320 (100, $[M+H]^+$). Anal. calculated for $C_{20}H_{33}NO_2$: C: 75.19, H: 10.41, N: 4.38. Found: C: 75.12, H: 10.37, N: 4.28.

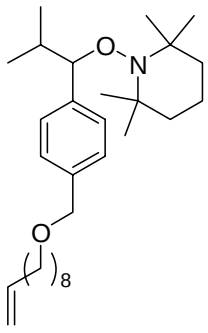
1-[1-(4-Iodomethyl-phenyl)-2-methyl-propoxy]-2,2,6,6-tetramethyl-piperidine (3)



Trimethylsilylchloride (1.90 g, 17.5 mmol, 3.00 eq) was added dropwise to the alkoxyamine **2b** (1.86 g, 5.83 mmol, 1.00 eq) and NaI (2.62 g, 17.5 mmol, 3.00 eq) in acetonitrile (14 mL) at 0 °C. The reaction mixture was allowed to warm up to r.t. during 5 h of stirring. After addition of water (10 mL) the phases were separated and the aqueous phase was extracted with Et_2O (10 mL). The combined organic layers were washed with Na_2SO_3 (aq, sat., 20 ml) and then dried over $MgSO_4$. After removal of the solvents *in vacuo* the crude product **3** was afforded as a brownish-yellow oil (2.42 g, 5.64 mmol, 97%), which was used without further purification.

^{1}H-NMR (300 MHz; $CDCl_3$): $\delta = 7.32$-7.26 (*m*, 2 H, Ar-H); 7.18-7.09 (*m*, 2 H, Ar-H); 4.50 (*d*, $J = 5.4$ Hz, 1 H, C*H*CH(CH_3)$_2$); 4.47 (*s*, 2 H, CH_2I); 2.60-2.45 (*m*, 1 H, C*H*(CH_3)$_2$); 1.58-0.75 (*m*, 24 H, $3 \times CH_2$, $1 \times$ CH(CH_3)$_2$, $2 \times$ C(CH_3)$_2$). ESI-MS: 430 (100, $[M+H]^+$), 320 (11, [(starting material)+H]$^+$); HRMS (ESI) calculated for $[M+H]^+$: 430.1607. Found: 430.1601.

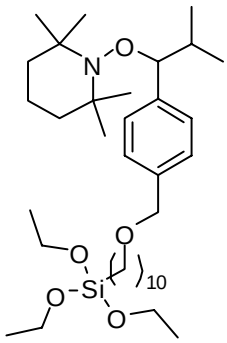
1-[1-(4-Dec-9-enyloxymethyl-phenyl)-2-methyl-propoxy]-2,2,6,6-tetramethyl-piperidine (3a)



9-Decen-1-ol (3.05 g, 19.6 mmol, 4.00 eq.) was diluted in THF (150 mL) and NaH (60% in mineral oil, 781 mg, 19.6 mmol, 4.00 eq) was added. The suspension was stirred first 15 min at r.t. and then refluxed for 2 h. Iodide **3** (2.09 g, 4.88 mmol, 1.00 eq) was added at r.t. to the suspension. The reaction mixture was stirred for 1 h at r.t. and then heated to reflux for 3 d. After cooling to r.t. the mixture was hydrolyzed using NH_4Cl (aq, sat., 20 mL) and then acidified with HCl (1M) to pH 4. Et_2O was added, the phases were separated and the aqueous phase was extracted with MTBE ($1 \times$) and CH_2Cl_2 ($2 \times$). The combined organic layers were dried with $MgSO_4$ and evaporated to dryness and the crude product was purified by flash chromatography (EtOAc/pentane, 1:40). The product **3a** was obtained as a pale yellow oil (1.96 g, 4.27 mmol, 88%).

