

# Face- and Edge-On Orientations of Octa-Acid and -Alcohol Substituted Tetraazaporphyrins in L- and LB-Monolayers

Mohamed Ahmida,<sup>a</sup> Scott Dufour,<sup>a</sup> Hui-Sheng Li,<sup>a</sup> Himadri Kayal,<sup>a</sup> Rolf Schmidt,<sup>b</sup>

Christine E. DeWolf<sup>b</sup> and S. Holger Eichhorn<sup>\*a</sup>

<sup>a</sup>Department of Chemistry and Biochemistry, University of Windsor,

Windsor, Ontario, Canada N9B 3P4

<sup>b</sup>Department of Chemistry and Biochemistry, Concordia University, 7141 Sherbrooke

St. West, Montréal, Québec, Canada H4B 1R6

Content	pages
1. Synthesis and spectroscopic characterization:	2-10
2. Thermal Analysis (DSC and TGA):	11-12
3. Titration:	13
4. Aggregation of octa-acid TAPs (UV-Vis):	14
5. Langmuir films of octa-acids (BAM and $\pi$ vs. A isotherms):	15-16
6. LB films of octa-acids (UV-Vis and AFM):	17-19
7. Langmuir films of octa-alcohols (BAM):	20
8. LB films of octa-alcohols (UV-Vis and AFM):	21-23

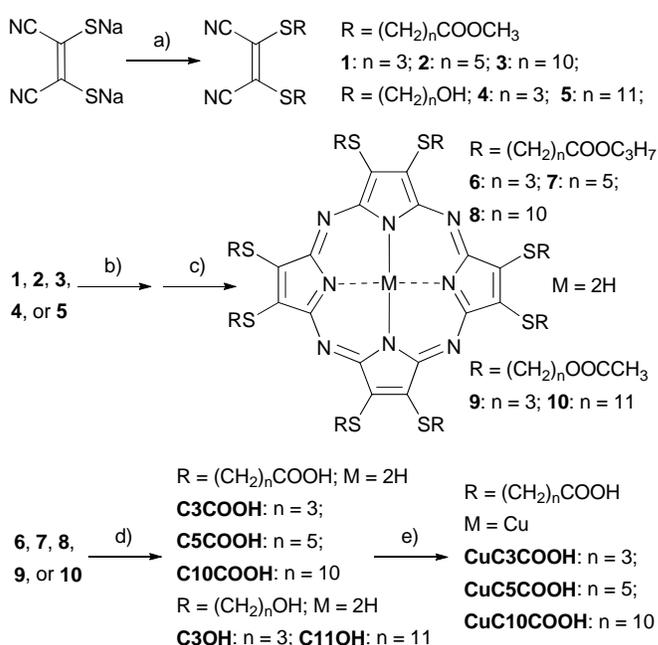
# 1 Synthesis

## 1.1 Materials

Reagents were used as received from Sigma-Aldrich, EM Science, and Fluka unless stated otherwise. Drying agents  $\text{MgSO}_4$  and molecular sieves (3 Å and 4 Å) were purchased from VWR. 1-Propanol and methanol were distilled and stored over 4 Å and 3 Å molecular sieves, respectively. Tetrahydrofuran and diethyl ether were obtained from a solvent purification system (Innovative Technology Inc. MA, USA, Pure-Solv 400). Column chromatography was performed using silica gel 60 (35-70 mesh ASTM, from EM Science). Thin layer chromatography was performed on Silica Gel 60 aluminum backed sheets (EM Science). 1,2-dicyanoethylene-1,2-dithiolate was prepared following the procedure of Schram and Hoffman.<sup>1</sup>

## 1.2 Instrumentation

$^1\text{H-NMR}$  &  $^{13}\text{C-NMR}$  spectra were run on Bruker NMR spectrometers (DRX 500 MHz, DPX 300 MHz, and DPX 300 MHz with auto-tune). Deuterated chloroform ( $\text{CDCl}_3$ ), DMSO ( $\text{CD}_3\text{SOCD}_3$ ), and pyridine ( $\text{C}_5\text{D}_5\text{N}$ ) were used as solvents and their residual proton signals functioned as reference signals. Multiplicities of the peaks are given as s = singlet, d = doublet, t = triplet, m = multiplet. Coupling constants are given in Hz and were only calculated for 1<sup>st</sup>-order systems. NMR data are presented in the following order (multiplicity, integration, coupling constant). Fourier Transform InfraRed spectra (FT-IR) were obtained on a Bruker Vector 22. Relative peak intensities and shapes are abbreviated as vs = very strong, s = strong, m = medium, w = weak, br = broad. Liquid samples were performed as films on potassium bromide windows and solid samples were run as potassium bromide pellets. Mass spectrometry measurements were performed by Kirk Green at the Regional Center for Mass Spectrometry (McMaster University). High resolution CI-MS was performed on a Micromass GCT (TOF) (Manchester, U.K.), and MALDI MS data were obtained on a Waters/Micromass Micro MX (Manchester, U.K.). UV/VIS absorption spectra were run on a Varian Cary 50 Conc UV-Visible Spectrophotometer. Elemental analyses were performed at the Centre for Catalysis and Materials Research at the University of Windsor on a PerkinElmer 2400 Series II CHNS/O Elemental Analyzer.



**Scheme 1.** Synthesis of octa-acid and -hydroxyl tetraazaporphyrins. Conditions: a) 2.2 eq  $\text{Br}(\text{CH}_2)_n\text{COOCH}_3$  ( $n = 3, 5, 10$ ), or  $\text{Br}(\text{CH}_2)_n\text{OH}$  ( $n = 3, 11$ ), DMF, 20 °C, 24 hrs, 65–78%; b)  $\text{Mg}(\text{OC}_3\text{H}_7)_2/\text{HOC}_3\text{H}_7$ , refl., 24 hrs, 55–60%; c) Acetic acid, 80 °C, 1–2 hrs, 75–80%; d) THF, 5 M KOH, refl., 2 hrs, 80–90%; e)  $\text{CuCl}_2$ , THF, 0.1 M NaOH, refl., 12–24 hrs, >90%.

### 1.3 General synthesis for 1-bromoalkanoic acid methyl esters

Bromoalkanoic acids ( $\text{Br}(\text{CH}_2)_n\text{COOH}$ ,  $n = 3, 5, 10$ ) (50 mmol) were combined with 60 mL of dry methanol and stirred until homogeneous. Concentrated sulfuric acid (0.5 mL) was slowly added and the solution was heated at reflux for 24 hrs (the condenser was equipped with a  $\text{CaCl}_2$  drying tube). The reaction mixture was then cooled to room temperature, poured into water (50 mL), and extracted with diethyl ether (5 x 25 mL). The combined ether layers were washed with water, an aqueous solution of sodium bicarbonate (5%), a saturated aqueous solution of NaCl and dried over  $\text{MgSO}_4$ . Evaporation of the ether gave pale yellow clear liquids as crude products. Analytically pure colourless samples were obtained by filtration through a plug of silica gel using a 1:4 mixture of ethyl acetate/hexane as eluent.

*4-Bromo-butyric acid methyl ester* ( $MW = 181 \text{ g/mol}$ )<sup>2</sup>

Yield: 5.6 g, (31 mmol, 65%);  $R_f$  (silica gel, 1:3 ethyl acetate/hexane): 0.35; IR ( $\text{cm}^{-1}$ ): 2927, 2854 (m,  $\nu(\text{C-H})$ ,  $\text{CH}_2$ ), 1740 (s,  $\nu(\text{C=O})$ , ester);  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ): 3.67 (s, 3H), 3.43 (t, 2H,  $J = 6.4$ ), 2.50 (t, 2H,  $J = 6.3$ ), 2.17 (tt, 2H,  $J = 6.4$  and 6.3); Spectral data agree with reported data.

*6-Bromo-hexanoic acid methyl ester* ( $MW = 209 \text{ g/mol}$ )<sup>2</sup>

Yield: 7.28 g, (34 mmol, 70%);  $R_f$  (silica gel, 1:3 ethyl acetate/hexane): 0.50; IR ( $\text{cm}^{-1}$ ): 2940, 2866 (m,  $\nu(\text{C-H})$ ,  $\text{CH}_2$ ), 1734 (s,  $\nu(\text{C=O})$ , ester);  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ): 3.67 (s, 3H), 3.40 (t, 2H,  $J = 6.7$ ), 2.33 (t, 2H,  $J = 6.9$ ), 1.88 (tt, 2H,  $J = 6.9$ ,  $J = 6.7$ ), 1.63 (m, 2H), 1.48 (m, 2H); Spectral data agree with reported data.

*11-Bromo-undecanoic acid methyl ester (MW = 279 g/mol)*<sup>3</sup>

Yield: 9.30 g, (33 mmol, 70%);  $R_f$  (silica gel, 1:3 ethyl acetate/hexane): 0.60; IR (cm<sup>-1</sup>): 2949, 2864 (m,  $\nu$ (C-H), CH<sub>2</sub>), 1739 (s,  $\nu$ (C=O), ester); <sup>1</sup>H-NMR (CDCl<sub>3</sub>): 3.65 (s, 3H), 3.39 (t, 2H, J = 6.8), 2.27 (t, 2H, J = 7.4), 1.84 (m, 2H), 1.60 (m, 2H), 1.27 (m, 12H); Spectral data agree with reported data.

