Synthesis and Aqueous Aggregation Properties of Amphiphilic Surface-Block Dendrimers

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Supporting Information

Instrumentation:

All solvents were dried and freshly distilled prior to use (DCM and pyridine with CaH₂, and THF with Na). All chemicals were purchased from Aldrich or Acros as highest purity grade and used without further purification. All reactions were performed under nitrogen atmosphere at room temperature unless specified otherwise. NMR spectra were recorded on a Varian INOVA spectrometer (for ¹H and ¹³C NMR, 400 MHz and 100.6 MHz respectively). Fast atom bombardment mass spectra (FAB-MS) were obtained on a JEOL JMS-SX102A spectrometer using a 3-nitrobenzyl alcohol matrix. MALDI-TOF mass spectra were obtained using a PerSpective Biosystems Voyager-DE Biospectrometry Workstation operating in the positive ion mode using 2-(4-hydroxyphenylazo)-benzoic acid (HABA). Elemental analysis was obtained from Atlantic Microlab, Inc. Size exclusion chromatography was performed using THF as the eluent on a Polymer Laboratories PLgel 3 μ m MIXED-E column (3 μ m bead size) and a Rainin HPLC system (temp = 25 °C; flow rate = 1.0 mL/min). Polystyrene standards (0.93K, 4.45K, and 12K; PDI = 1.03 - 1.05) were used for calibration. Light micrographs were obtained using an Olympus IX70 inverted light microscope. Tensiometric data was

obtained using a Kruss K12 Tensiometer in conjunction with a Metrohm Desimate 665. Fluorescence spectra were recorded on a Hitachi F2500 Fluorimeter. Thermal transition temperatures were measured using a TA Instruments DSCQ100 modulated differential scanning calorimeter. Transmission electron micrographs were obtained using a Philips CM10 TEM (negative staining with 2% uranyl acetate in water, Cu/Pd carbon coated grids).

Abbreviations:

EDCI = 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride, EtOAc = ethyl acetate, DCC = dicyclohexylcarbodiimide, DCM = dichloromethane, DCU = 1,3-dicyclohexylurea, DMAP = 4-(dimethylamino)pyridine, DPTS = 4-(dimethylamino)-pyridinium *p*-toluenesulfonate, Pd/C = 10 % palladium on activated carbon, THF = tetrahydrofuran.

Bulk hydration of compounds 2, 4, and 7:

When dissolved in aqueous solution, dendrimers **2**, **4** and **7** spontaneously form supramolecular aggregates. Due to the poor solubility of **5**, no hydration structures are observed. The morphology of the structures formed by **2**, **4** and **7** can be altered depending upon external factors such as temperature, concentration, and sample preparation. A selection of the supramolecular assemblies formed from these amphiphiles is shown in Figure S1. The micrographs displayed in Figures S1A, S1B, and S1C are obtained with an inverted light microscope by smearing 1 mg of dendritic amphiphile onto a glass microscope slide and subsequently hydrating with 1 drop of 200

mM buffered HEPES solution (pH = 7.4). Figure S1A shows vesicular structures obtained after hydrating compound **7** and heating to 50 °C for 5 minutes. Figure S1B shows the surface hydration of compound **4**. Worm-like tubules are observed after approximately five minutes of hydration and grow at an observable rate for an additional ten minutes. Figure S1C shows aggregates composed of compound **2** that are relatively uniform in appearance.

Figure S1. A) light micrograph of compound **7**; B) light micrograph of compound **4**; C) light micrograph of compound **2**. Note: All compounds hydrated with 200 mM buffered HEPES solution (pH = 7.4).

Scheme 1: Synthesis of Dendritic Compounds.

Reagents and Conditions:

Compound **8a**; reaction ‘a’

