Supplementary Material (ESI) for Chemical Communications

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

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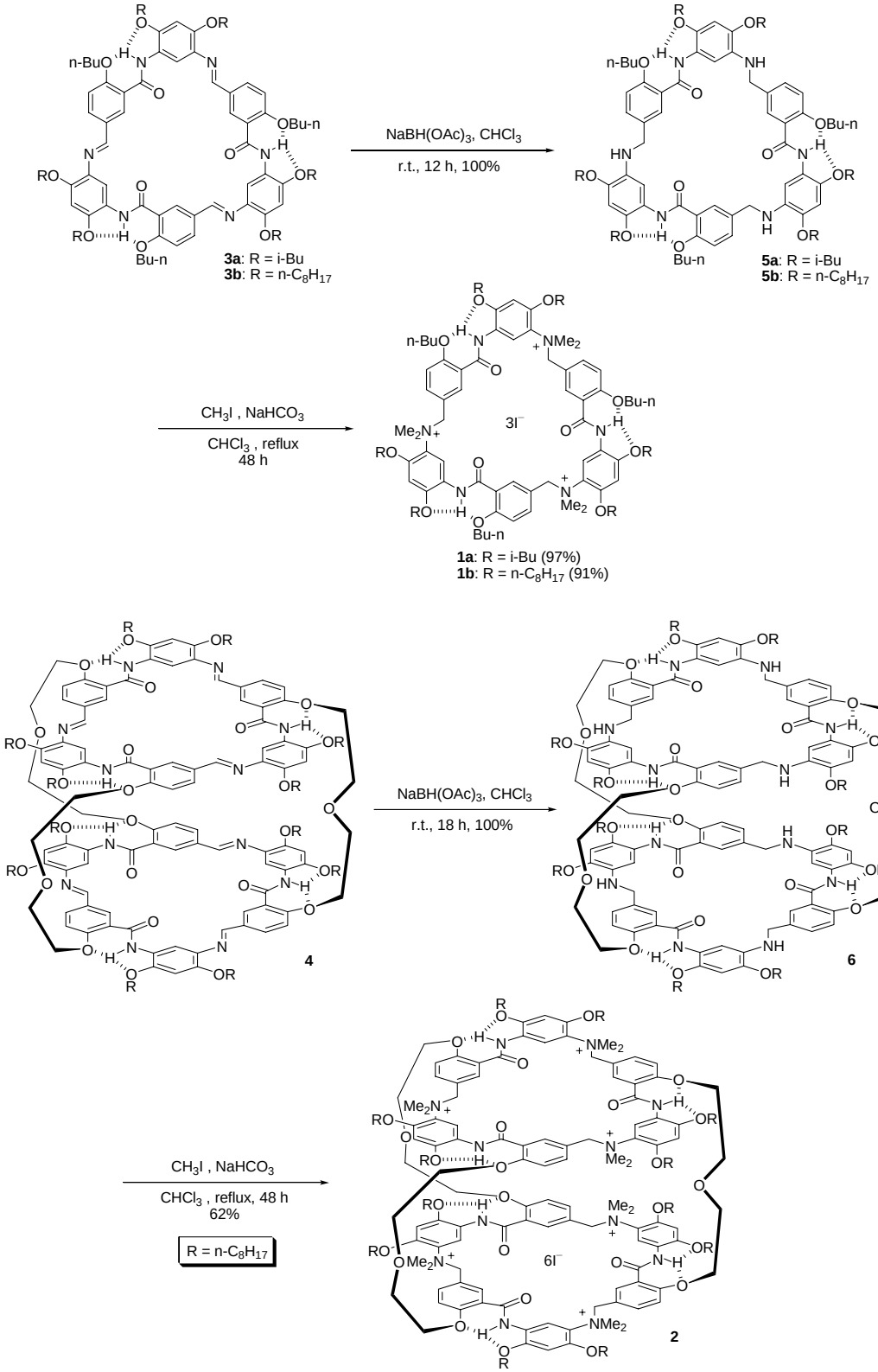