**1.4 General Synthesis of 1,2-dicyano-1,2-bis(methoxycarbonyl-alkylthio)ethylenes and 1,2-dicyano-1,2-bis(hydroxyalkylthio)ethylenes (1-5)**

Bromoalkyl esters (Br(CH<sub>2</sub>)<sub>n</sub>COOCH<sub>3</sub>, n = 3, 5, 10) or bromoalcohols (Br(CH<sub>2</sub>)<sub>n</sub>OH, n = 3, 11) (30 mmol) were added to 2.3 g (12.5 mmol) of disodium 1,2-dicyanoethylene-1,2-dithiolate in dry 1-propanol to produce an orange solution that gradually darkened to crimson red. The solutions were stirred for 24 hrs, evaporated, and purified by column chromatography on silica gel using 1:3 mixtures of CH<sub>2</sub>Cl<sub>2</sub>/hexane as eluent to give the pure products as dark red viscous oils.

*cis-1,2-dicyano-1,2-bis(4-oxo-4-methoxybutylthio)ethylene (MW = 342 g/mol), 1*

Yield: 2.73 g, (8 mmol, 65%);  $R_f$  (1:4 ethyl acetate/hexane): 0.45; <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$ : 3.69 (s, 6H), 3.20 (t, 4H, J = 7.2), 2.49 (t, 4H, J = 7.1), 2.04 (tt, 4H, J = 7.2 and 7.1); <sup>13</sup>C-NMR (CDCl<sub>3</sub>): 173.15, 121.15, 111.82, 51.89, 33.83, 32.02, 29.11; IR (cm<sup>-1</sup>): 2928, 2855 (m,  $\nu$ (C-H), CH<sub>2</sub>), 2262 (m,  $\nu$ (C $\equiv$ N) nitrile), 1740 (s,  $\nu$ (C=O), ester) 1644 (m,  $\nu$ (C=C)); HR-MS (m/z) [CI]: Theoretical: 343.0789 [M+H]<sup>+</sup>; Found: 343.0786.

*cis-1,2-dicyano-1,2-bis(6-oxo-6-methoxyhexylthio)ethylene (MW = 398 g/mol), 2*

Yield: 3.23 g, (8.1 mmol 65%);  $R_f$  (1:4 ethyl acetate/hexane): 0.55; <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$ : 3.67 (s, 6H), 3.10 (t, 4H, J = 7.2), 2.31 (t, 4H, J = 6.4), 1.69 (m, 8H), 1.47 (m 4H); <sup>13</sup>C-NMR (CDCl<sub>3</sub>): 173.66, 121.04, 112.02, 51.50, 34.79, 33.68, 29.51, 27.74, 24.23; IR (cm<sup>-1</sup>): 2928, 2855 (m,  $\nu$ (C-H), CH<sub>2</sub>), 2255 (m,  $\nu$ (C $\equiv$ N) nitrile), 1740 (s,  $\nu$ (C=O), ester), 1650 (m,  $\nu$ (C=C)); HR-MS (m/z) [CI]: Theoretical: 398.1342 (M<sup>+</sup>); Found: 398.1334.

*cis-1,2-dicyano-1,2-bis(11-oxo-11-methoxyundecylthio)ethylene (MW = 539 g/mol), 3*

Yield: 4.37 g, (8.1 mmol, 65%);  $R_f$  (1:4 ethyl acetate/hexane): 0.60; <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$ : 3.67 (s, 6H), 3.11 (t, 4H, J = 7.3), 2.30 (t, 4H, J = 6.4), 1.69 (m, 4H), 1.60 (m, 4H), 1.41 (m, 24H); <sup>13</sup>C-NMR (CDCl<sub>3</sub>) : 174.18, 121.06, 112.08, 52.37, 34.33, 33.87, 32.81, 29.81, 29.26, 29.15, 28.90, 28.81, 26.68; IR (cm<sup>-1</sup>): 2938, 2845 (m,  $\nu$ (C-H), CH<sub>2</sub>), 2250 (m,  $\nu$ (C $\equiv$ N) nitrile), 1740 (s,  $\nu$ (C=O), ester), 1647 (m,  $\nu$ (C=C)); HR-MS (m/z) [CI]: Theoretical: 538.2920 (M<sup>+</sup>); Found: 538.2899.

The spectroscopic data of *cis*-1,2-dicyano-1,2-bis(11-hydroxypropylthio)ethylene (**4**) and *cis*-1,2-dicyano-1,2-bis(11-hydroxyundecylthio)ethylene (**5**) agree with the reported values.<sup>4</sup>

### 1.5 General synthesis of [2,3,7,8,12,13,17,18-octakis(1-propyloxy-4-carbonyl butyl-1-thio)-5,10,15,20-tetraazaporphyrinato]magnesium(II)

Magnesium turnings (486 mg, 20 mmol) and a small crystal of iodine were added to dry 1-propanol (160 mL) and heated at reflux until all Mg has been reacted (about 24 hrs). Equivalents (20 mL, 2.5 mmol) of the freshly prepared mixtures of magnesium propanolated in propanol were added to solutions of **1-5** (8 mmol) in dry 1-propanol (10 mL) and heated to reflux under argon for 24 hrs. The red solutions turned into a deep blue, the color of the magnesium tetraazaporphyrinato derivatives, within 1-2 hrs. Half of the solvent of the deep blue solutions was removed in vacuum and the crude products were precipitated by the addition of 150 mL of deionized water. The precipitates of the crude products were collected on a glass sintered filter, washed with deionized water, and converted to the metal-free TAPs without further purification.

### 1.6 General synthesis of 2,3,7,8,12,13,17,18-octakis(propanyloxyalkylthio)-5,10,15,20-tetraazaporphyrins (**6-8**) and 2,3,7,8,12,13,17,18-octakis(acetyloxyalkylthio)-5,10,15,20-tetraazaporphyrins (**9** and **10**, both not isolated as pure compounds)

Magnesium TAPs (1.2 mmol) were dissolved in 70 mL of glacial acetic acid and stirred at 80 °C for 1-2 hrs. Demetallation causes a splitting of the Q-band absorptions, which was monitored by UV-Vis spectroscopy. Complete demetallation gives a deep violet solution that was poured into 300 mL of deionized water. The products precipitated out as dark solids over several hours and were thoroughly washed with deionized water. Further purification was achieved by precipitation from acetone solution with methanol and water. Analytically pure samples of **6-8** were obtained by column chromatography on silica gel with a 1:5 mixture of ethyl acetate/hexane as eluent.

TAPs **9** and **10** were not purified but hydrolyzed to the octa-alcohols as crude products.

*2,3,7,8,12,13,17,18-octakis(4-oxo-4-propyloxybutylthio)-5,10,15,20-tetraazaporphyrin*, (*MW* = 1594 g/mol), **6**

Yield: 1.52 g, (0.95 mmol, 76%);  $R_f$  (1:3 ethyl acetate/hexane): 0.25;  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 4.15 (t, 16H,  $J = 6.5$ ), 3.96 (t, 16H,  $J = 6.6$ ), 2.68 (t, 16 H,  $J = 7.2$ ), 2.21 (tt, 16H,  $J = 7.2$ ), 1.57 (m, 16H), 0.86 (t, 24H,  $J = 7.2$ );  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 172.48, 150.59, 139.41, 68.02, 34.07, 30.73, 27.80, 21.66, 10.63; IR ( $\text{cm}^{-1}$ ): 3292.24 (m,  $\nu(\text{N-H})$ , inner core NH), 2930 (m,  $\nu(\text{C-H})$ ,  $\text{CH}_2$ ), 1735 (s,  $\nu(\text{C=O})$ , propyl ester); UV/VIS ( $\lambda_{\text{max}}$  in nm) THF, ( $\epsilon / \text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ ): 357 (44 100), 505 (20000), 638 (26000), 708 (35000); EA: Theoretical; 53.61% C; 7.15% N; 6.56% H; Found: 53.53% C; 7.40% N, 6.70% H.

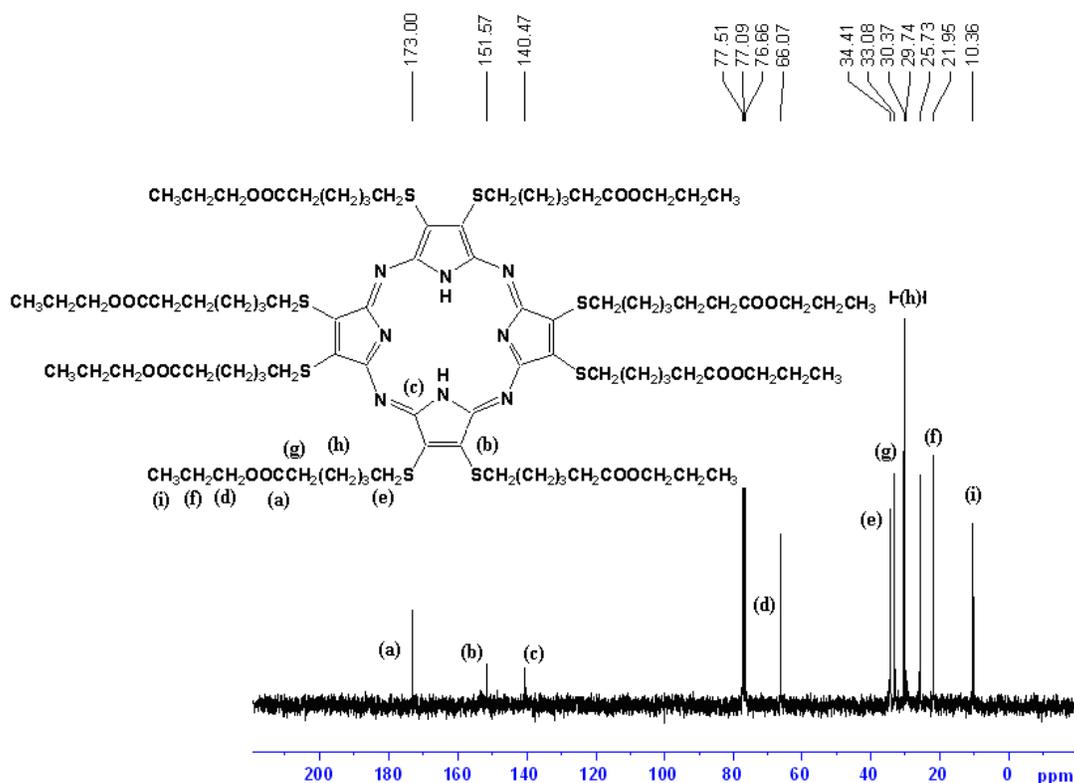
*2,3,7,8,12,13,17,18-octakis(6-oxo-6-propyloxypentylthio)-5,10,15,20-tetraazaporphyrin,*