Compound **8** (0.45 g, 0.58 mmol) was dissolved in 75 mL of CH_2Cl_2 with 0.63 g (2.77 mmol) of myristic acid, 0.34 g (1.16 mmol) of DPTS, and 0.72 g (3.47 mmol) of DCC. The reaction was stirred for 16 hours. The DCU precipitate was filtered and the solution was evaporated. The residue was resuspended in 50 mL of ethanol, cooled to 0 °C for 6 hours and filtered. The precipitate was resuspended in 75 mL of CH_2Cl_2 , washed with 75 mL of H_2O , dried over Na_2SO_4 , and the solvent evaporated to yield 0.84 g of

product (89% yield). ^1H NMR (CDCl_3): δ 0.80-0.89 (t, 12H, $-\text{CH}_3$), 1.08 (s, 9H, t-butyl), 1.14-1.34 (m, 80H, myristic $-\text{CH}_2-$), 1.50-1.64 (m, 8H, $\text{C}(=\text{O})-\text{CH}_2-\text{CH}_2-\text{CH}_2-$), 2.22-2.33 (t, 8H, $\text{C}(=\text{O})-\text{CH}_2-\text{CH}_2-$), 2.53-2.83 (m, 12H, succinic $-\text{CH}_2-\text{CH}_2$), 4.08-4.34 (m, 12H, $-\text{CH}_2-\text{CH}-\text{CH}_2-$), 5.18-5.30 (m, 3H, $-\text{CH}_2-\text{CH}-\text{CH}_2-$), 7.32-7.44, 7.61-7.67 (m, 10H, phenyl CH) ppm. ^{13}C NMR (CDCl_3): δ 14.25, 22.67, 24.81, 26.85, 28.81, 28.79, 29.12, 29.24, 29.36, 29.53, 29.64, 31.97, 34.05, 61.88, 62.34, 69.17, 127.66, 130.13, 135.28, 138.77, 171.34, 171.69, 173.32 ppm. FAB-MS: 1620.1 m/z (MH^+) (theory: 1620.29 m/z (M^+)). Elemental analysis: C, 68.84%; H, 9.69% (theory: C, 68.94%; H, 9.58%). SEC: $M_w = 2168$, $M_n = 2135$, PDI = 1.02.

Compound **9**; reaction ‘b’

Compound **8a** (0.81 g, 0.50 mmol) of was dissolved in 100 mL of THF. Next, 0.55 g (1.75 mmol) of tetrabutylammonium fluoride trihydrate was added to the solution. The mixture was stirred for 1 hour. After one hour the reaction was complete as indicated by TLC. The solution was diluted with 25 mL of H_2O and acidified with 1N HCl to a pH of 3. The product was extracted into EtOAc, dried over Na_2SO_4 , rotoevaporated and dried on the vacuum line. The product was purified by column chromatography (0-3% MeOH in CH_2Cl_2) to afford 0.60 g of product (87% yield). $R_f = 0.23$ (3% MeOH in CH_2Cl_2). ^1H NMR (CDCl_3): δ 0.82-0.88 (t, 12H, $-\text{CH}_3$), 1.20-1.31 (m, 80H, myristic $-\text{CH}_2-$), 1.53-1.64 (m, 8H, $-\text{C}(=\text{O})-\text{CH}_2-\text{CH}_2-\text{CH}_2-$), 2.26-2.33 (t, 8H, $-\text{C}(=\text{O})-\text{CH}_2-\text{CH}_2-$), 2.60-2.68 (m, 12H, $-\text{CH}_2-\text{CH}_2-$), 4.11-4.34 (m, 12H, $-\text{CH}_2-\text{CH}-\text{CH}_2-$), 5.19-5.35 (m, 3H, $-\text{CH}_2-\text{CH}-\text{CH}_2-$) ppm. ^{13}C NMR (CDCl_3): δ 14.16, 22.78, 24.98, 28.56, 28.87, 29.07, 29.24, 29.47, 29.63, 29.87, 32.01, 34.04, 62.02, 62.64, 69.16, 69.93,

171.47, 171.68, 173.51 ppm. FAB-MS: 1382.9 m/z ($M-H^+$) (theory: 1381.9 m/z (M^+)). Elemental analysis: C, 66.72%; H, 9.91% (theory: C, 66.92%; H, 9.92%). SEC: M_w = 2074, M_n = 2040, PDI = 1.02.