Compound 5a. A solution of **3a** (0.20 g, 0.15 mmol) and $NaBH(OAc)_3$ (1.05 g, 4.95 mmol) in chloroform (15 mL) was stirred at r.t. for 12 h and then washed with water (3 × 15 mL) and brine (15 m). Upon removal of the solvent, compound **4a** was obtained as a pale yellow solid (0.20 g, 100%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.75 (s, 3H), 8.17 (s, 3H), 7.50 (s, 3H), 7.32

(d, *J* = 8.40 Hz, 3H), 6.87 (d, *J* = 8.40 Hz, 3H), 6.48 (s, 3H), 4.52 (m, 9H), 4.31 (t, *J* = 6.75 Hz, 6H), 3.76 (d, *J* = 6.60 Hz, 6H), 3.67 (d, *J* = 6.90 Hz, 6H), 2.16-2.03 (m, 6H), 1.82-1.77 (m, 6H), 1.38-1.26 (m, 6H), 1.08-0.86 (m, 45H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.0, 155.4, 142.9, 141.3, 133.0, 132.0, 131.0, 129.3, 122.8, 122.1, 112.9, 107.0, 100.0, 75.4, 69.3, 46.7, 30.9, 28.4, 28.4, 19.5, 19.3, 19.0, 13.7. MS (MALDI-TOF): *m/z* 1344.5 $[M+Na]^+$. HRMS (MALDI-TOF): Calcd for $C_{78}H_{108}N_6O_{12}Na$ $[M + Na]^+$: 1343.7942. Found: 1343.7918.

Compound 5b. Pale yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 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, $CDCl_3$): δ 163.1, 155.9, 142.5, 139.9, 132.7, 131.8, 131.1, 122.8, 122.6, 113.1, 113.0, 104.9, 99.9, 70.8, 69.5, 69.0, 31.8, 31.7, 30.9, 29.5, 29.4 (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 $C_{102}H_{156}N_6O_{12}Na$ $[M + Na]^+$: 1680.1632. Found: 1680. 1674.

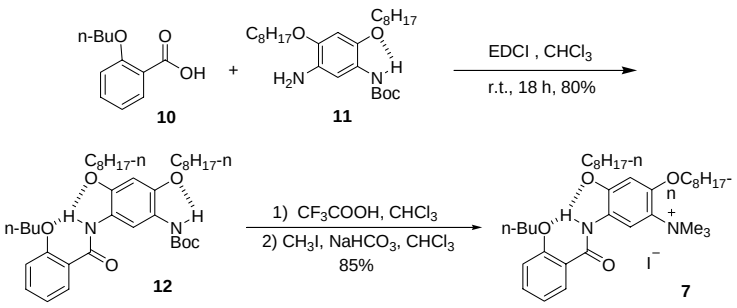
Compound 6. Pale yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.62 (s, 6H), 8.04 (d, *J* = 2.4 Hz, 6H), 7.10 (d, *J* = 6.9 Hz, 6H), 6.86 (s, 6H), 6.65 (d, *J* = 8.1, 6H), 6.53 (s, 6H), 4.70-4.46 (m, 18 H), 4.07-3.81 (m, 24H), 3.67 (d, *J* = 6.7 Hz, 6H), 3.54 (d, *J* = 6.8 Hz, 6H), 3.22 (s, 12H), 1.86 (t, *J* = 6.7 Hz, 12H), 1.51-1.19 (m, 132H), 0.89-0.86 (m, 36H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 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, 29.6, 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 $C_{192}H_{282}N_{12}O_{27}Na$ $[M + Na]^+$: 3211.0924. Found: 3211.0955.

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 reside was subjected to column chromatography (CH_2Cl_2/MeOH 50:1) to give compound **1a** as a pale yellow solid (94 mg, 97%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 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, $CDCl_3$): δ 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 $C_{29}H_{45}N_2O_5$ $[M+ 3MeOH]^{3+}$: 501.3337. Found: 501.3323.