IR: 2927*s*, 2854*m*, 1463*m*, 1360*s*, 1258*w*, 1241*w*, 1209*w*, 1099*s*, 1012*m*, 988*m*, 967*m*, 909*s*, 844*w*, 810*m*. ^{1}H-NMR (400 MHz; $CDCl_3$): δ = 7.25-7.23 (*m*, 2 H, Ar-H); 7.19-7.17 (*m*, 2 H, Ar-H); 5.81 (*ddt*, J_1 = 6.7 Hz, J_2 = 10.2 Hz, J_3 = 16.9 Hz, 1 H, CH_2=C*H*); 5.01-4.91 (*m*, 2 H, CH_2=CH); 4.52 (*d*, *J* = 5.3 Hz, 1 H, C*H*CH$(CH_3)_2$); 4.48 (*s*, 2 H, Ar-CH_2); 3.47 (*t*, *J* = 6.7 Hz, 2 H, OCH_2CH_2); 2.58-2.50 (*m*, 1 H, C*H*$(CH_3)_2$); 2.06-2.01 (*m*, 2 H, CH_2CH=CH_2); 1.65-0.61 (*m*, 36 H, $9 \times CH_2$, $2 \times C(CH_3)_2$, $1 \times CH(CH_3)_2$). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 139.6 (C), 139.2 (CH), 136.8 (C), 128.8 ($2 \times$ CH), 126.4 ($2 \times$ CH), 114.1 (CH_2), 91.1 (CH), 72.9 (CH_2), 70.6 (CH_2), 59.9 ($2 \times$ C), 40.7 ($2 \times CH_2$), 33.8 (CH_2), 31.1 (CH, $2 \times CH_3$), 29.8 ($2 \times CH_2$), 29.4 ($2 \times CH_2$), 29.1 (CH_2), 26.2 (CH_2), 20.2 ($2 \times CH_3$), 17.2 (CH_2), 16.1 ($2 \times CH_3$). ESI-MS: 480 (100, $[M+Na]^+$), 458 (56, $[M+H]^+$); Anal. calculated for $C_{30}H_{51}NO_2$: C: 78.72, H: 11.23, N: 3.06. Found: C: 78.69, H: 11.40, N: 3.00.

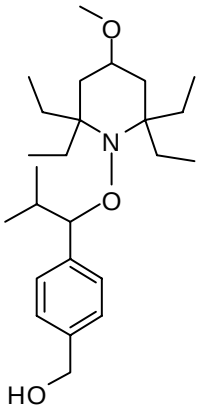
2,2,6,6-Tetramethyl-1-{2-methyl-1-[4-(10-triethoxysilanyl-decyloxymethyl)-phenyl]-propoxy}-piperidine (4)



The olefin **3a** (429 mg, 937 µmol, 1.00 eq) was dissolved in triethoxysilane (0.17 mL, 0.94 mmol, 1.00 eq) and heated up to 40 °C. Karstedt-catalyst (2.4% Pt, 0.08 mL, 0.01 mmol, 1 mol-%) was added during 10 min in two steps and the reaction mixture was stirred in the dark for 2 h at 40 °C. After addition of cyclohexane (0.80 mL) and propylenecarbonate (0.80 mL) the phases were separated. The organic phase was evaporated to dryness. Flash chromatography (MTBE/pentane, 1:30) yielded **4** as a colorless oil (244 mg, 392 µmol, 42%, 68% based on reisolated starting material).

IR: 3437*m*, 2970*s*, 2875*m*, 2362*w*, 1461*m*, 1418*w*, 1377*w*, 1213*w*, 1149*w*, 1086*s*, 1036*m*, 1007*s*, 906*w*, 837*w*, 803*w*, 789*w*. ^{1}H-NMR (300 MHz; $CDCl_3$): δ = 7.29-7.22 (*m*, 2 H, Ar-H); 7.21-7.14 (*m*, 2 H, Ar-H); 4.52 (*d*, *J* = 5.8 Hz, 1 H, C*H*CH$(CH_3)_2$); 4.48 (*s*, 2 H, Ar-CH_2); 3.81 (*t*, *J* = 7.0 Hz, 2 H, OCH_2CH_2); 3.47 (*t*, *J* = 6.7 Hz, 6 H, CH_2CH_3), 2.60-2.47 (*m*, 1 H, C*H*$(CH_3)_2$); 1.67-0.57 (*m*, 51 H, $12 \times CH_2$, $3 \times CH_2CH_3$, $2 \times C(CH_3)_2$, $1 \times CH(CH_3)_2$). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 139.5 (C), 136.7 (C), 128.7 ($2 \times$ CH), 126.4 ($2 \times$ CH), 91.0 (CH), 72.9 (CH_2), 70.6 (CH_2), 59.8 ($2 \times$ C), 58.3 ($3 \times CH_2$), 40.5 ($2 \times CH_2$), 33.2 (CH_2), 31.1 (CH, $2 \times CH_3$), 29.8 (CH_2), 29.6 (CH_2), 29.5 ($2 \times CH_2$), 29.3 (CH_2), 26.2 (CH_2), 22.8 (CH_2), 20.1 ($2 \times CH_3$), 18.3 ($3 \times CH_3$), 17.2 (CH_2), 16.0 ($2 \times CH_3$), 10.4 (CH_2). ESI-MS: 644 (5, $[M+Na]^+$), 622 (100, $[M+H]^+$); HRMS (ESI) calculated for $[M+H]^+$: 622.4867. Found: 622.4861. Anal. calculated for $C_{36}H_{67}NO_5Si$: C: 69.51, H: 10.86, N: 2.25. Found: C: 69.21, H: 10.94, N: 2.09.