Compound **10**; reaction 'c'

Compound **9** (0.71 g, 0.52 mmol) was dissolved in 50 mL of CH_2Cl_2 with 0.11 g (0.62 mmol) of *cis*-1,3-*O*-benzylidene glycerol, 0.08 g (0.26 mmol) of DPTS, and 0.16 g (0.78 mmol) of DCC. The reaction was stirred for 48 hours. The DCU precipitate was filtered and the solution was evaporated. The residue was resuspended in a minimum of EtOH and then cooled to 0 °C for 24 hours. The resulting precipitate was collected via suction filtration and placed under vacuum to afford 0.73 g of product (92% yield). 1H NMR ($CDCl_3$): δ 0.81-0.92 (t, 12H, $-CH_3$), 1.21-1.38 (m, 80H, myristic $-CH_2-$), 1.51-1.69 (m, 8H, $C(=O)-CH_2-CH_2-CH_2-$), 2.24-2.35 (t, 8H, $C(=O)-CH_2-CH_2-$), 2.58-2.80 (m, 12H, succinic $-CH_2-CH_2-$), 4.06-4.35 (m, 16H, $-CH_2-CH-CH_2-$), 4.72 (s, 1H, $-CH_2-CH-CH_2-$), 5.18-5.32 (m, 3H, $-CH_2-CH-CH_2-$), 5.54 (s, 1H, CH), 7.30-7.41 (m, 3H, arom. CH), 7.45-7.51 (m, 2H, arom. CH) ppm. ^{13}C NMR ($CDCl_3$): δ 14.00, 22.57, 24.73, 24.85, 28.56, 28.72, 28.88, 29.03, 29.18, 29.26, 29.38, 29.53, 29.56, 29.59, 31.83, 33.91, 61.79, 62.36, 66.31, 68.95, 69.53, 72.27, 101.163, 125.91, 128.31, 128.36, 129.14, 137.84, 171.40, 171.51, 171.71, 172.17, 173.40 ppm. MALDI-MS: 1566.13 m/z ($M+Na^+$) (theory: 1544.08 m/z (M^+)). Elemental analysis: C, 67.55%; H, 9.73% (theory: C, 67.67%; H, 9.53%). SEC: M_w = 2285, M_n = 2267, PDI = 1.01.

Compound **11**; reaction 'd'

Compound **10** (0.71 g, 0.46 mmol) was dissolved in THF (30 mL) and 10% Pd/C (0.7 g) was added. The solution was then placed in a Parr tube on a hydrogenator and shaken under 60 psi. H₂ for 16 hours. The solution was then filtered over wet celite, concentrated, and placed on a high vacuum line to yield 0.65 g of product (98% yield). ¹H NMR (CDCl₃): δ 0.81-0.89 (t, 12H, -CH₃), 1.17-1.35 (m, 80H, alkyl -CH₂-), 1.52-1.63 (m, 8H, C(=O)-CH₂-CH₂-CH₂-), 2.26-2.33 (t, 8H, C(=O)-CH₂-CH₂-), 2.58-2.71 (m, 12H, succinic -CH₂-CH₂-), 3.70-3.88 (m, 4H, -CH₂-CH-CH₂-), 4.08-4.38 (m, 12H, -CH₂-CH-CH₂-), 4.90-4.97 (q, 1H, -CH₂-CH-CH₂-), 5.17-5.30 (m, 3H, -CH₂-CH-CH₂-) ppm. ¹³C NMR (CDCl₃): δ 14.00, 22.59, 24.74, 28.59, 28.74, 29.03, 29.18, 29.26, 29.39, 29.57, 30.23, 31.83, 33.93, 61.79, 62.13, 62.34, 69.59, 75.72, 171.65, 171.81, 173.52 ppm. MALDI-MS: 1479.69 m/z (M+Na⁺) (theory: 1455.97 m/z (M⁺)). Elemental analysis: C, 66.18%; H, 9.86% (theory: C, 65.99%; H, 9.83%). SEC: M_w = 2273, M_n = 2271, PDI = 1.001.

Compound **8e**; reaction 'e'

Compound **8** (0.77 g, 0.99 mmol) was dissolved in 75 mL of CH₂Cl₂ with 0.99 g (4.76 mmol) of succinic acid monobenzyl ester, 0.58 g (1.98 mmol) of DPTS, and 1.23 g (5.91 mmol) of DCC. The reaction was stirred for 16 hours. The DCU precipitate was filtered and the solution was evaporated. The residue was resuspended in a minimum of CH₂Cl₂, cooled to 10 °C for 1 hour and filtered. The solution was concentrated under reduced pressure and purified by column chromatography (30-50% EtOAc in hexanes) to afford 1.21 g of product (79% yield). R_f = 0.18 (40% EtOAc in hexanes). ¹H NMR