Compound 1b. Pale yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 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, $CDCl_3$): δ 163.3, 156.1, 150.1, 147.4,

134.0, 132.7, 132.4, 125.8, 121.9, 121.7, 113.5, 113.0, 99.0, 70.2, 69.8, 69.6, 56.3, 31.7 (d), 30.9, 29.3, 29.2, 29.1, 29.1, 28.9, 26.2, 25.7, 22.6, 19.0, 14.1, 14.0, 13.8, 4.4. MS (ESI): *m/z* 582.1 $[M]^{3+}$. HRMS (ESI): Calcd for $C_{36}H_{57}N_2O_4$ $[M]^{3+}$: 581.4330. Found: 581.4313.

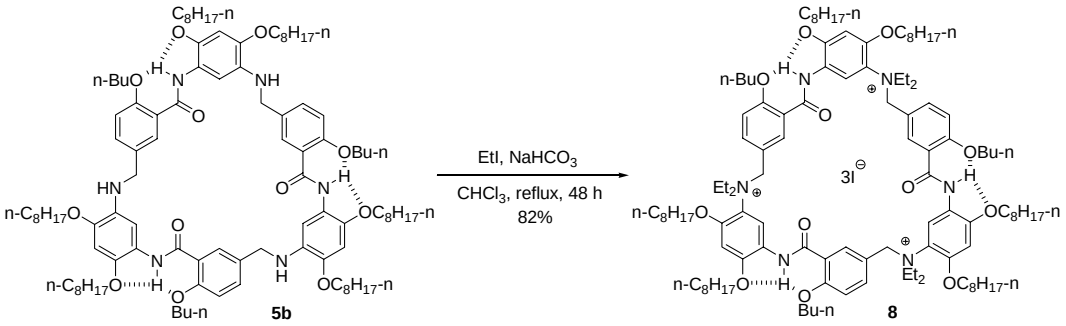
Compound 2. ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.10 (s, 6H), 8.87 (s, 6H), 8.07 (s, 6H), 7.44 (d, *J* = 5.7 Hz, 6H), 7.05 (d, *J* = 7.5 Hz, 6H), 6.70 (s, 6H), 4.45-4.35 (m, 30H), 4.18 (m, 24H), 3.94-3.86 (m, 42H), 1.89-1.78 (m, 24H), 1.37-1.11 (m, 120H), 0.89-0.80 (m, 36H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 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 $[M - 4I]^{5+}$.



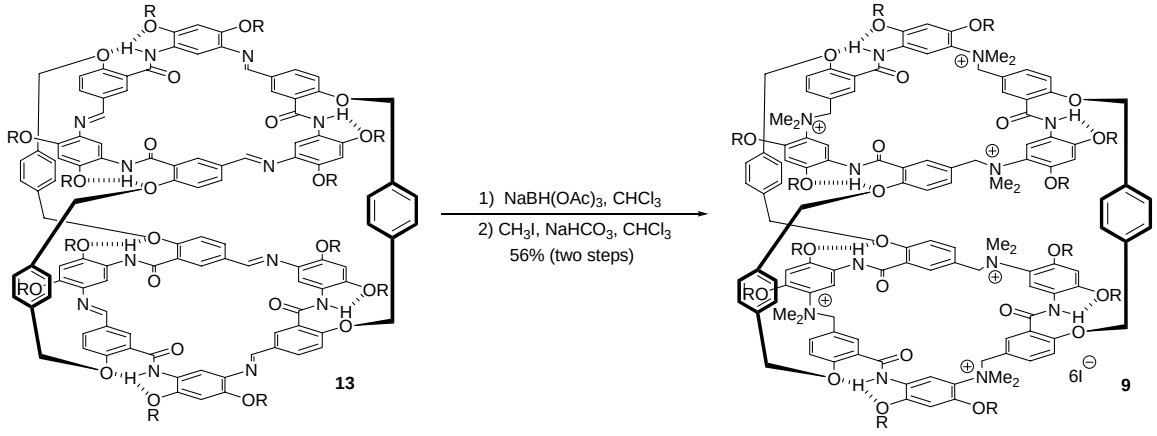
Compound 12. A solution of compounds **10** (0.41 g, 2.15 mmol) and EDCI (0.62 g, 3.23 mmol) in chloroform (10 mL) was stirred for 1 h and then compound **11** (1.00 g, 2.15 mmol) added. The mixture was stirred at r.t. for 18 h and then another part of chloroform (90 mL) added. The solution was washed with diluted hydrochloric acid (0.5 N, 100 mL × 2), water (100 mL) and brine (100 mL) and dried over sodium sulfate. After the solvent was removed with a rotavaor, the resulting residue was subjected to column chromatography (PE/CH_2Cl_2 10:1) to give compound **12** as a colorless oil (1.11 g, 80%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 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, $CDCl_3$): δ 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 $C_{38}H_{61}N_2O_6$ $[M + H]^+$: 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 at r.t. for 12 h and then chloroform (90 mL) added. The solution was washed with saturated sodium bicarbonate solution (100 mL × 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 (CH_2Cl_2/CH_3OH 50:1) to give **7** as a white solid (0.42 g, 85%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.23 (s, 1H), 9.12 (s, 1H), 8.18 (dd, J_1 = 6.0 Hz, J_2 = 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). ^{13}C NMR (125 MHz, $CDCl_3$): 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 $C_{36}H_{59}N_2O_4$ $[M + H]^+$: 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 subjected to column chromatograph (CH_2Cl_2/CH_3OH 50:1) to give compound **8** as a yellow solid (0.11 g, 82%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.21 (s, 3H), 9.05 (s, 3H), 8.19 (d, J = 2.1 Hz, 3H), 7.50 (dd, J_1 = 8.4 Hz, J_2 = 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). ^{13}C NMR (125 MHz, $CDCl_3$): 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 $C_{38}H_{62}N_2O_4I$ $[M - 3I]^{3+}$: 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 (CH_2Cl_2/MeOH 50:1) to give compound **9** as a pale yellow solid (56 mg, 56%). ^{1}H NMR (300 MHz, $CDCl_3$): 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). ^{13}C NMR (125 MHz, $CDCl_3$): 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 $[M + 6MeOH]^{6+}$, 1983.4 $[M - 2I]^{2+}$.

