Supporting Information

ω-Thiolation of phenolic surfactants enables controlled conversion between extended, bolaform and multilayer conformations

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Figure S1. AFM image of ODG SH deposited onto mica from an ultrapure water subphase at a surface pressure of 20 mN/m after 10 minutes relaxation time.
Figure S2. AFM images of a) bare template-stripped gold, b) SAM of ODG SH assembled on template-stripped gold, c) LB transfer of ODG SH from an ultrapure water supbase onto the template-stripped gold at pressure of 25 mN/m before an ethanol wash, d) LB transfer of ODG SH on a water supbase onto the template-stripped gold at pressure of 25 mN/m after an ethanol wash, e) tapping mode phase of c), f) tapping mode phase of d).
Figure S3. AFM image of ODG SH deposited onto mica from a pH 9 subphase at a surface pressure of 5 mN/m after 10 minutes relaxation time.
Figure S4. Surface pressure-molecular area isotherms of ODG SH as a function of subphase pH and relaxation time.
Figure S5. BAM images of ODG SH on a pH 9 subphase with 60 minutes relaxation at surface pressures of a) 10 mN/m, b) 12 mN/m, c) 15 mN/m, d) 22 mN/m.
Figure S6. AFM image of ODG SH deposited onto mica from a pH 9 subphase at a surface pressure of 12 mN/m after 60 minutes relaxation time.
Figure S7. BAM images of ODG SH on a pH 10 subphase at surface pressures of a) 7 mN/m, b) 8 mN/m, c) 9 mN/m, d) 10 mN/m, e) 11 mN/m, f) 12 mN/m. The ellipses in d) highlight two domains that differ in brightness due to their orientation.
Figure S8. AFM image of ODG SH deposited onto mica from a pH 10 subphase at a surface pressure of 16 mN/m after 10 minutes relaxation time.
Figure S9. BAM images of ODG SH on a pH 11 subphase at surface pressures of a) 0 mN/m, immediately after spreading, b) 15 mN/m, c) 14 mN/m (past the local maxima), d) 20 mN/m.
Figure S10. AFM image of ODG SH deposited onto mica from a pH 11 subphase at surface pressures of 5 and 15 mN/m after 10 minutes relaxation time.
Figure S11. Contour plot of X-ray intensity as a function of the in-plane ($Q_{xy}$) and out-of-plane ($Q_z$) vector components of ODG SH on a pH 11 subphase at a surface pressure of 15 mN/m.
Figure S12 Top: Photographic images of gold substrates immersed in ultrapure water for LB deposition showing differences in the meniscus due to wetting and Bottom: schematic of proposed film interaction with the gold substrate: a) hydrophilic gold and b) hydrophobic gold.
Table S1. Fitted peak positions in Qxy and Qz and corresponding full width at half maximum (FWHM). TW denotes a peak that was too weak to properly fit accurately in either position and width. The out-of-plane peak seen for ODG SH on subphases water and pH 10 could also be fit as two peaks yielding an intermediate tilt, in between NN and NNN, but the difference in tilt azimuth was minimal (120° vs 118°).
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<th>subphase</th>
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<th>15</th>
<th>20</th>
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<td>Pre-wash</td>
<td>1.11 ± 0.17</td>
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<td>3.09 ± 0.49</td>
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Table S2. Film thickness pre- and post-ethanol wash determined by ellipsometric measurements of ODG SH deposited onto gold by LB from the air-water interface.
Synthesis of 18-mercaptooctadecyl 3,4,5-trihydroxy benzoate

**Materials**: Octadecanedioic acid (95%+) was purchased from TCI America and used as received. Methyl 3,4,5-trihydroxybenzoate, N,N’-(dimethylamino)pyridine, N,N’-dicyclohexylcarbodiimide (99%), benzyl chloride (97%), sodium thiomethoxide (95%), 1M LiAlH4 in diethyl ether and 48% aq. HBr were purchased from Sigma Aldrich and used without further purification. 1,4-dimethylpyridinium p-toluenesulfonate (DPTS) was prepared according to ref.7.

H NMRs were recorded on a 400 MHz Varian and/or a 500 MHz Bruker instruments. C NMRs were recorded on a 500 MHz Bruker instrument with a frequency for the C at 125.7 MHz. Deuterated chloroform, methanol or DMSO were purchased from Cambridge Isotopes Laboratories Inc.

18-mercaptooctadecyl 3,4,5-trihydroxy benzoate was synthesised following the procedure shown in Scheme 1.