(CDCl₃): δ 1.08 (s, 9H, t-butyl), 2.55-2.81 (m, 28H, succinic -CH₂-CH₂), 4.06-4.37 (m, 12H, -CH₂-CH-CH₂-), 5.11 (s, 8H, benzyl -CH₂-), 5.18-5.29 (m, 3H, -CH₂-CH-CH₂-), 7.22-7.44, 7.61-7.67 (m, 30H, aromatic CH) ppm. ¹³C NMR (CDCl₃): δ 19.13, 26.81, 28.42, 28.64, 28.70, 28.91, 29.07, 30.56, 62.68, 66.72, 69.07, 73.69, 127.68, 128.23, 128.54, 130.06, 131.73, 135.21, 135.77, 171.64, 171.73, 171.90 ppm. FAB-MS: 1539.6 m/z (MH⁺) (theory: 1539.7 m/z (M⁺)). Elemental analysis: C, 63.35%; H, 6.02% (theory: C, 63.19%; H, 5.89%). SEC: M_w = 1739, M_n = 1704, PDI = 1.02.

Compound **12**; reaction 'f'

Compound **8e** (1.12 g, 0.73 mmol) was dissolved in 100 mL of THF. Next, 0.89 g (2.76 mmol) of tetrabutylammonium fluoride trihydrate was added to the solution. The mixture was stirred for 1 hour. After one hour the reaction was complete as indicated by TLC. The solution was diluted with 25 mL of H₂O and acidified with 1N HCl to a pH of 3. The product was extracted into EtOAc, dried over Na₂SO₄, rotoevaporated and dried on the vacuum line. The product was purified by column chromatography (0-3% MeOH in CH₂Cl₂) to afford 0.71 g of product (75% yield). R_f = 0.18 (3% MeOH in CH₂Cl₂). ¹H NMR (CDCl₃): δ 2.54-2.69 (m, 28H, -CH₂-CH₂), 4.11-4.31 (m, 12H, -CH₂-CH-CH₂-), 5.09 (s, 8H, benzyl -CH₂-), 5.18-5.25 (m, 3H, -CH₂-CH-CH₂-), 7.25-7.36 (m, 20H, aromatic CH) ppm. ¹³C NMR (CDCl₃): δ 28.57, 28.78, 28.94, 62.28, 62.43, 66.60, 69.16, 69.37, 128.24, 128.29, 128.61, 128.57, 171.33, 171.79, 171.95 ppm. FAB-MS: 1301.5 m/z (M-H⁺) (theory: 1301.3 m/z (M⁺)). Elemental analysis: C, 60.23%; H, 5.81% (theory: C, 60.00%; H, 5.58%). SEC: M_w = 1415, M_n = 1379, PDI = 1.03.

Compound **1**; reaction 'g'

Compound **12** (0.97 g, 0.75 mmol) was dissolved in 75 mL of CH₂Cl₂ with 0.19 g (0.90 mmol) of tetradecanol, 0.07 g (0.56 mmol) of DMAP, and 0.22 g (1.12 mmol) of EDCI. The reaction was stirred for 48 hours. The solution was concentrated under reduced pressure and purified by column chromatography (10-50% EtOAc in hexanes) to afford 0.88 g of product (79% yield). $R_f = 0.15$ (40% EtOAc in hexanes). ¹H NMR (CDCl₃): δ 0.82-0.90 (t, 3H, -CH₃), 1.16-1.37 (m, 22H, alkyl -CH₂-), 1.53-1.63 (m, 2H, -CH₂-CH₂-O-), 2.55-2.75 (m, 28H, succinic -CH₂-CH₂-), 4.00-4.07 (t, 2H, -CH₂-O-), 4.10-4.32 (m, 12H, -CH₂-CH-CH₂-), 5.11 (s, 8H, benzyl -CH₂-), 5.18-5.27 (m, 3H, -CH₂-CH-CH₂-), 7.26-7.40 (m, 20H, aromatic CH) ppm. ¹³C NMR (CDCl₃): δ 14.01, 22.59, 25.80, 28.55, 28.71, 28.76, 28.83, 28.90, 29.19, 29.26, 29.44, 29.51, 31.83, 62.23, 62.34, 64.94, 66.54, 69.13, 69.24, 128.28, 128.34, 128.50, 128.62, 135.81, 171.45, 171.67, 171.76, 171.87, 172.04, 172.25 ppm. MALDI-MS: 1519.96 m/z (M+Na⁺) (theory: 1497.62 m/z (M⁺)). Elemental analysis: C, 63.49%; H, 6.88% (theory: C, 63.36%; H, 6.73%). SEC: $M_w = 1708$, $M_n = 1664$, PDI = 1.03.