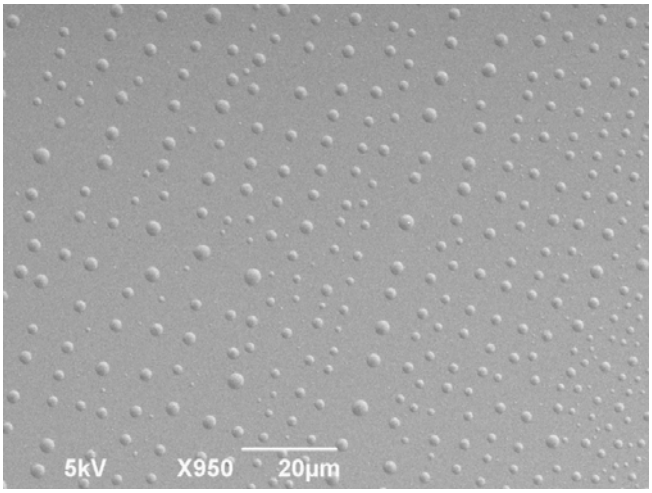


Fig S1. SEM image of **1b** in CH_2Cl_2 (3 mM).

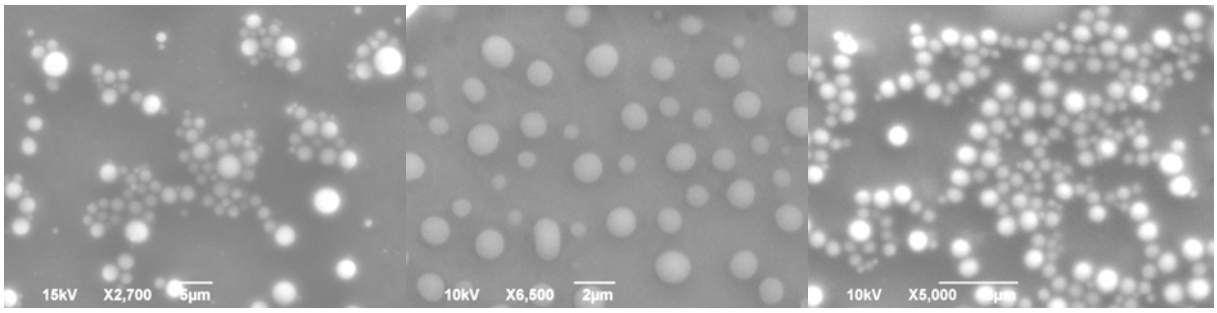


Fig. S2. SEM images of **1a** in $CHCl_3$/decalin (left) (1:1, v/v), $CHCl_3$/cyclohexane (middle) (1:0.4, v/v), and $CHCl_3$/n-octane (left) (1:1, v/v) (3mM).