(*MW* = 1794 g/mol), **7**

Yield: 1.61 g, (0.9 mmol, 72%); *R<sub>f</sub>* (1:3 ethyl acetate/hexane): 0.40; <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ: 4.10 (t, 16H, *J* = 7.2), 3.97 (t, 16H, *J* = 6.6), 2.29 (broad, 16H), 1.92 (broad, 16H), 1.60 (m, 48H), 0.88 (t, 24H, *J* = 7.2); <sup>13</sup>C-NMR (CDCl<sub>3</sub>) δ: 173.00, 151.57, 140.47, 66.07, 34.41, 33.08, 30.37, 29.74, 25.73, 21.95, 10.36; IR (cm<sup>-1</sup>): 3289 (m, ν(N-H) inner core NH), 2931, 2853 (m, ν(C-H), CH<sub>2</sub>), 1734 (m, ν(C=O), propyl ester); UV/VIS (λ max in nm) THF, (ε / dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>): 353 (44 100), 505 (20000), 641 (26000), 708 (34700); EA: Theoretical; 54.18% C; 7.02% N; 6.69% H; Found: 53.97% C; 7.32% N; 6.90% H.

*2,3,7,8,12,13,17,18-octakis(11-oxo-11-propyloxyundecylthio)-5,10,15,20-tetraazaporphyrin,* (*MW* = 2354 g/mol), **8**

Yield: 2.26 g, (0.96 mmol, 77%); *R<sub>f</sub>* (1:3 ethyl acetate/hexane): 0.68; <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ: 4.10 (t, 16H, *J* = 6.5), 4.01 (t, 16H, *J* = 6.5), 2.25 (broad, 16H), 1.91 (broad, 16H), 1.62 (m, 64H), 1.27 (m, 64H), 0.93 (t, 24H, *J* = 7.5); <sup>13</sup>C-NMR (CDCl<sub>3</sub>) δ: 173.88, 151.50, 140.83, 65.86, 34.44, 30.65, 29.61, 29.52, 29.43, 29.33, 29.24, 29.10, 25.10, 22.14, 10.42; IR (cm<sup>-1</sup>): 3286 (m, ν(N-H), inner core NH), 2920, 2851 (m, ν(C-H), CH<sub>2</sub>), 1734 (m, ν(C=O), propyl ester); UV/VIS (λ max in nm) THF, (ε / dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>): 353 (44 100), 502 (20000), 640 (26000), 708 (35000); EA: Theoretical; 64.36% C; 4.76% N; 9.16% H; Found: 63.95% C; 5.03% N; 9.45% H.



Example <sup>13</sup>C-NMR of TAP **7** in CDCl<sub>3</sub>

### 1.7 General synthesis of 2,3,7,8,12,13,17,18-octakis(carboxyalkylthio)-5,10,15,20-tetraazaporphyrins (C3COOH, C5COOH, and C10COOH) and 2,3,7,8,12,13,17,18-octakis(hydroxyalkylthio)-5,10,15,20-tetraazaporphyrins (C3OH and C11OH)

TAPs **6-10** (0.9 mmol) were dissolved in 70 mL of THF and 5 mL of 5 M KOH<sub>aq</sub> solution were added drop wise over 5 minutes under vigorous stirring at 50 °C. The solution was heated to reflux for 2 hrs and then evaporated to dryness. The residual green TAP salts were dissolved in water and slowly acidified with 1 M HCl<sub>aq</sub> until a pH of 6 (octa-alcohols) or 3 (octa-acids) was obtained. All TAPs precipitated as dark violet solids, which were collected on a filter and washed with cold MeOH. The octa-alcohol TAPs **C3OH** and **C11OH** were purified by column chromatography on silica as described previously. Their spectroscopic data agree with reported values.<sup>4</sup>

Purification of the octa-acid TAPs by chromatography on silica or RP-18 was not successful because of low solubility in the required eluents. They were purified by successive re-precipitations from hot THF by the addition of a small amount of 1M NaOH<sub>aq</sub> and then from 1M NaOH<sub>aq</sub> solution by the addition of 1 M HCl<sub>aq</sub>. All solutions in 1M NaOH<sub>aq</sub> are green in colour because the TAP is also deprotonated but turns back to purple when acidified. The TAPs precipitated out within 1-2 hrs at pH 3 of the aqueous solution.

All TAPs are dark purple in colour and are crystalline solids except for TAP **C3OH** that is amorphous and soft at room temperature.

*2,3,7,8,12,13,17,18-octakis(3-carboxypropylthio)-5,10,15,20-tetraazaporphyrin (MW = 1260 g/mol), C3COOH*

Yield: 910 mg, (0.72 mmol 80%); overall yield based on **1**: 25%

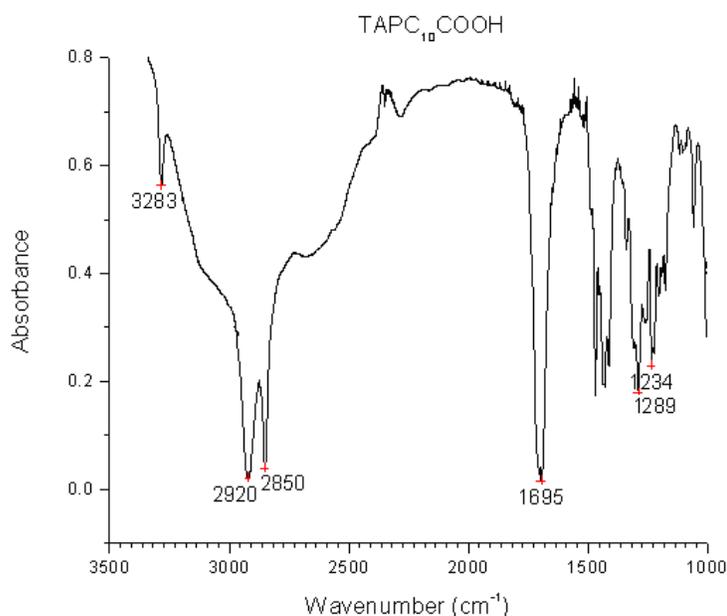
<sup>1</sup>H-NMR (d<sub>5</sub>Pyridine): 4.48 (t, 16H, J = 7 Hz), 2.49 (t, 16H, J = 7 Hz), 2.16 (tt, 16H, J = 16 Hz), -1.041 (s, 2H, 2(N-H)); IR (cm<sup>-1</sup>): 3284 (m, ν(N-H), inner core NH), 2918 (m, ν(C-H), CH<sub>2</sub>), 1697 (s, ν(C=O) carboxylic acid); MS [MALDI +ve ion]: Theoretical ((M+H)<sup>+</sup>): 1259; Found: 1259; EA: Theoretical \*4H<sub>2</sub>O: 43.29% C; 8.41% N; 5.00% H; Found: 43.19% C; 8.55% N; 5.20% H. The water content was verified by TGA-MS.

*2,3,7,8,12,13,17,18-octakis(3-carboxypentylthio)-5,10,15,20-tetraazaporphyrin (MW = 1484 g/mol), C5COOH*