```
HO
HO
HO
O

BnCl
K2CO3,
DMF, over night

BnO

4N NaOH
EtOH/THF 1/1(v:v) 5h, reflux

BnO

Br(CH2)18

DCC/DPTS
THF, rt, 36h

BnO

HO(CH2)18OH

HO(CH2)18COOCH3

LIAH4, THF (anh)

BnO

4N(anh)/H2SO4(cat)
reflux, over night

MeOH(anh)/H2SO4(cat)

HOOC(CH2)16COOH

CH3OOC(CH2)16COOCH3

HO(CH2)18OH

HBr, Toluene reflux, 3h

BnO

Br(CH3)18COO

DCC/DPTS
THF, rt, 36h

BnO

H2,1atm

10%
Pd/C
EtOAc

1)CH3SH, MeOH, rt, 48h

2) 0.1M HCl

Scheme 1. Synthesis of 18-mercaptooctadecyl 3,4,5-trihydroxy benzoate
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Synthesis of methyl 3,4,5-tri(benzyloxy)benzoate (2).1 Methyl 3,4,5-trihydroxy benzoate 1 (1 g, 5.42 mmol, 1 eq.) was dissolved in 50 ml of DMF and the solution was thoroughly degassed. Benzyl chloride (2 ml, 17.88 mmol, 3.3 eq.) followed by 2.99 g (21.68 mmol, 4 eq.) of oven dried K2CO3 were added and the suspension was stirred at 80 °C, overnight, under a positive pressure of inert gas. The reaction mixture was cooled at room temperature, the solids were removed by filtration and the filtrate was concentrated under reduced pressure. The residue was partitioned between ethyl acetate and water. The organic layer was separated and dried over MgSO4. The crude product was purified by column chromatography on silica gel (hexanes:ethyl acetate 1:1 (v:v)). The fractions with Rf = 0.83 were separated (2.09 g, 84.9%).

1H-NMR (500 MHz, CDC13) δ (ppm): 7.50-7.34 (m, 15H, PhCH2O), 7.30 (s, 2H, Har ortho to COOCH3), 5.17 (s, 4H, Har, PhCH2O meta to COOCH3), 5.15 (s, 2H, PhCH2O para to COOCH3), 3.92 (s, 3H, COOCH3).

13C-NMR (125 MHz, CDC13) δ (ppm): 166.69, 152.57, 142.40, 137.45, 136.66, 128.55, 128.53, 128.20, 128.03, 127.96, 127.55, 125.23, 109.07, 75.14, 71.23, 52.25.

Synthesis of 3,4,5-tris(benzyloxy)benzoic acid (3).2 Compound 2 (1.57 g, 3.47 mmol) was dissolved in 48 ml of a 1:1 (v:v) mixture of THF/EtOH. To the solution 4.8 ml 4N aq. KOH was added and the reaction mixture was refluxed for 5h. After cooling at room temperature, the reaction mixture was acidified with 2N aq. HCl and concentrated under reduced
pressure. To the residue CH$_2$Cl$_2$ and water were added. The organic phase was separated, dried over MgSO$_4$ and concentrated by rotary evaporation to afford compound 3 quantitatively (1.53 g). The compound was used for the next step without further purification.

1H-NMR (500 MHz, DMSO-d$_6$) δ (ppm): 12.94 (s (broad), 1H, COOH), 7.50-7.26 (m, 17H, PhCH2O and Har ortho to COOH), 5.19 (s, 4H, Har, PhCH2O meta to COOH), 5.06 (s, 2H, PhCH2O para to COOH).

13C-NMR (125 MHz, DMSO-d$_6$) δ (ppm): 167.27, 152.45, 141.39, 137.83, 137.30, 128.89, 128.66, 128.55, 128.36, 128.03, 126.48, 108.64, 74.68, 70.65.

Synthesis of 1,18-dimethyl octadecanediol (5). Octadecanediolic acid 4 (2.5 g, 7.95 mmol) was reflux overnight in 35 ml dry methanol containing 2 ml H$_2$SO$_4$ as catalyst. After cooling to room temperature, the solvent was partial removed under reduced pressure and the product was separated by precipitation from water. The white precipitate was taken into diethyl ether and washed with water. The organic layer was dried over MgSO$_4$ and concentrated under reduced pressure to give 2.63 g (96.6 %) of 1,18-dimethyl octadecanediol.

1H-NMR (500 MHz, CDCl$_3$) δ (ppm): 3.66 (s, 6H, COOCH$_3$), 2.29 (t, 4H, J=7.3 Hz, CH$_2$-COOCH$_3$), 1.61 (quint., 4H, CH$_2$-CH$_2$-COOCH$_3$), 1.28-1.24 (m, 24H, (CH$_2$)$_{12}$-CH$_2$-COOCH$_3$).