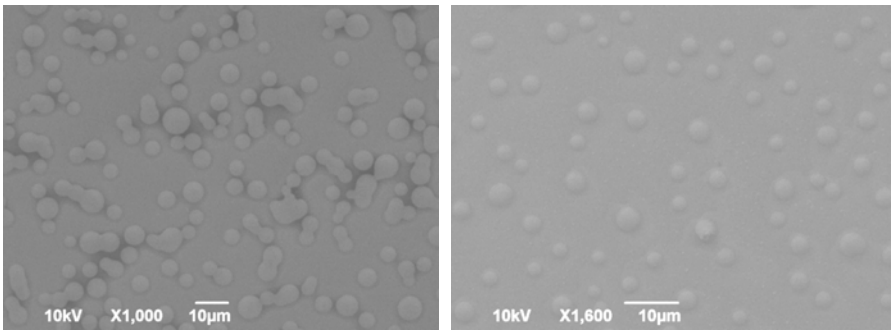


Fig. S3. SEM images of **1b** in $CHCl_3$/decalin (left) (1:0.6, v/v), b) $CHCl_3$/n-octane (right) (1:0.8, v/v) (3mM).

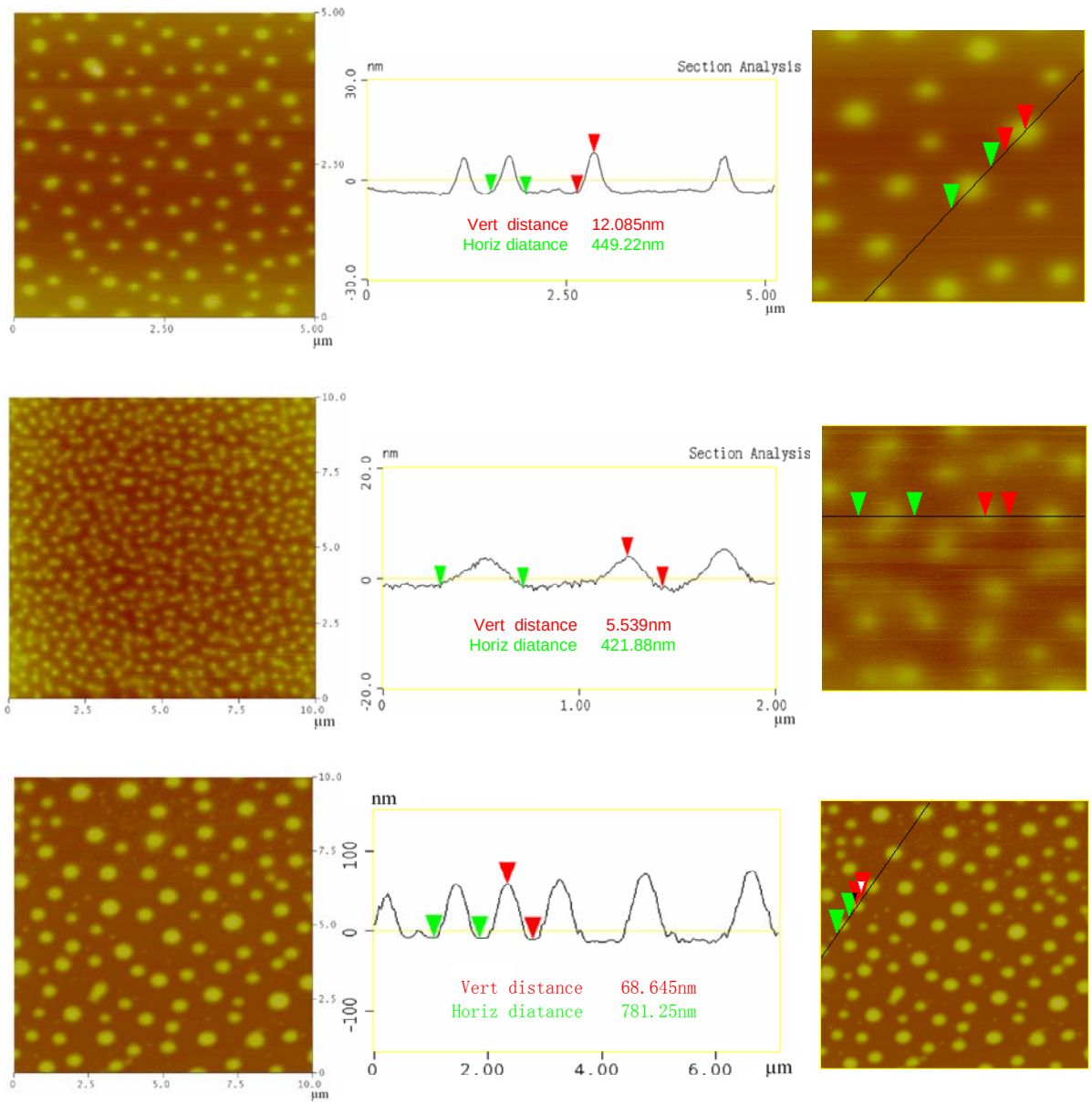


Fig. S4. Tapping-mode AFM images and cross-section analysis of **1a** (upper) in $CHCl_3$, **1a** (middle) in