Reverse vesicles formed by hydrogen bonded arylamide-derived triammonium cyclophanes and hexaammonium capsule

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**Compound 5a.** A solution of 3a (0.20 g, 0.15 mmol) and NaBH(OAc)₃ (1.05 g, 4.95 mmol) in chloroform (15 mL) was stirred at r.t. for 12 h and then washed with water (3 × 15 mL) and brine (15 mL). Upon removal of the solvent, compound 4a was obtained as a pale yellow solid (0.20 g, 100%). ¹H NMR (300 MHz, CDCl₃): δ 9.75 (s, 3H), 8.17 (s, 3H), 7.50 (s, 3H), 7.32 (s, 3H), 7.32 (s, 3H).
Compound 5b. Pale yellow solid. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 10.08 (d, $J = 8.4$ Hz, 3H), 8.24 (d, $J = 11.4$ Hz, 3H), 8.07 (s, 3H), 7.52 (dd, $J_1 = 11.4$ Hz, $J_2 = 8.7$ Hz, 3H), 7.00 (t, $J = 8.1$ Hz, 3H), 6.5 (d, $J = 6.0$ Hz, 3H), 4.67 (s, 3H), 4.37 (s, 3H), 4.22-4.16 (m, 6H), 3.98-3.94 (m, 12H), 1.92-1.73 (m, 21H), 1.47-1.25 (m, 66H), 0.89-0.82 (m, 27H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 163.1, 155.9, 143.1, 141.9, 133.7, 131.9, 130.5, 128.3, 124.4, 121.9, 113.6, 106.5, 101.2, 71.5, 71.0, 69.2, 69.1, 45.1, 31.8, 29.9, 29.5, 29.3 (d), 29.3, 26.1, 25.9, 22.6, 19.1, 14.1 (d), 13.8. MS (MALDI-TOF): m/z 1680.8 [M + Na]$^+$. HRMS (MALDI-TOF): Calcd for C$_{102}$H$_{156}$N$_6$O$_{12}$Na [M + Na]$^+$: 1680.1632. Found: 1680.1674.

Compound 6. Pale yellow solid. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 9.62 (s, 6H), 8.04 (d, $J = 2.4$ Hz, 6H), 7.10 (d, $J = 6.9$ Hz, 6H), 6.86 (s, 6H), 6.65 (d, $J = 8.1$ Hz, 6H), 6.53 (s, 6H), 4.70-4.46 (m, 18 H), 4.07-3.81 (m, 24H), 3.67 (d, $J = 6.7$ Hz, 6H), 3.54 (d, $J = 6.8$ Hz, 6H), 3.22 (s, 12H), 1.86 (t, $J = 6.7$ Hz, 12H), 1.51-1.19 (m, 132H), 0.89-0.86 (m, 36H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 162.7, 155.2, 143.1, 141.9, 133.7, 131.9, 130.5, 128.3, 124.4, 121.9, 113.6, 106.5, 101.2, 71.5, 71.0, 69.2, 69.1, 45.1, 31.8, 29.9, 29.5, 29.3 (d), 26.2, 26.1, 22.7, 22.6, 14.1. MS (MALDI-TOF): m/z 3189.4 [M + H]$^+$. HRMS (MALDI-TOF): Calcd for C$_{192}$H$_{282}$N$_{12}$O$_{27}$Na [M + Na]$^+$: 3211.1255. Found: 3211.1282.