13C-NMR (125 MHz, CDCl$_3$) δ (ppm): 174.57, 51.65, 34.34, 29.87, 29.85, 29.81, 29.67, 29.47, 29.37, 25.18.

Synthesis of 1,18-octadecanediol (6). 3,1,18-dimethyl octadecanediol (2.39 g, 7.60 mmol, 1 eq.) was dissolved in 160 ml THF (anh.). To the vigorously stirred solution, 19.5 ml 1M LiAlH$_4$ in Et$_2$O (2.56 eq.) was added dropwise. After the complete addition, the reaction mixture was heated at reflux for 20 h. The reaction was cooled at room temperature and excess LiAlH$_4$ was quenched with water (added very slowly) until gas generation stopped. 31 ml 15 % aq. NaOH was added to the mixture and the formed precipitate was removed by filtration and washed with hot THF. The filtrate was extracted three times with Et2O. The combined organic layers were dried over MgSO$_4$ and concentrated under reduced pressure. 1.75 g (80.3%) of the product was obtained.

1H-NMR (500 MHz, CDCl$_3$) δ (ppm): 3.66 (t, 4H, J=7 Hz, CH$_2$OH), 1.37 (quint, 4H, CH$_2$-CH$_2$-OH), 1.40-1.25 (m, 28H, (CH$_2$)$_{14}$-CH$_2$-CH$_2$OH).

13C-NMR (125 MHz, CDCl$_3$) δ (ppm): 63.13, 32.82, 29.66, 29.62, 29.60, 29.44, 25.75.

Synthesis of 18-bromooctadecan-1-ol (7). 1,18-octadecanediol (1.63 g, 5.71 mmol) was heated at reflux, for 4 h, in 16 ml of toluene to which 1.3 ml 48% aq. HBr was added. The reaction mixture was cooled at room temperature and the contents of the flask transferred to a separatory funnel. The organic phase was separated and concentrated under reduced pressure. Dichloromethane was added to the residue and the organic phase was further washed with water, sat. NaHCO$_3$ and brine, dried over MgSO$_4$, filtered and concentrated. The crude product was purified by column chromatography (SiO$_2$, hexanes:ethyl acetate, 4:1 (v:v)). The fractions with Rf = 0.36 were separated to give 0.67 g (33.78 %) of the product, as a white powder.

1H-NMR (400 MHz, CDCl$_3$) δ (ppm): 3.63 (t, 2H, J=6.4 Hz, CH$_2$OH), 3.40 (t, 2H, J=7.2 Hz, CH$_2$Br) 1.84 (quint, 2H, CH$_2$-CH$_2$-OH), 1.48 – 1.28 (m, 28 H, (CH$_2$)$_{14}$-CH$_2$-CH$_2$OH).

13C-NMR (125 MHz, CDCl$_3$) δ (ppm): 63.13, 34.10, 32.86, 32.83, 29.68, 29.67, 29.63, 29.61, 29.56, 29.45, 28.79, 28.20, 25.75.

Synthesis of 18-bromooctadecyl 3,4,5-tri(benzyloxy)benzoate 8. 3,4,5-tri(benzyloxy)benzoic acid 3 (1.14 g, 2.60 mmol, 1eq.), 18-bromooctadecan-1-ol 7 (1.09 g, 3.12 mmol, 1.2 eq.) and 1,4-dimethylpyridinium p-toluenesulfonate (DPTS) (0.22 g, 0.78 mmol, 0.3 eq.) were dissolved in 45 ml dry CH$_2$Cl$_2$ under an inert atmosphere. To the chilled solution, N,N'-Dicyclohexylcarbodiimide (DCC) was added dropwise as a solution in 6 ml dry CH$_2$Cl$_2$. The reaction mixture was stirred at room temperature for 2 days under a positive pressure of inert gas. The solids were removed by filtration and the filtrate was concentrated under reduced pressure. The crude product was purified by column chromatography on silica (hexanes:ethyl acetate 1:1 (v:v)). The fractions with RF = 0.76 were separated. Further purification was performed in order to remove traces of the N,N'-dicyclohexylurea by suspending the product in MeOH and stirring it at room temperature for 0.5 h. Finally the solids were separated by filtration and washed with MeOH on filter. 0.609 g (37.05 %) of 8 was obtained.
**1H-NMR (500 MHz, CDCl3) δ (ppm):** 7.45-7.26 (m, 17H, PhCH2O and Har ortho to COO-CH2~), 5.16 (s, 4H, Har, PhCH2O meta to COO-CH2~), 5.13 (s, 2H, PhCH2O para to COO-CH2~), 4.29 (t, 2H, J=6.5 Hz, COO-CH2~), 3.42 (t, 2H, J=7.0 Hz, ~CH2-Br), 1.87 (quint, 2H, ~CH2-CH2-Br), 1.76 (quint, 2H, COO-CH2-CH2~), 1.49-1.24 (m, 28 H, ~ (CH2)14-CH2-CH2Br).