Compound **2**; reaction 'h'

Compound **1** (0.17 g, 0.11 mmol) was dissolved in THF (20 mL) and 10% Pd/C (0.1 g) was added. The solution was then placed in a Parr tube on a hydrogenator and shaken under 50 psi. H₂ for 12 hours. The solution was then filtered over wet celite, concentrated, and placed on a high vacuum line at 50 °C for 48 hours to yield 0.12 g of product (98% yield). ¹H NMR (CDCl₃): δ 0.82-0.88 (t, 3H, -CH₃), 1.20-1.35 (m, 22H, alkyl -CH₂-), 1.55-1.64 (m, 2H, -CH₂-CH₂-O-), 2.58-2.71 (m, 28H, succinic -CH₂-CH₂-),

4.02-4.08 (t, 2H, $-\text{CH}_2\text{-O}-$), 4.13-4.38 (m, 12H, $-\text{CH}_2\text{-CH-CH}_2-$), 5.21-5.31 (m, 3H, $-\text{CH}_2\text{-CH-CH}_2-$) ppm. ^{13}C NMR (CDCl_3): δ 14.01, 22.59, 25.79, 28.48, 28.78, 28.86, 29.19, 29.27, 29.44, 29.51, 29.57, 30.23, 31.83, 62.28, 65.13, 69.20, 69.34, 171.59, 171.84, 171.92, 172.19, 172.62, 177.24 ppm. MALDI-MS: 1158.72 m/z ($\text{M}+\text{Na}^+$) (theory: 1137.13 m/z (M^+)). Elemental analysis: C, 53.98%; H, 6.86% (theory: C, 53.87%; H, 6.74%). SEC: $M_w = 1482$, $M_n = 1451$, PDI = 1.02.

Compound **3**; reaction 'i'

Compound **12** (0.97 g, 0.75 mmol) was dissolved in 75 mL of CH_2Cl_2 with 0.46 g (0.90 mmol) of 1,3-di-*O*-tetradecanoylglycerol, 0.07 g (0.56 mmol) of DMAP, and 0.22 g (1.12 mmol) of EDCI. The reaction was stirred for 48 hours. The solution was concentrated under reduced pressure and purified by column chromatography (10-50% EtOAc in hexanes) to afford 1.00 g of product (74% yield). $R_f = 0.12$ (40% EtOAc in hexanes). ^1H NMR (CDCl_3): δ 0.82-0.89 (t, 6H, $-\text{CH}_3$), 1.17-1.31 (m, 40H, $-\text{CH}_2-$), 1.54-1.62 (m, 4H, $\text{C(=O)-CH}_2\text{-CH}_2-$), 2.25-2.32 (t, 4H, C(=O)-CH_2-), 2.57-2.68 (m, 28H, succinic $-\text{CH}_2\text{-CH}_2-$), 4.09-4.30 (m, 16H, $-\text{CH}_2\text{-CH-CH}_2-$), 5.11 (s, 8H, benzyl $-\text{CH}_2-$), 5.18-5.26 (m, 4H, $-\text{CH}_2\text{-CH-CH}_2-$), 7.28-7.37 (m, 20H, aromatic CH) ppm. ^{13}C NMR (CDCl_3): δ 14.02, 22.60, 24.75, 28.55, 28.71, 28.78, 28.92, 29.05, 29.20, 29.27, 29.41, 29.57, 31.85, 33.92, 61.78, 62.23, 66.55, 69.26, 69.54, 126.29, 128.35, 128.46, 128.63, 135.82, 171.41, 171.87, 172.04, 173.41 ppm. MALDI-MS: 1818.27 m/z ($\text{M}+\text{Na}^+$) (theory: 1796.04 m/z (M^+)). Elemental analysis: C, 64.29%; H, 7.35% (theory: C, 64.20%; H, 7.30%). SEC: $M_w = 2034$, $M_n = 1978$, PDI = 1.03.