Compound 1a. To a stirred suspension of 5a (72 mg, 0.054 mmol) and sodium bicarbonate (0.18 g, 2.16 mmol) in chloroform (10 mL) was added methyl iodide (6.5 mL, 0.10 mol) slowly. The mixture was stirred under reflux for 48 h and cooled. The solid was filtrated off and the filtrate concentrated with a rotavapor. The resulting residue was subjected to column chromatography (CH$_2$Cl$_2$/MeOH 50:1) to give compound 1a as a pale yellow solid (94 mg, 97%). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 10.14 (s, 3H), 9.11 (s, 3H), 8.21 (s, 3H), 7.52 (d, $J_1 = 7.6$ Hz, $J_2 = 1.8$ Hz, 3H), 6.99 (d, $J = 7.6$ Hz, 3H), 6.68 (s, 3H), 4.48 (s, 6H), 4.25 (t, $J = 6.6$ Hz, 6H), 4.03 (s, 18H), 3.95-3.91 (m, 12H), 1.87-1.83 (m, 6H), 1.61 (m, 6H), 1.45-1.42 (m, 6H), 1.14-0.92 (m, 45H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 163.4, 156.1, 150.2, 147.5, 134.0, 132.7, 132.4, 125.8, 121.8, 113.7, 113.2, 99.0, 76.0, 69.7, 56.3, 30.8, 28.3, 28.1, 19.7, 19.2, 18.0, 13.8, 4.5. MS (ESI): m/z 501.4 [M + 3MeOH]$^{3+}$. HRMS (ESI): Calcd for C$_{29}$H$_{45}$N$_2$O$_5$ [M+ 3MeOH]$^{3+}$: 501.3337. Found: 501.3323.

Compound 1b. Pale yellow solid. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 10.17 (s, 3H), 9.12 (s, 3H), 8.21 (d, $J = 2.3$ Hz, 3H), 7.52 (dd, $J_1 = 8.6$ Hz, $J_2 = 2.3$ Hz, 3H), 6.99 (d, $J = 8.6$ Hz, 3H), 6.69 (s, 3H), 4.48 (s, 6H), 4.30-4.12 (m, 18H), 4.00 (s, 18H), 1.96-1.85 (m, 18H), 1.49-1.24 (m, 66H), 0.96-0.80 (m, 27H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 163.3, 156.1, 150.1, 147.4,
Compound 2. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 10.10 (s, 6H), 8.87 (s, 6H), 8.07 (s, 6H), 7.44 (d, $J = 5.7$ Hz, 6H), 7.05 (d, $J = 7.5$ Hz, 6H), 6.70 (s, 6H), 4.45-4.35 (m, 30H), 4.18 (m, 24H), 3.94-3.86 (m, 42H), 1.89-1.78 (m, 24H), 1.37-1.11 (m, 120H), 0.89-0.80 (m, 36H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 162.8, 155.9, 150.3, 147.5, 133.8, 132.7, 131.8, 124.9, 121.7, 121.3, 114.8, 99.4, 70.5, 70.2, 69.5, 69.1, 56.3, 31.6, 31.5, 29.5, 29.2, 29.1, 29.0, 28.7, 26.1, 25.6, 22.5, 14.0, 13.9, 4.7. MS (MALDI-TOF): $m/z$ 697.4 [M + Na]$^+$. HRMS (MALDI-TOF): Calcd for C$_{38}$H$_{61}$N$_2$O$_6$ [M + H]$^+$: 641.4546. Found: 641.4524.

Compound 12. A solution of compounds 10 (0.41 g, 2.15 mmol) and EDCI (0.62 g, 3.23 mmol) in chloroform (10 mL) was stirred for 1 h and then compound 11 (1.00 g, 2.15 mmol) added. The mixture was stirred at r.t. for 18 h and then another part of chloroform (90 mL) added. The solution was washed with saturated hydrochloric acid (0.5 N, 100 mL x 2), water (100 mL) and brine (100 mL) and dried over sodium sulfate. After the solvent was removed with a rotavapor, the resulting residue was subjected to column chromatography (PE/CH$_2$Cl$_2$ 10:1) to give compound 12 as a colorless oil (1.11 g, 80%). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 9.96 (s, 1H), 9.05 (s, 1H), 8.30 (d, $J = 8.0$ Hz, 1H), 7.43 (t, $J = 6.5$ Hz, 1H), 7.08 (t, $J = 6.5$ Hz, 1H), 7.00 (d, $J = 8.0$ Hz, 1H), 6.73 (s, 1H), 6.50 (s, 1H), 4.19 (t, $J = 6.9$ Hz, 2H), 4.02-3.94 (m, 4H), 2.05-1.74 (m, 6H), 1.53 (s, 9H), 1.48-1.22 (m, 22H), 0.97-0.82 (m, 9H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 162.8, 156.7, 144.4, 144.2, 132.6, 132.4, 122.9, 121.7, 121.4, 121.2, 113.9, 112.6, 98.5, 69.8, 69.3, 69.2, 31.7 (d), 30.9, 29.3 (d), 29.2 (d), 29.1, 28.3 (d), 26.0, 25.8, 22.6 (d), 19.1, 14.0 (d), 13.7. MS (MALDI-TOF): $m/z$ 664.2 [M + Na]$^+$. HRMS (MALDI-TOF): Calcd for C$_{38}$H$_{61}$N$_2$O$_6$ [M + H]$^+$: 641.4546. Found: 641.4524.