{4-[2-Methyl-1-(2,2,6,6-tetraethyl-4-methoxy-piperidin-1-yloxy)-propyl]-phenyl}-methanol (5a)

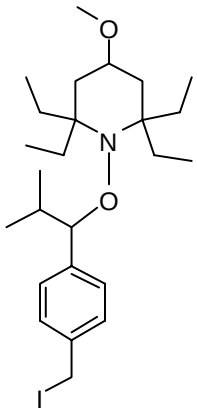


Bromide **2** (337 mg, 1.40 mmol, 1.00 eq), 2,2,6,6-tetraethyl-4-methoxy-piperidin-1-oxyl[1] (342 mg, 1.41 mmol, 1.01 eq), Cu powder (93 mg, 1.5 mmol, 1.05 eq), $Cu(OTf)_2$ (5 mg, 0.01 mmol, 1 mol-%) and 4,4'-di-*tert*-butyl-2,2'-bipyridyl (15 mg, 56 µmol, 4 mol-%) were suspended under an argon atmosphere in benzene (1.2 mL). The reaction mixture was stirred in a sealed tube under an argon atmosphere at 75 °C for 18 h. The solids were removed by filtration over silica gel (washing with CH_2Cl_2). Without further purification the crude alkoxyamine (max. 1.40 mmol, 1.00 eq) was completely dissolved in THF (25 ml). $LiAlH_4$ (66 mg, 1.7 mmol, 1.25 eq) was added to the solution at r.t. and the reaction mixture was stirred for 1.5 h. The reaction was stopped by addition of water (82 µL). After 5 min NaOH (aq, 15%, 82 µL) and after further 5 min water (164 µL) was added. After 20 min stirring, the colorless precipitate was filtered and washed with CH_2Cl_2. The filtrate was dried over $MgSO_4$ and the solvent was removed under reduced pressure. After purification of the crude product using flash chromatography (MTBE/pentane, 1:8), the alcohol **5a** was isolated as a colorless solid (518 mg, 1.28 mmol, 92%).

mp = 104 °C. IR: 3437*w*,*br*, 2970*s*, 2875*m*, 2362*w*, 1509*m*, 1460*m*, 1417*m*, 1213*w*, 1148*m*, 1058*s*, 1035*m*, 1007*s*, 906*w*, 837*m*, 803*m*, 789*m*. ^{1}H-NMR (300 MHz; $CDCl_3$): δ = 7.25 (*m*, 2 H, Ar-H); 7.15 (*m*, 2 H, Ar-H); 4.68 (*s*, 2 H, C*H*$_2$OH); 4.53 (*d*, *J* = 4.4 Hz, 1 H, C*H*CH(CH$_3$)$_2$); 3.41-3.19 (*m*, 4 H, C*H*(CH$_3$)$_2$, OCH$_3$); 2.51-0.34 (m, 32 H, 1 × C*H*OCH$_3$, 1 × CH$_2$O*H*, 2 × C*H*$_2$CHOCH$_3$, 4 × C*H*$_2$CH$_3$, 4 × CH$_2$C*H*$_3$, 2 × CH(C*H*$_3$)$_2$). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 139.5 (C), 138.9 (C), 128.4 (2 × CH), 125.6 (2 × CH), 89.2 (CH), 71.2 (CH), 65.3 (2 × C, CH_2), 55.6 (CH_3), 36.1 (CH_2), 35.7 (CH_2), 31.9 (CH), 30.6 (CH_2), 29.2 (CH_2), 27.4 (CH_2), 26.9 (CH_2), 20.1 (CH_3), 15.4 (CH_3), 10.1 (CH_3), 9.9 (CH_3), 8.2 (CH_3), 7.8 (CH_3). ESI-MS: 428 (62, $[M+Na]^+$), 406 (100, $[M+H]^+$). Anal. calculated for $C_{25}H_{43}NO_3$: C: 74.03, H: 10.69, N: 3.45. Found: C: 73.73, H: 10.68, N: 3.35.