Compound **4**; reaction 'j'

Compound **3** (0.10 g, 0.05 mmol) was dissolved in THF (20 mL) and 10% Pd/C (0.1 g) was added. The solution was then placed in a Parr tube on a hydrogenator and shaken under 50 psi. H₂ for 12 hours. The solution was then filtered over wet celite, concentrated, and placed on a high vacuum line at 50 °C for 48 hours to yield 0.08 g of product (97% yield). ¹H NMR (CDCl₃): δ 0.82-0.88 (t, 6H, -CH₃), 1.20-1.33 (m, 40H, myristic -CH₂-), 1.53-1.62 (m, 4H, C(=O)-CH₂-CH₂-CH₂-), 2.67-2.33 (t, 4H, C(=O)-CH₂-CH₂-), 2.56-2.72 (m, 21H, succinic -CH₂-CH₂-), 4.08-4.38 (m, 16H, -CH₂-CH-CH₂-), 5.18-5.30 (m, 4H, -CH₂-CH-CH₂-) ppm. ¹³C NMR (CDCl₃): δ 14.01, 22.59, 28.65, 28.79, 28.85, 29.03, 29.18, 29.27, 29.39, 29.57, 29.60, 31.83, 33.93, 61.79, 62.26, 69.34, 69.57, 171.59, 171.82, 172.20, 173.60, 177.16 ppm. MALDI-MS: 1458.34 m/z (M+Na⁺) (theory: 1435.55 m/z (M⁺)). Elemental analysis: C, 56.93%; H, 7.52% (theory: C, 56.89%; H, 7.44%). SEC: M_w = 1872, M_n = 1840, PDI = 1.02.

Compound **5**; reaction 'k'

Compound **12** (0.20 g, 0.14 mmol) was dissolved in pyridine (12 mL). Succinic anhydride (0.04 g, 0.41 mmol) was added and the reaction stirred for 24 h. Next, the solvent was removed under vacuum and the resulting waxy solid was resuspended in a minimum of ethanol. This solution was cooled to 4 °C, and the resulting precipitate was isolated via suction filtration. The precipitate was recrystallized from ethanol to afford 0.09 g of product (37% yield). ¹H NMR (CDCl₃): δ 0.84-0.95 (t, 12H, -CH₃), 1.16-1.38 (m, 80H, -CH₂-), 1.59-1.68 (m, 8H, C(=O)-CH₂-CH₂-), 2.26-2.38 (t, 8H, C(=O)-CH₂-), 2.56-2.76 (m, 20H, succinic -CH₂-CH₂-), 4.08-4.37 (m, 16H, -CH₂-CH-CH₂-), 5.18-5.27

(m, 4H, -CH₂-CH-CH₂-) ppm. ¹³C NMR (CDCl₃): □ 14.00, 22.58, 24.73, 28.57, 28.73, 29.02, 29.17, 29.26, 29.38, 29.52, 29.55, 29.58, 31.82, 33.92, 61.79, 62.35, 69.57, 171.54, 171.79, 171.87, 173.49, 173.56 ppm. MALDI-MS: 1678.37 m/z (M+Na⁺) (theory: 1656.12 m/z (M⁺)). Elemental analysis: C, 64.29%; H, 9.61% (theory: C, 63.82%; H, 9.13%). SEC: M_w = 2160, M_n = 2160, PDI = 1.00.

Compound **6**; reaction 'I'

Compound **11** (0.24 g, 0.17 mmol) was dissolved in 30 mL of THF with 0.52 g (0.40 mmol) of compound **12**, 0.05 g (0.17 mmol) of DPTS, and 0.10 g (0.50 mmol) of DCC. The reaction was stirred for 84 hours. The solution was filtered, concentrated under reduced pressure and purified by column chromatography (0-9% acetone in DCM) to afford 0.33 g of product (50% yield). R_f = 0.11 (7% acetone in DCM). ¹H NMR (CDCl₃): □ 0.82-0.89 (t, 12H, -CH₃), 1.19-1.32 (m, 80H, -CH₂-), 1.53-1.63 (m, 8H, C(=O)-CH₂-CH₂-), 2.25-2.62 (t, 8H, C(=O)-CH₂-), 2.56-2.79 (m, 68H, succinic -CH₂-CH₂), 4.10-4.32 (m, 40H, -CH₂-CH-CH₂-), 5.09 (s, 16H, benzyl -CH₂-), 5.17-5.26 (m, 10H, -CH₂-CH-CH₂-), 7.25-7.38 (m, 40H, aromatic CH) ppm. ¹³C NMR (CDCl₃): □ 13.99, 22.56, 24.72, 26.06, 28.52, 28.68, 28.74, 28.88, 29.01, 29.16, 29.24, 29.37, 29.51, 29.54, 29.57, 31.81, 33.89, 61.74, 62.20, 66.50, 69.22, 69.51, 128.26, 128.31, 128.47, 128.60, 171.39, 171.45, 171.69, 171.74, 171.79, 171.86, 171.95, 172.02, 173.37 ppm. MALDI-MS: 4044.73 m/z (M+Na⁺) (theory: 4022.44 m/z (M⁺)). Elemental analysis: C, 62.85%; H, 7.11% (theory: C, 62.70%; H, 7.07%). SEC: M_w = 4375, M_n = 4226, PDI = 1.04.