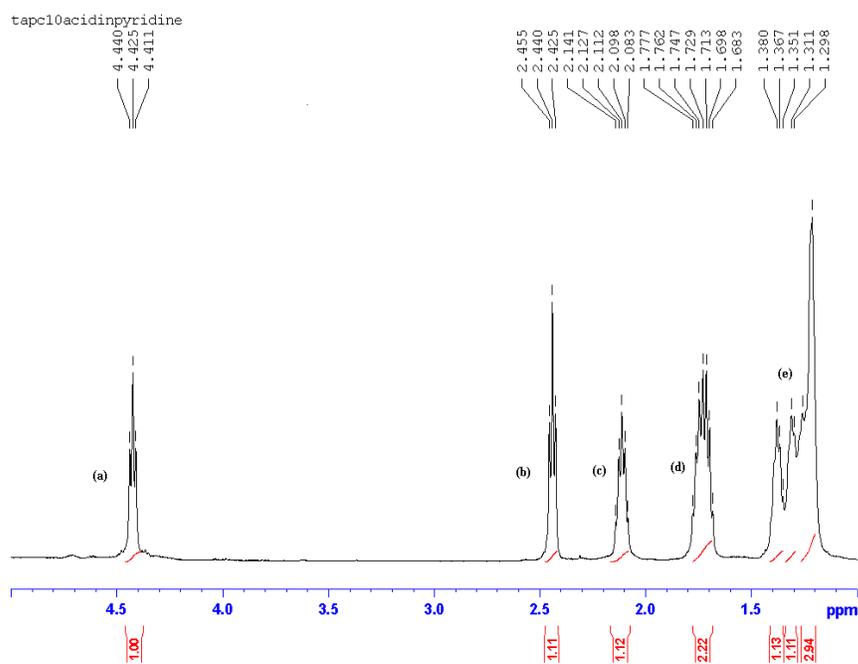
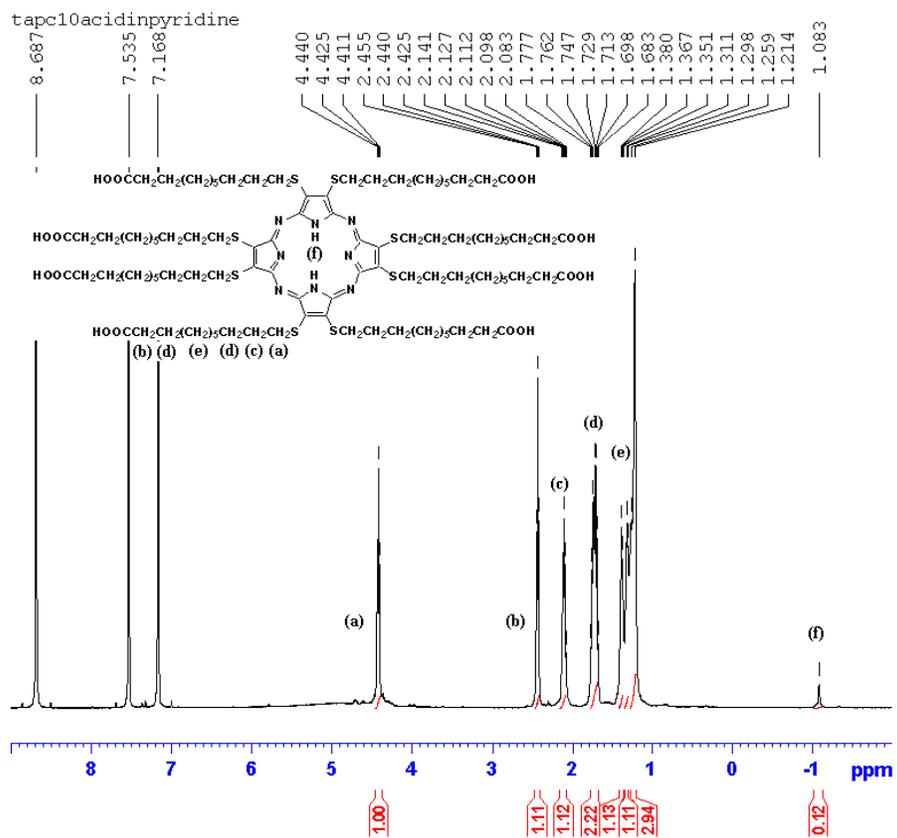
Yield: 1.10 g, (0.74 mmol, 82%); overall yield: 26%; <sup>1</sup>H-NMR (d<sub>5</sub>Pyridine): 4.38 (t, 16H, J = 7 Hz), 2.52 (t, 16H, J = 6.5 Hz), 2.13 (tt, 16H, J = 7 Hz), 1.89 (m, 32H), -1.15 (s, 2H 2(N-H)); IR (cm<sup>-1</sup>): 3285 (m, ν(N-H), inner core NH), 2928, 2856 (m, ν(C-H), CH<sub>2</sub>), 1696 (s, ν(C=O), carboxylic acid); MS [MALDI +ve ion]: Theoretical ((M+H)<sup>+</sup>): 1483; Found: 1483; EA: Theoretical\*2H<sub>2</sub>O: 50.57% C; 7.37% N; 6.23% H; Found: 50.36% C; 7.51% N; 6.32% H. The water content was verified by TGA-MS.

*2,3,7,8,12,13,17,18-octakis(3-carboxydecylthio)-5,10,15,20-tetraazaporphyrin* ( $MW = 2045 \text{ g/mol}$ ), **C10COOH**

Yield: 1.44 grams, (0.71 mmol, 78%); overall yield: 28%;  $^1\text{H-NMR}$  ( $d_5$  Pyridine): 4.43 (t, 16H,  $J = 7.5$ ), 2.44 (t, 16H,  $J = 7.5$ ), 2.11 (tt, 16H,  $J = 7.0$ ), 1.73 (m, 32H), 1.37 (m, 16H), 1.30 (m, 16H), 1.26 (m, 48H), -1.08 (s, 2H, 2(N-H)); IR ( $\text{cm}^{-1}$ ): 3288 (m,  $\nu(\text{N-H})$ , inner core NH), 2919, 2850 (m,  $\nu(\text{C-H})$ ,  $\text{CH}_2$ ), 1695 (s,  $\nu(\text{C=O})$  carboxylic acid); MS [MALDI +ve ion]: Theoretical  $((\text{M}+\text{H})^+)$ : 2044; Found: 2044; EA: Theoretical  $*2\text{H}_2\text{O}$ : 60.02% C; 5.38% N; 8.43% H; Found: 59.88% C; 5.40% N; 8.50% H. The water content was verified by TGA-MS.



IR of **C10COOH** as thin film on KBr. Hydrolysis of the ester groups to carboxylic acids is monitored by the change in the carbonyl stretching mode ( $\nu_{\text{C=O, ester}} = 1740 \text{ cm}^{-1}$ ,  $\nu_{\text{C=O, acid}} = 1695 \text{ cm}^{-1}$ ) and the broad O-H stretching absorption of the carboxylic acid between  $3300\text{-}2500 \text{ cm}^{-1}$ . The peak at  $3283 \text{ cm}^{-1}$  belongs to the N-H stretching mode and confirms that the macrocycle is metal-free.



<sup>1</sup>H-NMR of C10COOH in pyridine (top) and expanded region (bottom)

### 1.8 General synthesis of [2,3,7,8,12,13,17,18-octakis(carboxyalkylthio)-5,10,15,20-tetraazaporphyrinato]copper(II) (CuC3COOH, CuC5COOH, and CuC10COOH)

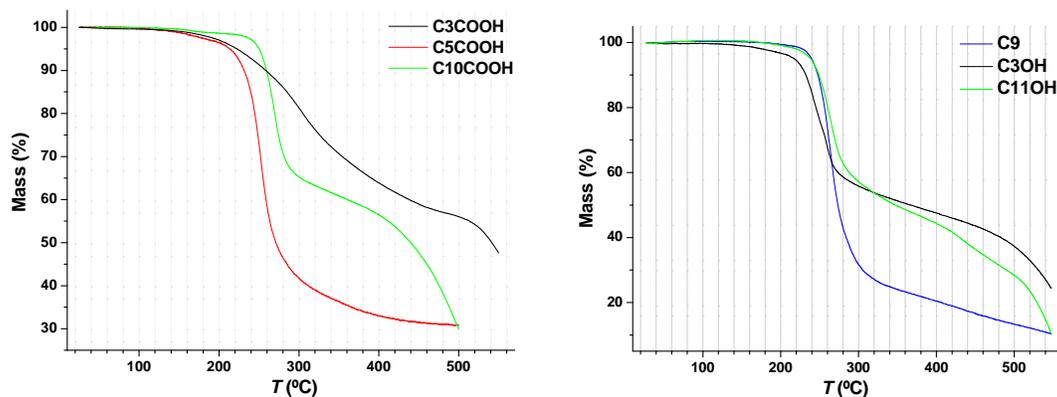
Octa-acid TAPs **C3COOH**, **C5COOH**, or **C10COOH** (0.1 mmol) were added to a solution of Cu(II) acetate (0.2 mmol) in THF and heated to reflux for 12-24 hrs. Completion of the metallation was confirmed by UV-Vis spectroscopy before deionized water was added to precipitate out the copper TAPs. The TAPs were washed with 9:1 mixture of deionized water and acetic acid until the aqueous phase is colourless (all copper salts are removed) and finally re-precipitated from hot THF by the addition of deionized water.

*[2,3,7,8,12,13,17,18-octakis(propane acid thio)-5,10,15,20-tetraazaporphyrinato]copper(II)* (MW = 1322 g/mol), **CuC3COOH**  
Yield: 120 mg, (0.091 mmol, 91 %) UV-VIS: 361 (41 200), 502 (14 700), 669 (53 000)  
IR (cm<sup>-1</sup>): 2921, 2850 (m, ν(C-H), CH<sub>2</sub>), 1699 (s, ν(C=O), carboxylic acid) EA  
Theoretical\*3 H<sub>2</sub>O; 43.64%C; 8.48%N; 4.27%H; Found: 43.92%C; 8.12%N; 4.60%H.

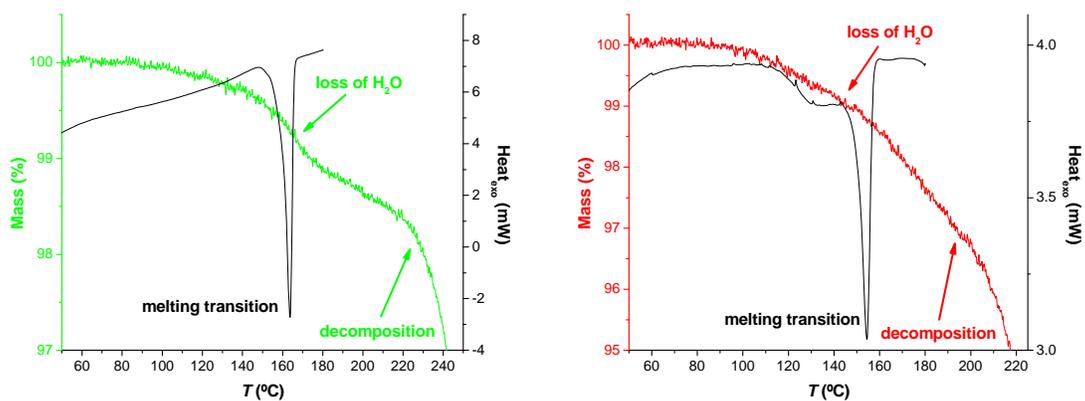
*[2,3,7,8,12,13,17,18-octakis(hexanoic acid thio)-5,10,15,20-tetraazaporphyrinato]copper(II)* (MW = 1546 g/mol), **CuC5COOH**  
Yield: 144 mg, (0.093 mmol, 93%) UV/VIS: 361 (41 200), 502 (14 700), 670 (52 500) IR  
(cm<sup>-1</sup>): 2929 (m, ν(C-H), CH<sub>2</sub>), 1700 (m, ν(C=O), carboxylic acid) EA  
Theoretical\*2H<sub>2</sub>O: 49.74%C; 7.25%N; 5.74%H; Found: 50.02%C; 6.90%N; 6.01%H.