[1] T. Schulte, K. O. Siegenthaler, H. Luftmann, M. Letzel, A. Studer, *Macromolecules* **2005**, *38*, 6833-6844.

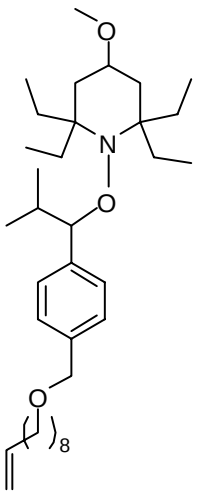
2,2,6,6-Tetraethyl-1-[1-(4-iodomethyl-phenyl)-2-methyl-propoxy]-4-methoxy-piperidine (5b)



Trimethylsilylchloride (198 mg, 1.82 mmol, 3.00 eq) was added dropwise to the alkoxyamine **5a** (247 mg, 609 µmol, 1.00 eq) and NaI (273 mg, 1.82 mmol, 3.00 eq) in acetonitrile (2 mL) at 0 °C. The reaction mixture was allowed to warm up to r.t. during 5 h of stirring. After addition of water (2 mL) the phases were separated and the aqueous phase was extracted with Et_2O (4 mL). The combined organic layers were washed with Na_2SO_3 (aq, sat., 5 mL) and then dried over $MgSO_4$. After removal of the solvents *in vacuo* the crude product **5b** was obtained as a brownish-yellow oil (310 mg, 601 µmol, 99%), which was used without further purification.

^{1}H-NMR (300 MHz; $CDCl_3$): δ = 7.23-7.16 (*m*, 2 H, Ar-H); 7.06-6.96 (*m*, 2 H, Ar-H); 4.47-4.31 (*m*, 3 H, C*H*CH$(CH_3)_2$, CH_2I); 3.35-3.13 (*m*, 4 H, C*H*$(CH_3)_2$, OCH_3); 2.39-0.52 (*m*, 31 H, 1 × C*H*OCH_3, 2 × C*H*$_2$CHOCH_3, 4 × C*H*$_2$C*H*$_3$, 4 × C*H*$_2$C*H*$_3$, 2 × CH(C*H*$_3$)$_2$). ESI-MS: 538 (5, $[M+Na]^+$), 516 (100, $[M+H]^+$), 502 (16); HRMS (ESI) calculated for $[M+H]^+$: 516.2338. Found: 516.2325.

1-[1-(4-Dec-9-enyloxymethyl-phenyl)-2-methyl-propoxy]-2,2,6,6-tetraethyl-4-methoxy-piperidine (5c)

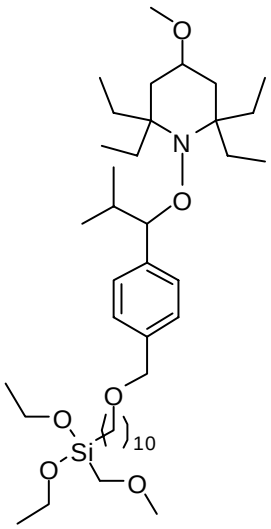


9-Decen-1-ol (167 mg, 1.07 mmol, 4.00 eq.) was diluted in THF (10 mL) and NaH (60% in mineral oil, 43 mg, 1.1 mmol, 4.0 eq) was added. The suspension was stirred for 15 min at r.t. and then refluxed for 2 h. Iodide **5b** (138 mg, 268 µmol, 1.00 eq) was added at r.t. to the suspension. The reaction mixture was stirred for 20 min at r.t. and then heated to reflux for 4.5 h. After cooling to r.t. the mixture was hydrolyzed using NH_4Cl (aq, sat., 2 mL) and then acidified with HCl (1M) to pH 4. Et_2O was added, the phases were separated and the aqueous phase was extracted with MTBE (1 ×) and CH_2Cl_2 (2 ×). The combined organic layers were dried with $MgSO_4$, evaporated to dryness and the crude product was purified by flash chromatography (MTBE/pentane, 1:40). The product **5c** was obtained as a pale yellow oil (123 mg, 226 µmol, 85%).