Compound 7; reaction 'm'

Compound 6 (0.09 g, 0.024 mmol) was dissolved in THF (20 mL) and 10% Pd/C (0.1 g) was added. The solution was then placed in a Parr tube on a hydrogenator and shaken under 50 psi. H₂ for 12 hours. The solution was then filtered over wet celite, concentrated, and placed on a high vacuum line at 50 °C for 48 hours to yield 0.07 g of product (95% yield). ¹H NMR (CDCl₃): δ 0.82-0.89 (t, 12H, -CH₃), 1.18-1.32 (m, 80H, -CH₂-), 1.53-1.64 (m, 8H, C(=O)-CH₂-CH₂-), 2.26-2.33 (t, 8H, C(=O)-CH₂-), 2.56-2.72 (m, 68H, succinic -CH₂-CH₂-), 4.08-4.37 (m, 40H, -CH₂-CH-CH₂-), 5.18-5.27 (m, 10H, -CH₂-CH-CH₂-) ppm. ¹³C NMR (CDCl₃): δ 14.01, 22.59, 24.59, 28.76, 29.03, 29.18, 29.26, 29.39, 29.53, 29.56, 29.59, 30.22, 31.83, 33.93, 61.78, 62.26, 69.35, 69.54, 171.61, 171.83, 171.88, 171.92, 172.08, 172.16, 172.24, 172.38, 173.51, 176.78 ppm. MALDI-MS: 3302.34 m/z (M+H⁺) (theory: 3301.46 m/z (M⁺)). Elemental analysis: C, 55.85%; H, 7.30% (theory: C, 56.03%; H, 7.14%). SEC: M_w = 3944, M_n = 3844, PDI = 1.03.

Area Per Molecule Calculations (*ApM*):

The *ApM* at the air/water interface was calculated using the Gibbs Equation. For compounds 2, 4 and 7 the slope of the plot of the change in surface tension versus log molar concentration of surfactant under isothermal conditions (24 °C) was determined to be -21 ± 2 , -45 ± 2 and -26 ± 5 (mN L mol⁻¹), respectively. The Surface excess (Γ , mol m⁻²) was calculated according to Equation 1 where '*R*' is the gas constant (J mol⁻¹ K⁻¹), '*T*' is the absolute temperature (K), '*c*' is the concentration (mol L⁻¹), and ' σ ' is the surface tension (N m⁻¹).

$$\Gamma = \frac{1}{2.303RT} \cdot \frac{\partial \sigma}{\partial \log c} \quad \text{Eq. (1.0)}$$

This resulted in surface excess values of 3.8×10^{-6} , 7.9×10^{-6} and 4.6×10^{-6} (mol m^{-2}) for compounds **2**, **4** and **7**, respectively. Next, the ApM (in units of square Angstroms, $\text{\AA}^2$) can be obtained from the following relationship where ' N ' is Avogadro's constant.

Results are reported in Table 1.

$$ApM = \frac{10^{20}}{N \cdot \Gamma} \quad \text{Eq. (2.0)}$$

Fluorescence Measurements:

A stock solution of pyrene (0.5 mM) in ethanol was added to test tubes. The ethanol was evaporated by a stream of nitrogen and thereafter under vacuum for 1 h. Amphiphile stock solutions in buffer (200 mM HEPES, pH = 7.4) above or below the cac were added to the tubes to give a final volume of 1 mL and a final pyrene concentration of 0.5 μM . The samples were incubated in the dark at 25 °C for 24 h, with intermittent vigorous mixing. Fluorescence spectra were recorded using $\lambda_{\text{ex}} = 320$ nm and monitoring emission at 350 - 400 nm.