Compound 7. A solution of 12 (0.46 g, 0.72 mmol) and trifluoroacetic acid (0.7 mL, 9.14 mmol) in chloroform (10 mL) was stirred for 12 h and then chloroform (90 mL) added. The solution was washed with saturated sodium bicarbonate solution (100 mL x 2), water (100 mL) and brine (100 mL) and dried over sodium sulfate. Upon removal of the solvent with a rotavapor, the corresponding intermediate amine was obtained as a colorless oil (0.39 g, 100%). The amine was dissolved in chloroform (10 mL). To the solution were added methyl iodide (8 mL, 0.13 mol) and sodium bicarbonate (1.01 g, 25.1 mmol). The suspension was
stirred under reflux for 5 h and then the solid filtrated off. After workup, the crude product was purified by column chromatography (CH2Cl2/CH3OH 50:1) to give 7 as a white solid (0.42 g, 85%). 1H NMR (300 MHz, CDCl3): δ 10.23 (s, 1H), 9.12 (s, 1H), 8.18 (dd, J1 = 6.0 Hz, J2 = 2.0 Hz, 1H), 7.49 (t, J = 6.0 Hz, 1H), 7.13-7.02 (m, 2H), 6.70 (s, 1H), 4.26-4.15 (m, 6H), 3.98 (s, 9H), 1.94-1.83 (m, 6H), 1.46-1.23 (m, 22H), 0.97-0.80 (m, 9H). 13C NMR (125 MHz, CDCl3): δ 163.9, 156.7, 150.0, 147.2, 133.6, 132.2, 125.7, 122.0, 121.5, 121.4, 112.9, 112.8, 99.0, 70.2, 69.8, 69.4, 56.2, 31.7, 31.6, 30.9, 29.2 (d ), 29.1 (d), 28.9, 26.2, 25.7, 22.5, 22.5, 19.0, 14.0, 14.0, 13.8. MS (ESI): m/z 583.4 [M + H]+. HRMS (ESI): Calcd for C36H59N2O4 [M + H]+: 583.4464. Found: 583.4469.