IR: 2960*m*, 2930*s*, 2877*m*, 2856*m*, 1640*w*, 1511*w*, 1376*w*, 1154*w*, 1100*m*, 1007*w*, 909*w*, 734*w*. ^{1}H-NMR (300 MHz; $CDCl_3$): δ = 7.26-7.20 (*m*, 2 H, Ar-H); 7.19-7.09 (*m*, 2 H, Ar-H); 5.81 (*ddt*, J_1 = 6.7 Hz, J_2 = 10.2 Hz, J_3 = 17.0 Hz, 1 H, CH_2=C*H*); 5.03-4.89 (*m*, 2 H, C*H*$_2$=CH), 4.5 (*d*, *J* = 4.4 Hz, 1 H, C*H*CH$(CH_3)_2$); 4.49 (*s*, 2 H, Ar-CH_2), 3.46 (*t*, *J* = 6.7 Hz, 2 H, OC*H*$_2$C*H*$_2$); 3.41-3.28 (*m*, 4 H, C*H*$(CH_3)_2$, OCH_3); 2.53-0.35 (*m*, 45 H, 1 × C*H*OCH_3, 13 × CH_2, 4 × CH_2C*H*$_3$, 1 × CH(C*H*$_3$)$_2$). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 139.3 (C), 139.2 (CH), 136.7 (C), 128.2 (2 × CH), 126.2 (2 × CH), 114.1 (CH_2), 89.9 (CH), 72.8 (CH_2), 71.2 (CH), 70.5 (CH_2), 65.3 (C), 65.2 (C), 55.6

(CH_3), 36.1 ($2 \times CH_2$), 35.8 (CH_2), 33.8 (CH_2), 31.9 (CH), 30.6 (CH_2), 29.7 (CH_2), 29.4 (CH_2), 29.2 (CH_2), 29.1 (CH_2), 28.9 (CH_2), 27.4 (CH_2), 26.9 (CH_2) 26.2 (CH_2), 20.1 (CH_3), 15.4 (CH_3), 10.1 (CH_3), 9.9 (CH_3), 8.2 (CH_3), 7.8 (CH_3). ESI-MS: 566 (26, $[M+Na]^+$), 544 (100, $[M+H]^+$); Anal. calculated for $C_{35}H_{61}NO_3$: C: 77.29, H: 11.31, N: 2.58. Found: C: 77.32, H: 11.33, N: 2.48.

2,2,6,6-Tetramethyl-4-methoxy-1-{2-methyl-1-[4-(10-triethoxysilanyl-decyloxy-methyl)-phenyl]-propoxy}-piperidine (5)



The olefin **5c** (120 mg, 221 µmol, 1.00 eq) was dissolved in triethoxysilane (40 µL, 0.22 mmol, 1.0 eq) and heated to 40 °C. Karstedt-catalyst (2.4% Pt, 20 µL, 2.2 µmol, 1 mol-%) was added in two portions (second portion after 10 min) and the reaction mixture was stirred in the dark for 2 h at 40 °C. After addition of cyclohexane (0.25 mL) and propylenecarbonate (0.25 mL) the phases were separated. The organic phase was evaporated to dryness. Purification by flash chromatography (MTBE/pentane, 1:40→1:5) yielded **5** as a colorless oil (73 mg, 0.10 mmol, 47%, 60% based on reisolated starting material).