*[2,3,7,8,12,13,17,18-octakis(undecanoic acid thio)-5,10,15,20-tetraazaporphyrinato]copper(II)* (MW = 2108 g/mol), **CuC10COOH**  
Yield: 197 mg, (0.093 mmol, 93%) UV/VIS: 362 (41 000), 502 (14 600), 668 (52 500) IR  
(cm<sup>-1</sup>): 2921, 2851 (s, ν(C-H), CH<sub>2</sub>), 1702 (s, ν(C=O), carboxylic acid); EA  
Theoretical\*2H<sub>2</sub>O; 59.30%C; 5.32%N; 8.04%H; Found: 59.49%C; 5.12%N; 8.40%H.

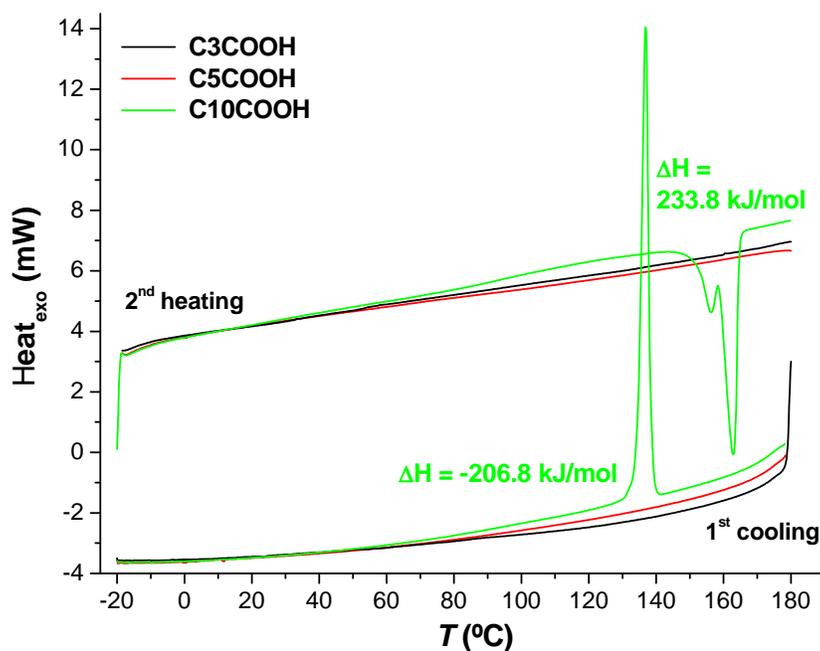
## 2 Thermal Analysis



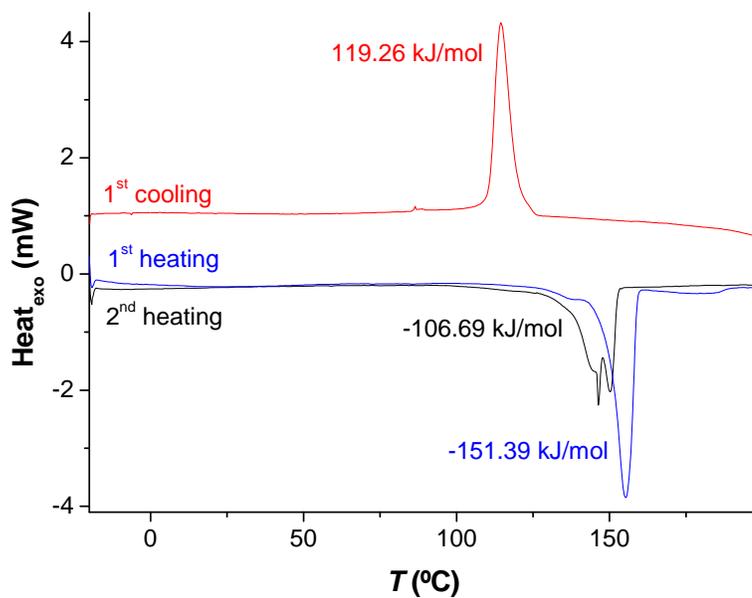
**Figure S1.** TGA curves of octa-acid TAPs (left) and octa-alcohol TAPs (right) in He at 5 °C/min. The TGA curve of 2,3,7,8,12,13,17,18-octakis(nonylthio)-5,10,15,20-tetraazaporphyrin (**C9**, right) is shown for comparison.



**Figure S2.** Expanded range of TGA and DSC (1<sup>st</sup> heating) curves of **C10COOH** (left) and **C5COOH** (right). The melting transitions coincide with the on-set of weight loss due to loss of water.

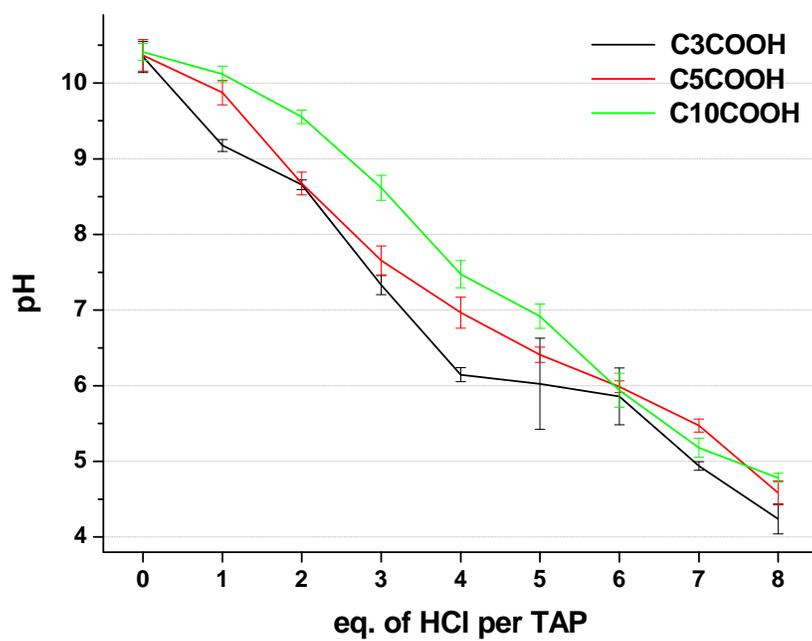


**Figure S3.** Reversible DSC curves of octa-acid TAPs at 5 °C/min. TAP C5COOH undergoes an irreversible endothermic transition at 154 °C in the 1<sup>st</sup> heating run (see Fig. S2).



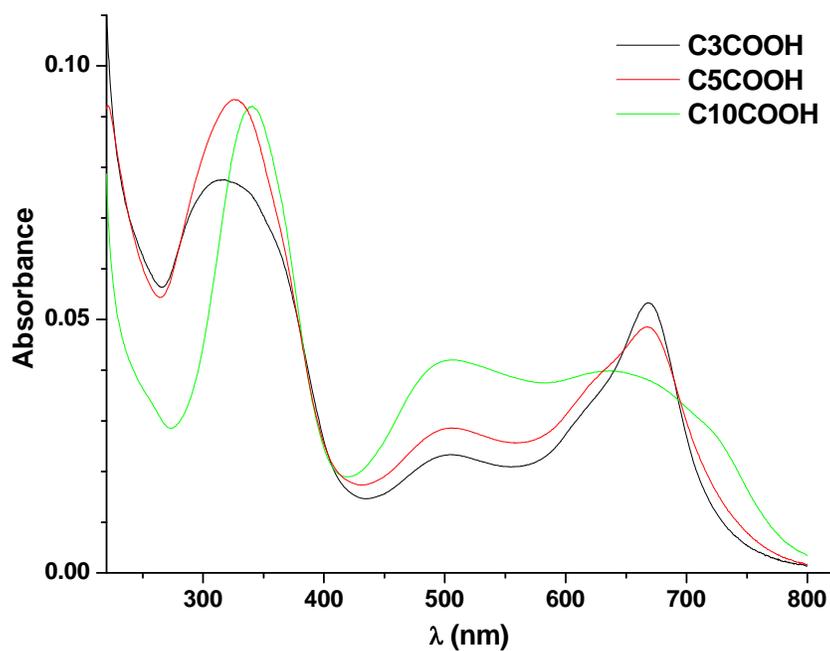
**Figure S4.** DSC curves of CuC10COOH at 10 °C/min.

### 3 Titration



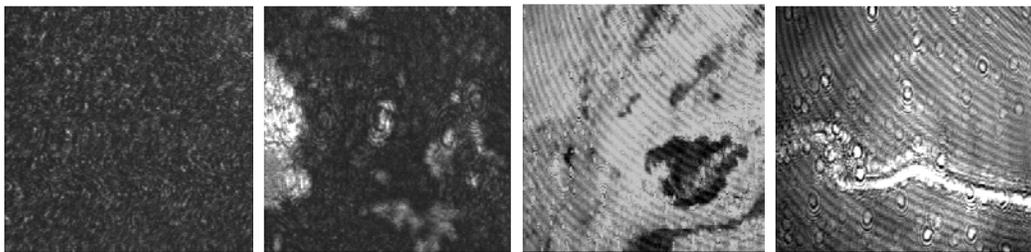
**Figure S5.** Titration of aqueous solutions of sodium octa-carboxylate TAPs with  $10^{-3}$  M  $\text{HCl}_{\text{aq}}$ . Values are averaged over 3 measurements and the standard deviation is given for each point.