CH_2Cl_2 and **1b** (down) in CH_2Cl_2 (the concentration was 0.3 mM).

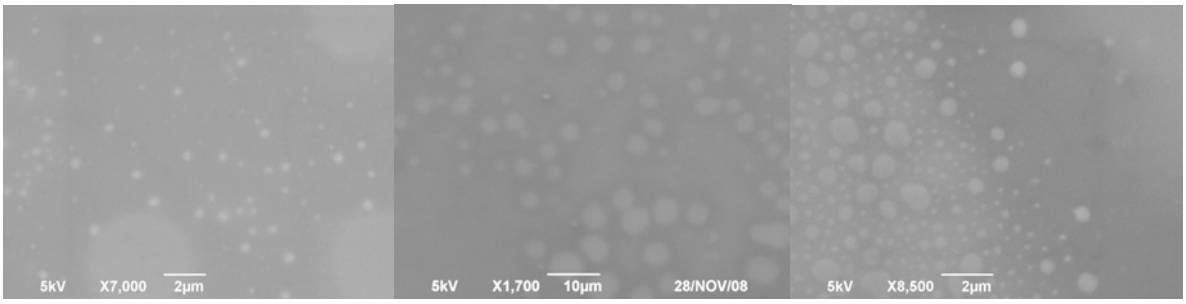


Fig. S5. SEM images of **3b** in $CHCl_3$ (left), **3b** in CH_2Cl_2 (middle) and **5b** in $CHCl_3$ (right) in CH_2Cl_2 (3 mM) in the presence of 10 equiv of hydrogen iodide.