Compound 8. A suspension of 5b (0.10 g, 0.06 mmol), ethyl iodide (10 mL, 0.12 mol) and sodium bicarbonate (0.49 g, 5.86 mmol) in chloroform (10 mL) was stirred under reflux for 48 h and then cooled. The solid was filtrated off and the solvent concentrated with a rotavapor. The resulting reside was subjecte d to column chromatograph (CH2Cl2/CH3OH 50:1) to give compound 8 as a yellow solid (0.11 g, 82%). 1H NMR (300 MHz, CDCl3): δ 10.21 (s, 3H), 9.05 (s, 3H), 8.19 (d, J = 2.1 Hz, 3H), 7.50 (dd, J1 = 8.4 Hz, J2 = 2.1 Hz, 3H), 6.98 (d, J = 8.4 Hz, 3H), 6.74 (s, 3H), 4.45 (s, 6H), 4.27-4.12 (m, 30H), 1.92-1.85 (m, 18H), 1.48-1.41 (m, 12H), 1.31-1.22 (m, 72H), 0.98-0.93 (t, J = 7.5 Hz, 9H), 0.86-0.80 (m, 27H). 13C NMR (125 MHz, CDCl3): δ 169.2, 162.9, 154.7, 150.3, 144.2, 133.9, 131.7, 131.2, 122.1, 121.5, 117.4, 112.6, 98.8, 69.4, 69.2, 68.2, 53.8, 41.3, 31.8, 31.7, 30.9, 29.3, 29.1, 26.3, 25.8, 23.5, 22.7, 22.6, 22.5, 19.6, 18.9, 14.1, 14.0. MS (ESI): m/z 736.8 [M − 3I]3+. HRMS (ESI): Calcd for C38H62N2O4I [M − 3I]3+: 737.3750. Found: 737.3749.
**Compound 9.** A solution of compound 13 (78 mg, 0.024 mmol) and NaBH(OAc)₃ (0.30 g, 1.43 mmol) in chloroform (10 mL) was stirred at r.t. for 12 h and then another part of chloroform (50 mL) added. The solution was washed with water (50 mL × 2) and brine (50 mL) and dried over sodium sulfate. Upon removal of the solvent under reduced pressure, the resulting hexamine intermediate (78 mg) was dissolved in chloroform (10 mL). To the solution were added methyl iodide (2.0 mL, 32.1 mmol) and sodium bicarbonate (0.68 g, 8.10 mmol). The suspension was then refluxed for 48 h and cooled. After the solid was filtrated off, the resulting solid was subjected to column chromatography (CH₂Cl₂/MeOH 50:1) to give compound 9 as a pale yellow solid (56 mg, 56%). ¹H NMR (300 MHz, CDCl₃): δ 10.29 (s, 6H), 9.11 (s, 6H), 8.19 (s, 6H), 7.46-7.40 (m, 18H), 6.99 (d, J = 8.4 Hz, 6H), 6.69 (s, 6H), 5.43 (s, 12H), 4.44 (s, 12H), 4.23 (s, 12H), 4.01-3.88 (m, 48H), 1.91 (m, 12H), 1.73 (s, 12H), 1.50-1.15 (m, 120H), 0.88-0.78 (m, 36H). ¹³C NMR (125 MHz, CDCl₃): δ 162.9, 155.4, 150.2, 147.6, 135.7, 133.8, 133.1, 132.4, 127.4, 125.3, 122.2, 121.5, 114.4, 112.8, 99.1, 70.8, 70.5, 69.7, 56.5, 31.9, 31.7, 31.7, 29.6, 29.3, 29.2, 29.1, 28.7, 26.9, 26.8, 26.2, 25.7, 22.6, 17.8, 14.1, 4.4. MS (ESI): m/z 609.7 [M + 6MeOH]⁺, 1983.4 [M – 2I]²⁺.

![Fig S1. SEM image of 1b in CH₂Cl₂ (3 mM).](image1)

![Fig. S2. SEM images of 1a in CHCl₃/decalin (left) (1:1, v/v), CHCl₃/cyclohexane (middle) (1:0.4, v/v), and CHCl₃/n-octane (left) (1:1, v/v) (3mM).](image2)
Fig. S3. SEM images of 1b in CHCl₃/decalin (left) (1:0.6, v/v), b) CHCl₃/n-octane (right) (1:0.8, v/v) (3mM).

Vert distance     12.085nm  
Horiz distance    449.22nm

Vert distance      5.539nm  
Horiz distance    421.88nm

Vert distance    68.645nm  
Horiz distance  781.25nm

Fig. S4. Tapping-mode AFM images and cross-section analysis of 1a (upper) in CHCl₃, 1a (middle) in CH₂Cl₂ and 1b (down) in CH₂Cl₂ (the concentration was 0.3 mM).
**Fig. S5.** SEM images of 3b in CHCl₃ (left), 3b in CH₂Cl₂ (middle) and 5b in CHCl₃ (right) in CH₂Cl₂ (3 mM) in the presence of 10 equiv of hydrogen iodide.

**Fig. S6.** Tapping-mode AFM images and cross-section analysis of 2 in CHCl₃ (left) and in CH₂Cl₂ (right) (the concentration was 0.15 mM).

**Fig. S7.** SEM images of 1b a) 0.3 mM, b) 0.6 mM, c) 1.5 mM, d) 2.4 mM and e) 3.0 mM, obtained by evaporation of its chloroform solutions on mica.
Fig. S8. The XRD profiles of the aggregates of a) 1a and b) 1b. The samples were prepared by evaporating their chloroform solutions of 3.0 mM.

Fig. S9. SEM images of 1b, obtained by evaporation of its chloroform solution (0.3 mM) on mica.