## 4 Aggregation Studies by UV/VIS Spectroscopy

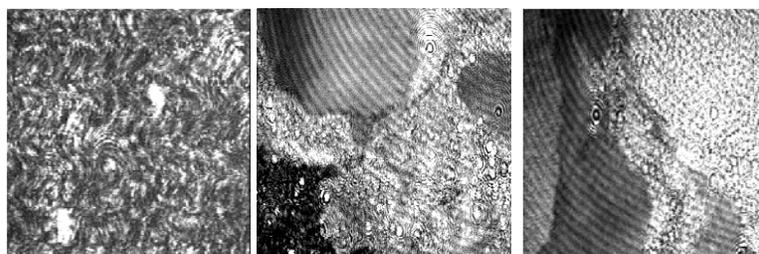


**Figure S6.** UV/VIS spectra of  $10^{-6}$  M solutions of octa-acid TAPs in  $10^{-3}$  M  $\text{NaOH}_{\text{aq}}$  that indicate aggregation of TAPs **C10COOH** and **C5COOH** while **C3COOH** is not aggregated. The absorption spectra show only two Q-bands, similar to the spectra of metallated TAPs, because the inner NH protons of the TAPs have been abstracted by the base to form a dianionic macrocycle.

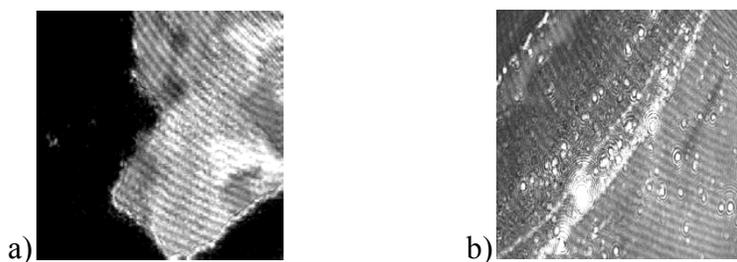
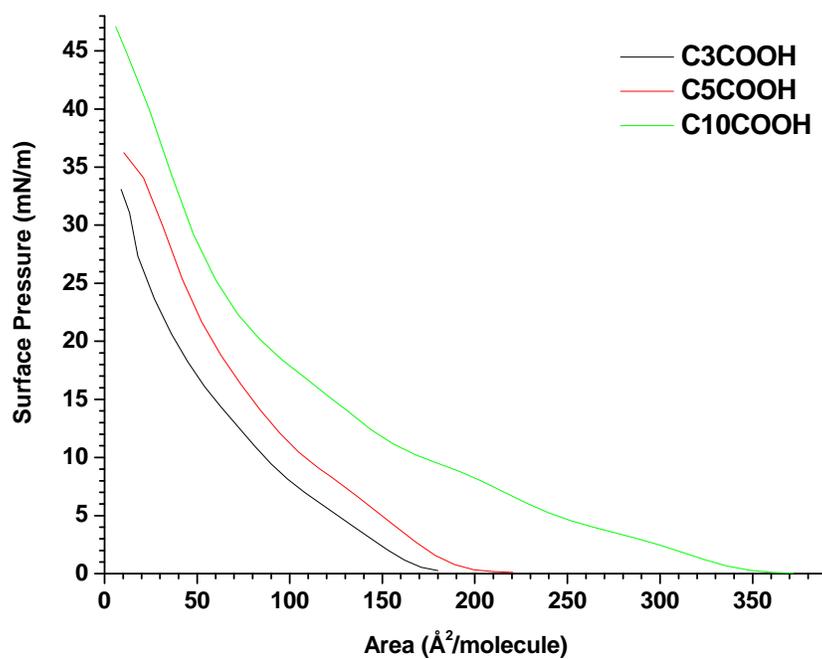
## 5 Langmuir Monolayers of Octa-acid TAPs



**Figure S7.** BAM images (imaged area 220 x 220  $\mu\text{m}$ ) of **C3COOH** on pure water (pH = 6.5) at surface pressures of 0 mN/m, 5 mN/m, 16 mN/m, and 31 mN/m from left to right. 3-Dimensional aggregates already appear at low surface pressure (e.g. image at 5 mN/m) but are persistent and increasing in number at surface pressures above 20 mN/m

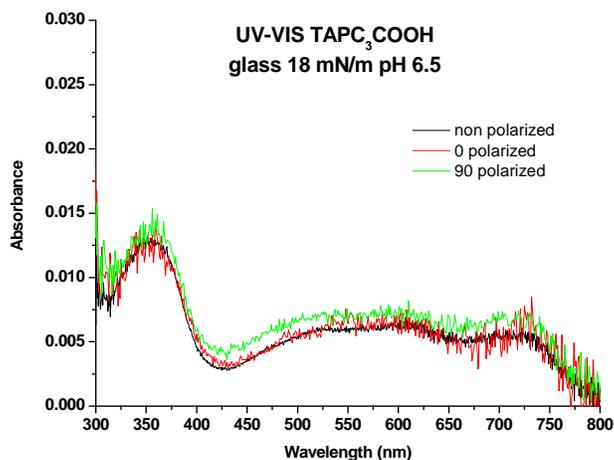


**Figure S8.** BAM images (imaged area 220 x 220  $\mu\text{m}$ ) of **C5COOH** on pure water (pH = 6.5) at surface pressures of 0 mN/m, 5 mN/m, and 20 mN/m from left to right. 3-Dimensional aggregates already appear at low surface pressure but are persistent and increasing in number at surface pressures above 18 mN/m

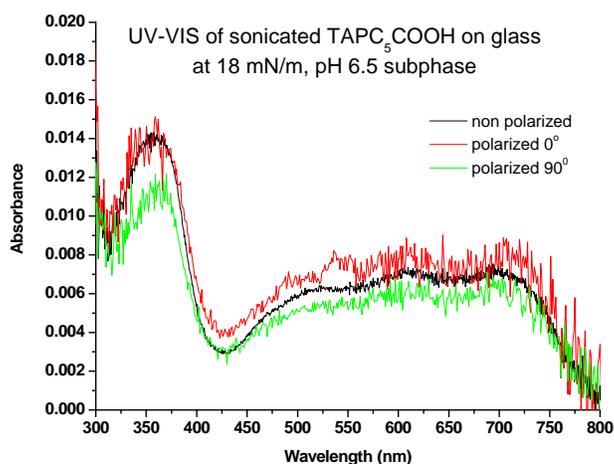


**Figure S9.**  $\pi$  vs. A isotherms of octa-acid TAPs at pH = 3.0 of the aqueous subphase and BAM images of the Langmuir film of **C10COOH** at (a) 7 mN/m (210  $\text{\AA}^2/\text{molecule}$ ) and (b) 28 mN/m (90  $\text{\AA}^2/\text{molecule}$ )

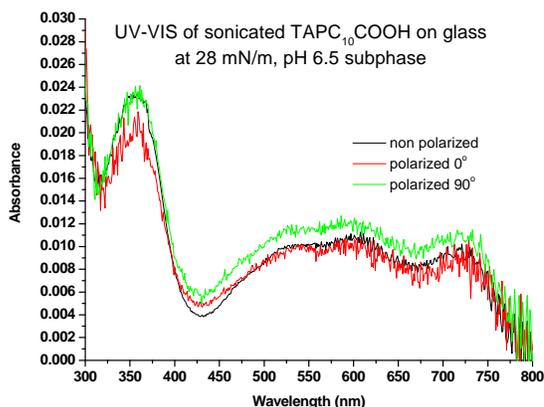
## 6 LB Monolayers of Octa-acid TAPs



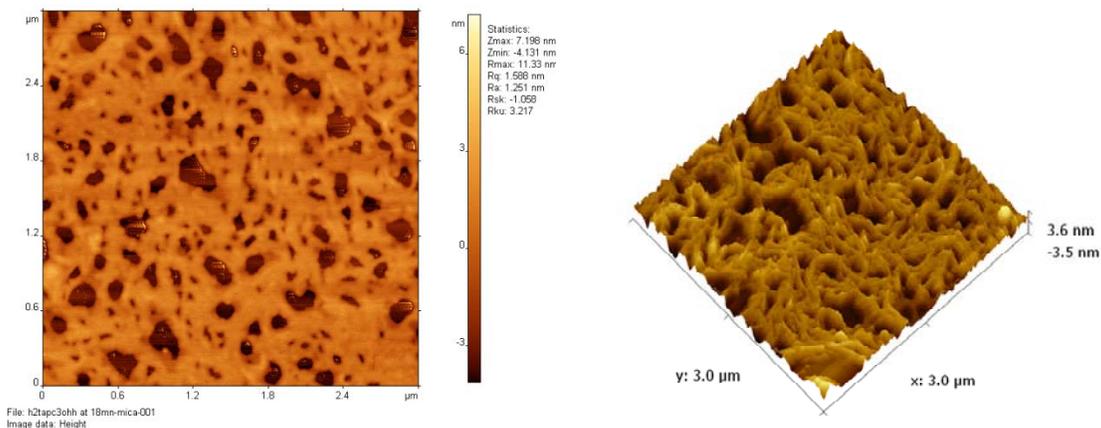
**Figure S10.** UV-Vis absorption spectra of an LB film of **C3COOH** on glass that was transferred by Z-deposition on the upstroke at a speed of  $2 \text{ mm min}^{-1}$  and symmetric compression. The aqueous subphase had a pH of 6.5 and the transfer pressure was 18 mN/m. Shown are absorption spectra with depolarized light and linearly polarized light. Orientations  $0^\circ$  and  $90^\circ$  indicate polarizations parallel and orthogonal to the direction of the upstroke, respectively.