IR: 2971*s*, 2928*s*, 2879*m*, 2856*m*, 1463*m*, 1387*w*, 1364*w*, 1199*w*, 1165*m*, 1102*s*, 1082*s*,1008*w*, 957*m*, 790*m*. ^{1}H-NMR (300 MHz; $CDCl_3$): δ= 7.25-7.17 (*m*, 2 H, Ar-H); 7.15-7.09 (*m*, 2 H, Ar-H); 4.52 (*d*, J = 4.4 Hz, 1 H, C*H*CH(CH_3)$_2$); 4.49 (*s*, 2 H, Ar-CH_2); 3.81 (*q*, J = 7.0 Hz, 6 H, CH_2CH$_3$); 3.46 (*t*, J = 6.7 Hz, 2 H, OCH_2CH$_2$); 3.39-3.29 (*m*, 4 H, C*H*(CH_3)$_2$, OCH_3); 2.50-0.54 (*m*, 58 H, $1 \times$ C*H*OCH$_3$, $15 \times CH_2$, $9 \times CH_3$). ^{13}C-NMR (75 MHz, $CDCl_3$): δ= 139.3 (C), 136.7 (C), 128.2 ($2 \times$ CH), 126.2 ($2 \times$ CH), 89.2 (CH), 72.8 (CH_2), 71.2 (CH), 70.5 (CH_2), 65.3 (C), 65.2 (C), 58.3 ($3 \times CH_2$), 55.7 (CH_3), 36.1 ($2 \times CH_2$), 35.8 (CH_2), 33.2 (CH_2), 31.9 (CH), 30.6 (CH_2), 29.7 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 29.3 (CH_2), 29.2 (CH_2), 27.4 (CH_2), 26.9 (CH_2) 26.2 (CH_2), 22.8 (CH_2), 20.1 (CH_3), 18.3 ($3 \times CH_3$), 15.4 (CH_3), 10.4 (CH_2), 10.1 (CH_3), 9.9 (CH_3), 8.2 (CH_3), 7.8 (CH_3). ESI-MS: 731 (95, $[M+Na]^+$), 709 (100, $[M+H]^+$), 537 (16), 458 (19); Anal. calculated for $C_{41}H_{77}NO_6Si$: C: 69.54, H: 10.96, N: 1.98. Found: C: 69.81, H: 10.83, N: 1.89.

Langmuir-Blodgett (LB) Procedures

All experiments were conducted in a commercial LB-through (KSV 3000). The subphase (MilliQ DI Water, 18.2 MΩcm) was temperature controlled at (24.0 ± 0.1) °C, air temperature varied between 24.0 and 24.5 °C. A DPPC solution in chloroform as well as chloroform solutions of **4** and **5** at a concentration of 1 mg/ml were prepared. The DPPC solution was then parted and mixed with a solution containing appropriate amounts of **4** and **5** to yield DPPC solutions with 2.5 mol-%, 5 mol-%, 7.5 mol-%, and 10 mol-% **4**, respectively 10 mol-% **5**. For the measurement of isotherms 20 µl of the respective

solvent was spread onto the water surface and then allowed to evaporate for about 15 min. After that isotherms were measured with a maximum barrier speed of 10 mm/min. The resulting isotherms for pure DPPC, pure **4** and a mixture of 10 mol-% of **4** in DPPC are shown in *Figure S1*. The silicon substrates for the transfer (Si 100, natural oxide layer) were cutted into 5×2 cm² pieces and then cleaned subsequentially for 10 min each step in chloroform, isopropanol, and DI water (as above) and then treated with an oxygen plasma (TePla 100-E, 300 W) for 2 min. The substrates were submerged into the trough and 20 µl of the mixed solutions were spread. The film was compressed to a lateral pressure of 5.0 mN/m with a maximum speed of 45 cm²/min after waiting for 1 h to evaporate the solvent and to hydrolyze the triethoxy functions of **4** respectively **5**. After this the film was let rest again for about 10 min to stabilize. Then the substrate was lifted with a speed of 15 mm/min, while the lateral pressure was kept constant by further compression.

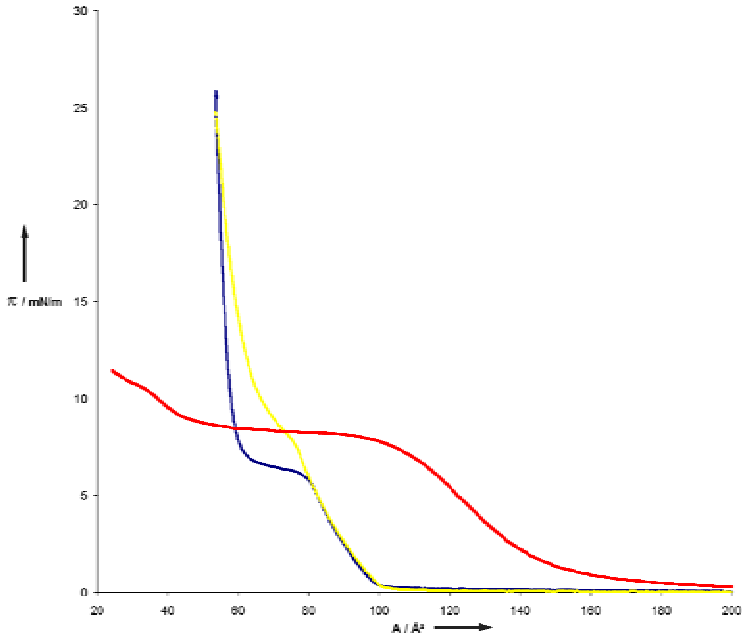


Figure S1: Surface pressure-molecular area (π-A) isotherms of **4** (red), DPPC (blue) and mixed DPPC/**4** (10 mol-% of **4**, yellow) monolayers at the air/water interface at r.t.