**13C-NMR (125 MHz, CDCl3) δ (ppm):** 166.19, 152.50, 142.34, 137.45, 136.71, 128.53, 128.19, 128.01, 127.94, 127.54, 125.60, 109.11, 75.13, 71.26, 65.28, 34.08, 32.85, 29.70, 29.67, 29.65, 29.63, 29.59, 29.55, 29.45, 29.33, 28.78, 28.73, 28.19, 26.05.

Synthesis of 18-bromooctadecyl 3,4,5-trihydroxy benzoate (9). 18-bromooctadecyl 3,4,5-tri(benzyloxy)benzoate (0.6096 g, 0.79 mmol) was dissolved in 15 ml EtOAc and the resulted solution was thoroughly degassed for 0.5 h. 0.143 g of 10% Pd/C was added and the reaction mixture was stirred at room temperature overnight under an applied atmospheric pressure of H2. The reaction was quenched by addition of CH2Cl2 and the reaction mixture was filtered through a Celite pad. The filtrate was concentrated under reduced pressure to give 0.3908 g (89.8%) of pure 9 that was used for the next step without further purification.

**1H-NMR (400 MHz, CDCl3) δ (ppm):** 7.31 (s, 2H, Har ortho to COO-CH2~), 4.27 (t, 2H, J=6.8 Hz, COO-CH2~), 3.41 (t, 2H, J=6.8 Hz, ~CH2-Br), 1.85 (quint, 2H, ~CH2-CH2-Br), 1.74 (quint., 2H, COO-CH2-CH2~), 1.44-1.23 (m, 28 H, ~ (CH2)14-CH2-CH2Br).

Synthesis of 18-(acetylthio)octadecyl 3,4,5-trihydroxybenzoate (10). Compound 9 (0.39 g, 0.78 mmol, 1eq.) was dissolved in 8 ml of DMF. The solution was cooled at -78ºC and potassium thioacetate (0.106 g, 0.93 mmol, 1.2 eq.) was added dropwise as a solution in 1 ml DMF. The reaction mixture was stirred at room temperature for 24 h then extracted with EtOAc. The organic layers were washed with Na2CO3, dried over MgSO4 and concentrated. The crude product was suspended in MeOH and stirred at room temperature, and then the solids were separated by filtration and dried to give 10 quantitatively.

**1H-NMR (500 MHz, CDCl3) δ (ppm):** 7.25 (s, 2H, Har ortho to COO-CH2~), 4.25 (t, 2H, J=6.5 Hz, COO-CH2~), 2.86 (t, 2H, J=7.5 Hz, ~CH2-SCOCH3), 2.32 (s, 3H, ~CH2-SCOCH3), 1.72 (quint, 2H, ~CH2-CH2-SCOCH3), 1.56 (quint, 2H, COO-CH2-CH2~), 1.45-1.20 (m, 28 H, ~ (CH2)14-CH2-CH2- SCOCH3).

**13C-NMR (125 MHz, DMSO-d6) δ (ppm):** 196.56, 167.03, 144.00, 136.53, 121.97, 109.69, 65.17, 36.94, 31.86, 30.65, 29.66, 29.65, 29.63, 29.60, 29.57, 29.54, 29.47, 29.31, 29.22, 29.12, 28.82, 28.72, 26.04.

Synthesis of 18-mercaptooctadecyl 3,4,5-trihydroxybenzoate (11). To a stirred solution of 10 (0.135 g, 0.27 mmol, 1 eq.) in 3 ml MeOH (degassed), sodium thiomethoxide (~ 1 M final concentration) is added and the reaction mixture is stirred at room temperature for 48 h under a positive pressure of Argon. To the solution 12 ml 0.1 M aq. HCl (degassed) was added. After stirring for a few minutes, the reaction mixture was extracted with CH2Cl2. The combined organic layers were washed with brine, dried over MgSO4, filtered and concentrated to give 11 (120 mg, 97.1 %) with a purity of 97.4 %.

**1H-NMR (400 MHz, CDCl3) δ (ppm):** 7.28 (s, 2H, Har ortho to COO-CH2~), 4.27 (t, 2H, J=6.4 Hz, COO-CH2~), 2.53 (q, 2H, J=9.5 Hz, ~CH2-SH), 1.74 (quint, 2H, COO-CH2-CH2~), 1.59 (quint, 2H, -CH2-CH2SH), 1.45-1.25 (m, 29 H, ~ (CH2)14-CH2-CH2SH).