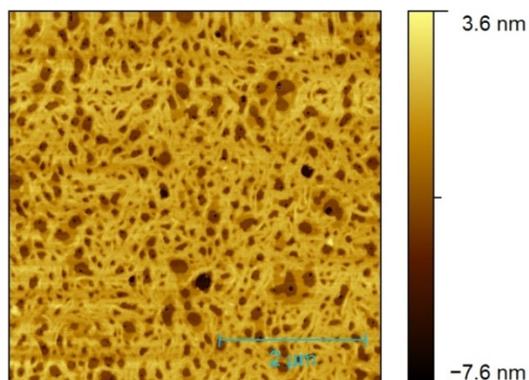
**Figure S11.** UV-Vis absorption spectra of an LB film of **C5COOH** on glass that was transferred by Z-deposition on the upstroke at a speed of  $2 \text{ mm min}^{-1}$  and symmetric compression. The aqueous subphase had a pH of 6.5 and the transfer pressure was 18 mN/m. Shown are absorption spectra with depolarized light and linearly polarized light. Orientations  $0^\circ$  and  $90^\circ$  indicate polarizations parallel and orthogonal to the direction of the upstroke, respectively.



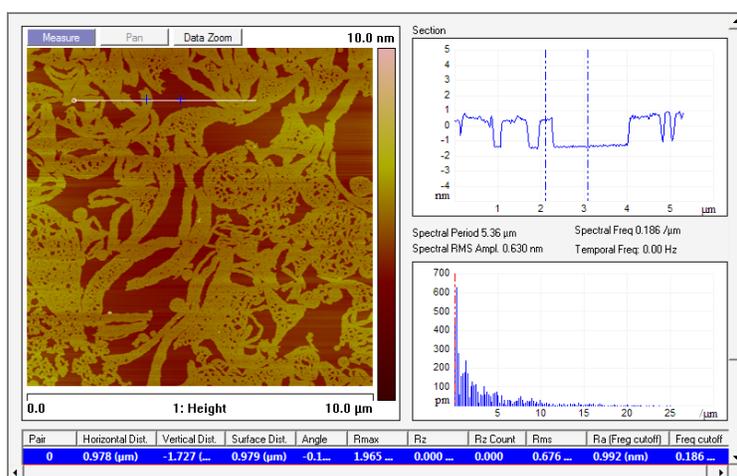
**Figure S12.** UV-Vis absorption spectra of an LB film of **C10COOH** on glass that was transferred by Z-deposition on the upstroke at a speed of  $2 \text{ mm min}^{-1}$  and symmetric compression. The aqueous subphase had a pH of 6.5 and the transfer pressure was 28 mN/m. Shown are absorption spectra with depolarized light and linearly polarized light. Orientations  $0^\circ$  and  $90^\circ$  indicate polarizations parallel and orthogonal to the direction of the upstroke, respectively.



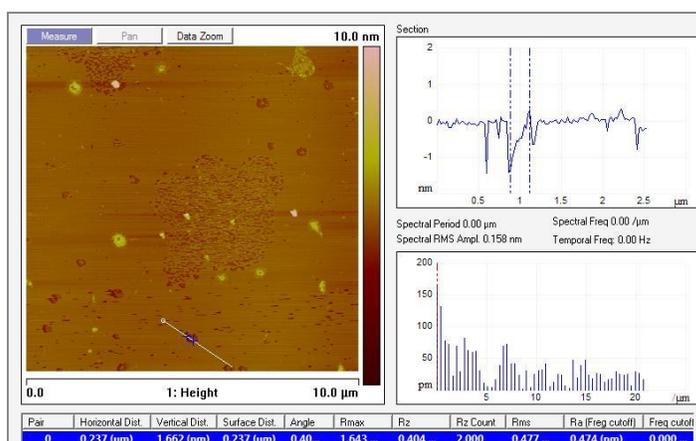
**Figure S13.** AFM image of the LB film of **C3COOH** transferred by Z-deposition on the upstroke at a speed of  $2 \text{ mm min}^{-1}$  onto mica at symmetric compression. The aqueous subphase had a pH of 6.5 and the transfer pressure was 18 mN/m.



**Figure S14.** AFM image of the LB film of **C5COOH** transferred by Z-deposition on the upstroke at a speed of  $2 \text{ mm min}^{-1}$  onto mica at symmetric compression. The aqueous subphase had a pH of 6.5 and the transfer pressure was 18 mN/m.

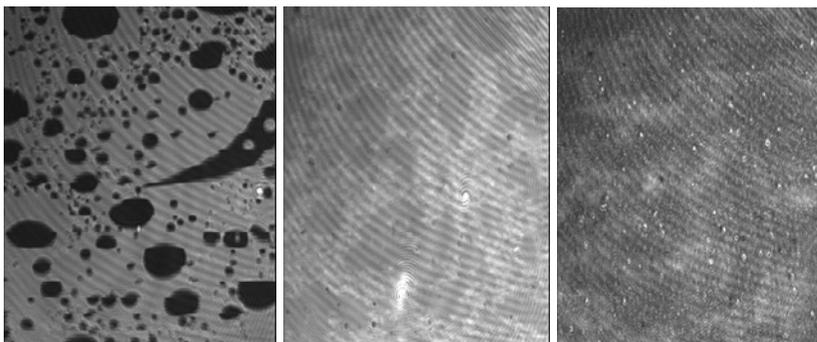


**Figure S15.** Example AFM profile measurement of the LB film of **C10COOH** transferred by Z-deposition on the upstroke at a speed of  $2 \text{ mm min}^{-1}$  onto mica at symmetric compression. The aqueous subphase had a pH of 6.5 and the transfer pressure was 2.5 mN/m.

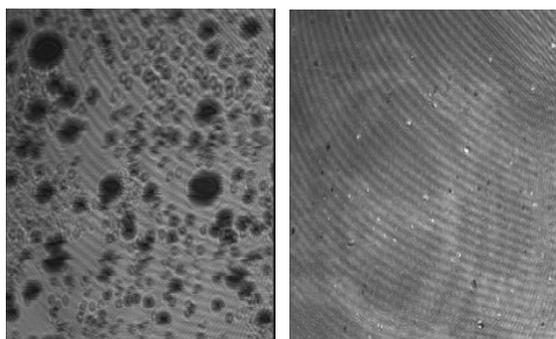


**Figure S16.** Example AFM profile measurement of the LB film of **C10COOH** transferred by Z-deposition on the upstroke at a speed of  $2 \text{ mm min}^{-1}$  onto mica at symmetric compression. The aqueous subphase had a pH of 6.5 and the transfer pressure was 20 mN/m.

## 7 Langmuir Monolayers of Octa-alcohol TAPs

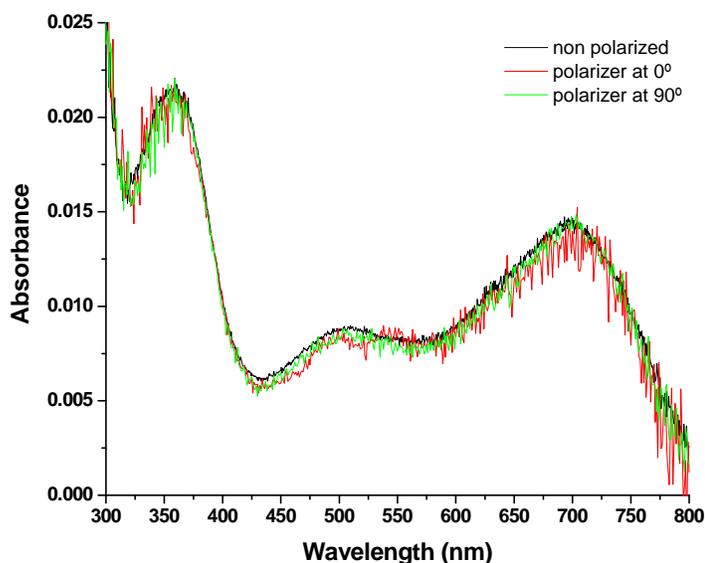


**Figure S17.** BAM images (imaged area 220 x 220  $\mu\text{m}$ ) of **C3OH** on pure water (pH = 6.5) at surface pressures of 0 mN/m, 15 mN/m, and 25 mN/m from left to right.

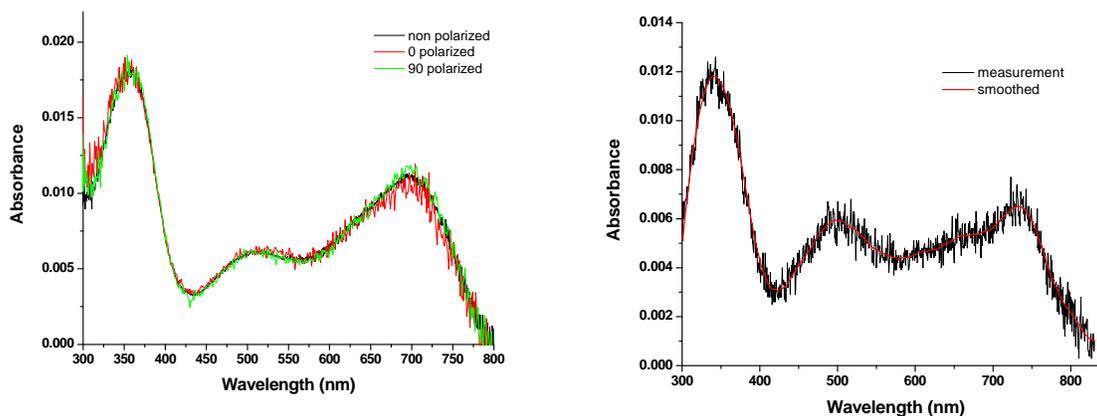


**Figure S18.** BAM images (imaged area 220 x 220  $\mu\text{m}$ ) of **C11OH** on pure water (pH = 6.5) at surface pressures of 0 mN/m (left) and 20 mN/m (right).