Typical Procedure for the Surface Initiated Polymerization of Styrene using 4

A Schlenk tube was charged with 2,2,6,6-tetramethyl-1-(1-phenyl-ethoxy)-piperidine (**6**) (5.4 mg, 21 µmol, 0.2 mol-%) and styrene (1.18 ml, 10.3 mmol, 1.00 eq). The tube was subjected to three freeze-thaw cycles, a structured silicon wafer containing immobilized alkoxyamine initiator **4** (after LB transfer, the silicon wafer was heated under vacuum (0.01 bar) at 80 °C for 2 h to immobilize the alkoxyamine on the surface, washed twice with $CHCl_3$ in an ultrasonic bath to remove the DPPC and then dried) was added and sealed off under argon. The polymerization was carried out under argon at 125 °C for 24 h. The resulting mixture was cooled to r.t., dissolved in CH_2Cl_2. The wafer was taken

out of the solution, continuously extracted with CH_2Cl_2 for at least 14 h and AFM measurements were carried out. CH_2Cl_2 was removed from the styrene/polystyrene solution under reduced pressure and residual monomer was removed in a vacuum-drying cabinet at 60 °C for 12 h. Conversion was evaluated gravimetically; molecular weight and polydispersity index (PDI) were determined by size exclusion chromatography. Conversion = 73%; M_n = 32300 g/mol; PDI = 1.30.

Typical Procedure for the Surface Initiated Polymerization of Styrene using 5

A Schlenk tube was charged with 2,2,6,6-tetraethyl-4-methoxy-1-(1-phenyl-ethoxy)-piperidine (**7**) (6.4 mg, 18 µmol, 0.2 mol-%) and styrene (1.06 ml, 9.21 mmol, 1.00 eq). The tube was subjected to three freeze-thaw cycles, a structured silicon wafer containing immobilized alkoxyamine initiator **5** (after LB transfer, the silicon wafer was heated under vacuum (0.01 bar) at 60 °C for 2 h to immobilize the alkoxyamine on the surface, washed twice with $CHCl_3$ in an ultrasonic bath to remove the DPPC and then dried) was added and sealed off under argon. The polymerization was carried out under argon at 105 °C for 24 h. The resulting mixture was cooled to r.t., dissolved in CH_2Cl_2. The wafer was taken out of the solution, continuously extracted with CH_2Cl_2 for at least 14 h and AFM measurements were carried out. CH_2Cl_2 was removed from the styrene/ polystyrene solution under reduced pressure and residual monomer was removed in a vacuum-drying cabinet at 60 °C for 12 h. Conversion was evaluated gravimetically; molecular weight and polydispersity index (PDI) were determined by size exclusion chromatography. Conversion = 76%; M_n = 29400 g/mol; PDI = 1.21.

Typical Procedure for the Surface Initiated Polymerization of n-Butyl Acrylate

A Schlenk tube was charged with 2,2,6,6-tetraethyl-4-methoxy-1-(1-phenyl-ethoxy)-piperidine (**7**) (5.3 mg, 15 µmol, 2mol-%) and n-butyl acrylate (1.09 ml, 7.63 mmol, 1.00 eq). The tube was subjected to three freeze-thaw cycles, a structured silicon wafer containing immobilized alkoxyamine initiator **5** (after LB transfer, the silicon wafer was heated under vacuum (0.01 bar) at 60 °C for 2 h to immobilize the alkoxyamine on the surface, washed twice with $CHCl_3$ in an ultrasonic bath to remove the DPPC and then dried) was added and sealed off under argon. The polymerization was carried out under argon at 105 °C for 24 h. The resulting mixture was cooled to r.t., dissolved in CH_2Cl_2. The wafer was taken out of the solution, continuously extracted with CH_2Cl_2 for at least 14 h and AFM measurements were carried out. CH_2Cl_2 was removed from the n-butyl acrylate/poly-n-butyl acrylate solution under reduced pressure and AFM measurements were performed. CH_2Cl_2 was removed under reduced pressure and residual monomer was removed in a vacuum-drying cabinet at 60 °C for 12 h. Conversion was evaluated gravimetically; molecular weight and polydispersity index (PDI) were determined by size exclusion chromatography. Conversion = 67%; M_n = 43800 g/mol; PDI = 1.21.

Determination of the chain density on the substrates

The graft density σ was estimated from

$$\sigma = L\rho N_A/M_n \qquad (1)$$

where L is the thickness of graft layer (determined by AFM-measurements), ρ is the bulk density of styrene (0.906 g/cm^3), respectively n-butyl-acrylate, N_A is the Avogadro number and M_n is the number-average molecular weight.[2]
The calculated graft densities σ of the polystyrene chains prepared from immobilized alkoxyamine initiator **4** are presented in *Table S1*.

Table S1: Chain densities of the structured wafers derived from immobilized alkoxyamine initiator **4**.

percentage of admixing of 4 **[%]**	**height L [nm]**	M_n **[g/mol] of polymer synthesized in solution (PDI)**	**chain density** σ **[nm^2]**
2.5	4.5 ± 0.1	22 850 (1.28)	0.11
5.0	3.7 ± 0.2	22 000 (1.23)	0.09
7.5	6.8 ± 0.2	32 900 (1.28)	0.11
10.0	8.0 ± 0.2	32 300 (1.30)	0.14
12.5	7.0 ± 0.2	31 400 (1.23)	0.12
15.0	10.0 ± 0.2	40 400 (1.35)	0.14

[2] C. Yoshikawa, A. Goto, Y. Tsujii, T. Fukuda, T. Kimura, K. Yamamoto, A. Kishida, *Macromolecules* **2006**, *39*, 2284.

Large area survey of stripe pattern

The DPPC stripe patterns can generally extend over large surface areas[3]. Here the typical dimension of the substrates used during LB deposition was 5×2 cm². Unfortunately a quick large area survey by optical means was not feasible for our system because of the small periodicity and the thin film thickness. Alternatively AFM images were taken at several different positions all over the substrate to make sure that the whole substrate was covered uniformly by the stripe pattern. These random sample images show a complete coverage of the substrate by the alternating DPPC (LE) mixed with alkoxyamine initiator / DPPC (LC) stripe pattern over the whole sample surface. The primary substrates where then cutted into smaller pieces (10×5 mm²) for the SIP. After the SIP once again several locations all over each sample where checked to ensure the uniformity of the polymerized pattern. A typical sample image is shown in *Figure S2*.

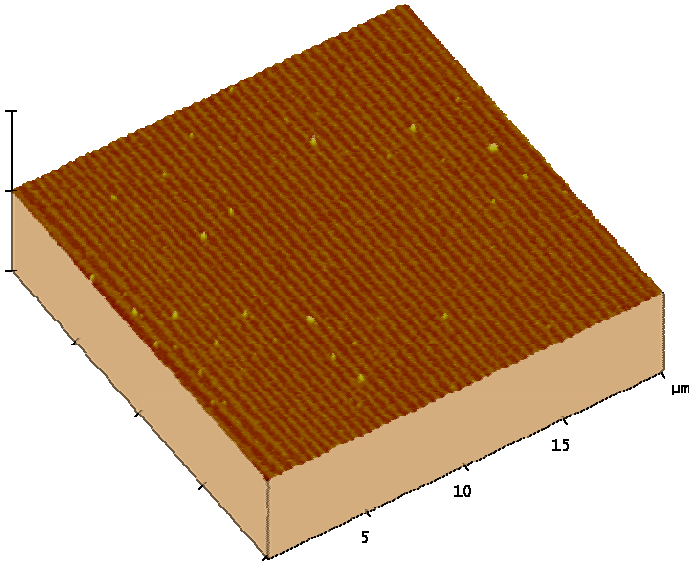


Figure S2: 20×20 µm² AFM image of a sample with 10 mol-% of **5** after SIP of styrene.

[3] X. Chen, M. Hirtz, H. Fuchs, L. Chi, *Adv. Mater.* **2005**, *17*, 2881.