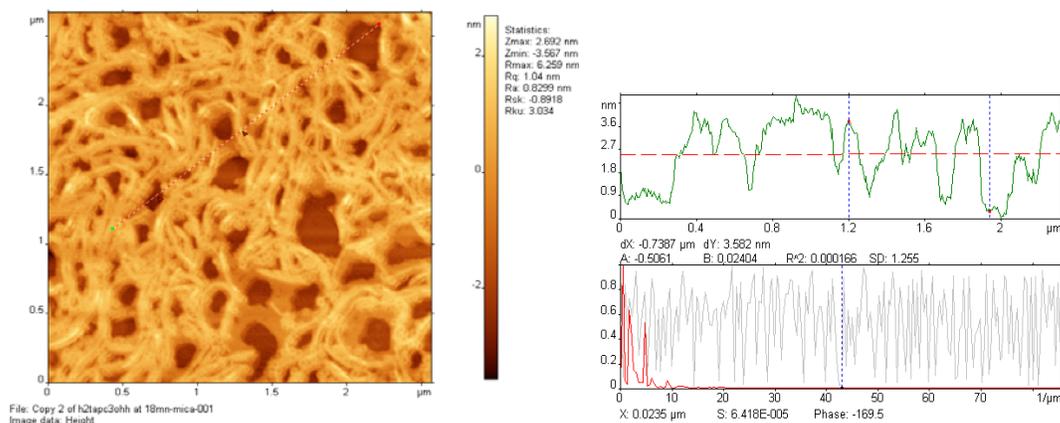
## 8 LB Monolayers of Octa-alcohol TAPs



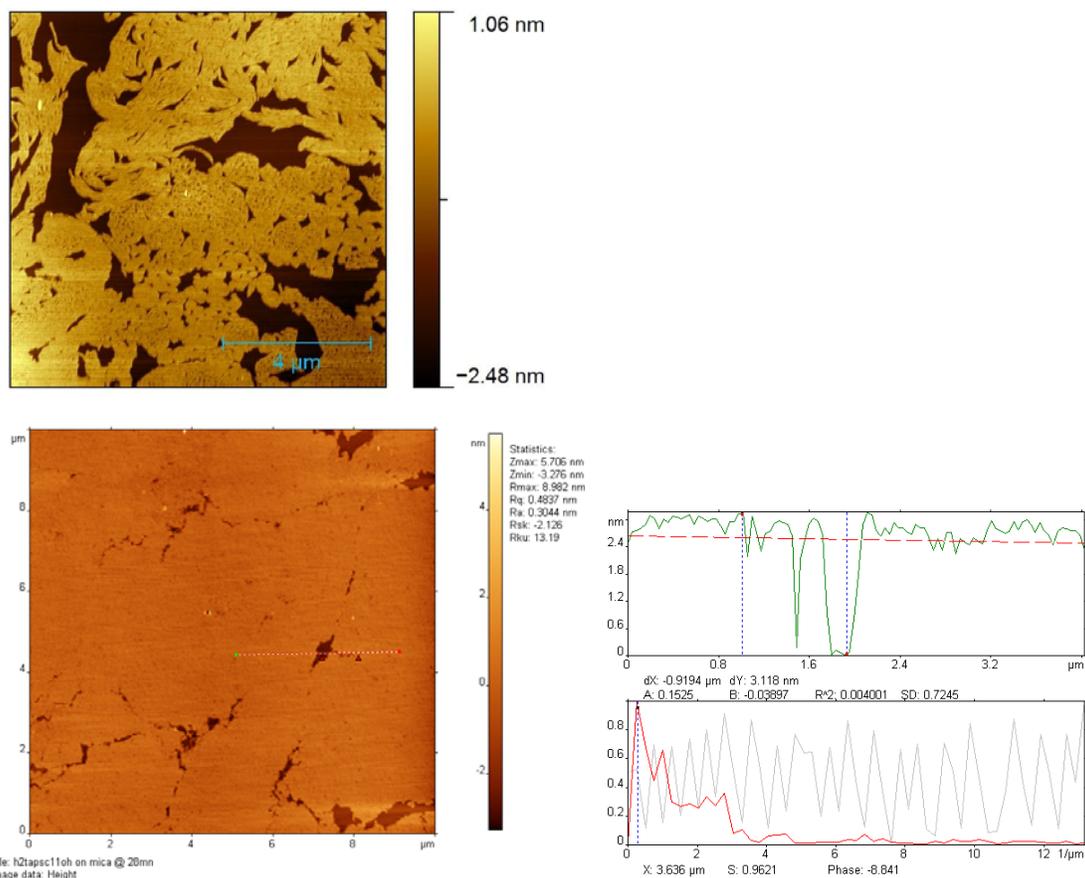
**Figure S19.** UV-Vis absorption spectra of an LB film of **C30H** on glass that was transferred by Z-deposition on the upstroke at a speed of  $2 \text{ mm min}^{-1}$  and symmetric compression. The aqueous subphase had a pH of 6.5 and the transfer pressure was 28 mN/m. The incoming light beam was depolarized or linearly polarized parallel (0) and orthogonal (90) to the dipping direction.



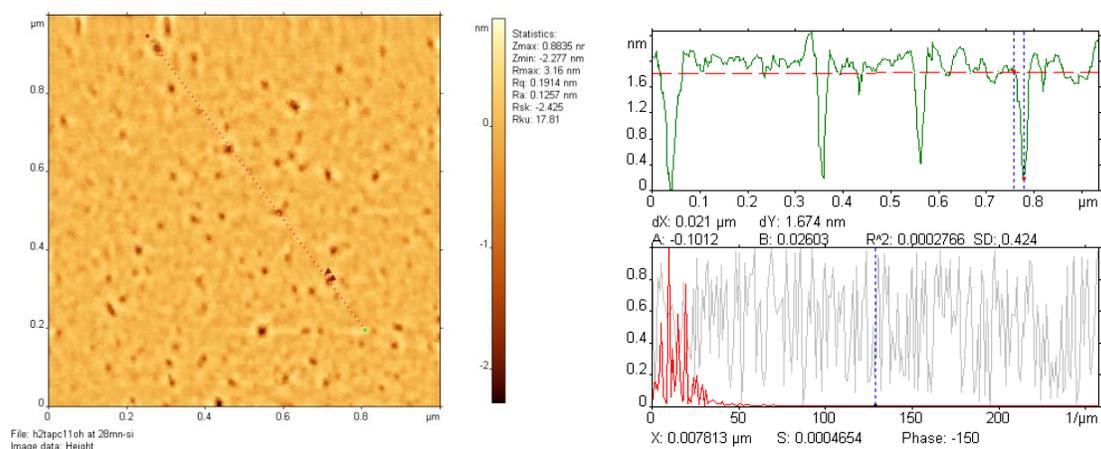
**Figure S20.** UV-Vis absorption spectra of LB films of **C11OH** on glass that were transferred by Z-deposition on the upstroke at a speed of  $2 \text{ mm min}^{-1}$  and symmetric compression. The pH of the aqueous subphase was 6.5 and the transfer pressures were 28 mN/m (left) and 18 mN/m (right). The incoming light beam was depolarized or linearly polarized parallel (0) and orthogonal (90) to the dipping direction (left).



**Figure S21.** AFM image and profile of an LB film of **C30OH** on mica that was transferred by Z-deposition on the upstroke at a speed of  $2 \text{ mm min}^{-1}$  and symmetric compression. The aqueous subphase had a pH of 6.5 and the transfer pressure was  $18 \text{ mN/m}$ . A height profile across holes was used to determine the thickness of the 3-dimensional features to about  $3.6 \text{ nm}$  on average and a maximum of  $4.8 \text{ nm}$ .



**Figure S22.** AFM images of LB films of **C11OH** on mica that were transferred by Z-deposition on the upstroke at a speed of  $2 \text{ mm min}^{-1}$  and symmetric compression. The aqueous subphase had a pH of 6.5 and the transfer pressure was  $18 \text{ mN/m}$  (top) and  $28 \text{ mN/m}$  (bottom). A height profile across holes was used to determine the thickness of the film transferred at  $28 \text{ mN/m}$  to about  $2.7 \text{ nm}$  on average and a maximum of  $3.1 \text{ nm}$ .



**Figure S23.** AFM image of an LB film of **C11OH** on a silicon wafer that was transferred by Z-deposition on the upstroke at a speed of  $2 \text{ mm min}^{-1}$  and symmetric compression. The aqueous subphase had a pH of 6.5 and the transfer pressure was 28 mN/m. The height profile across holes was used to determine the thickness of the film to about 2.0 nm on average and a maximum of 2.5 nm.

1. C. J. Schramm and B. M. Hoffman, *Inorg. Chem.*, 1980, **19**, 383.
2. S. Wolfe, M.-C. Wilson, M.-H. Cheng, G. V. Shustov and C. I. Akuche, *Can. J. Chem.*, 2003, **81**, 937.
3. H. C. Brown and C. F. Lane, *J. Am. Chem. Soc.*, 1970, **92**, 6660.
4. H. Eichhorn, M. Rutloh, D. Woehrl, J. Stumpe and U. B. B. G. Inst. Org. Makromol. Chem, *J. Chem. Soc., Perkin Trans. 2*, 1996, 1801.