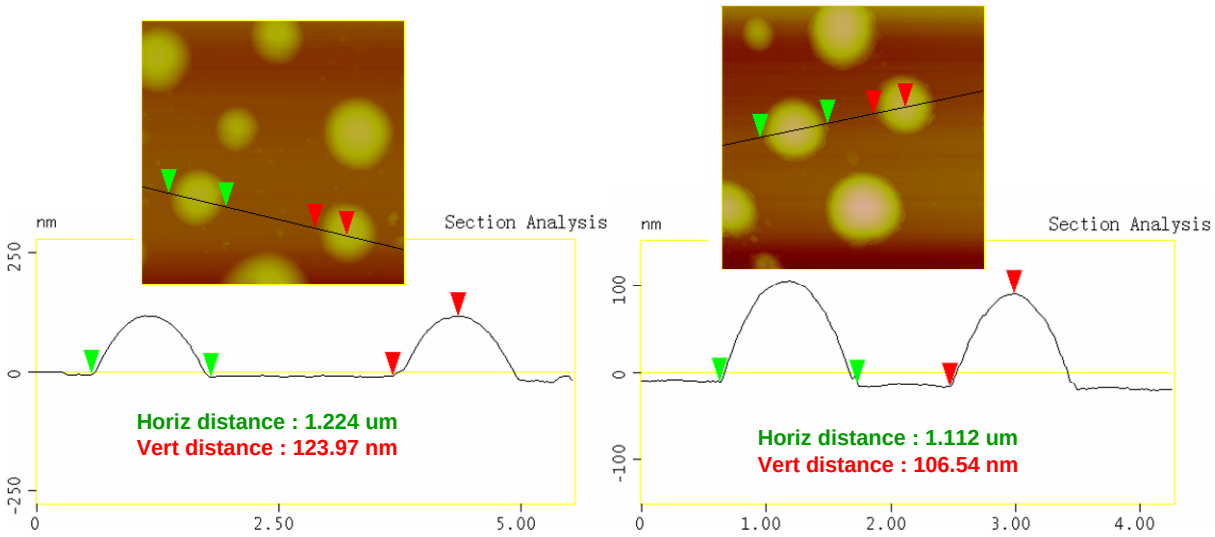


Fig. S6. Tapping-mode AFM images and cross-section analysis of **2** in $CHCl_3$ (left) and in CH_2Cl_2 (right) (the concentration was 0.15 mM).

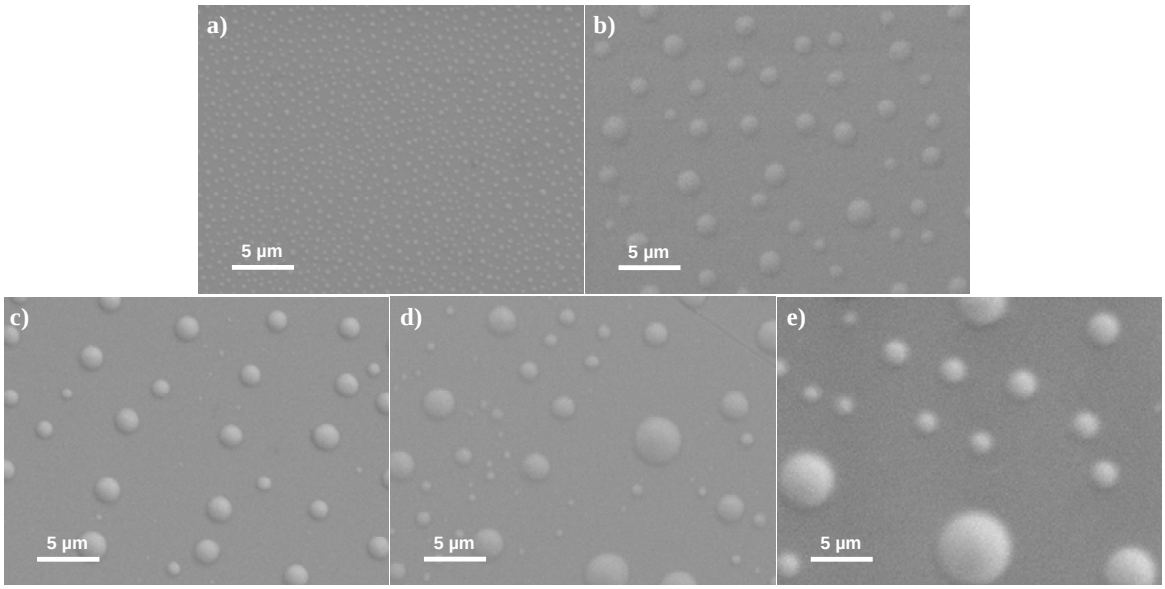


Fig. S7. SEM images of **1b** a) 0.3 mM, b) 0.6 mM), c) 1.5 mM, d) 2.4 mM and e) 3.0 mM, obtained by evaporation of its chloroform solutions on mica.

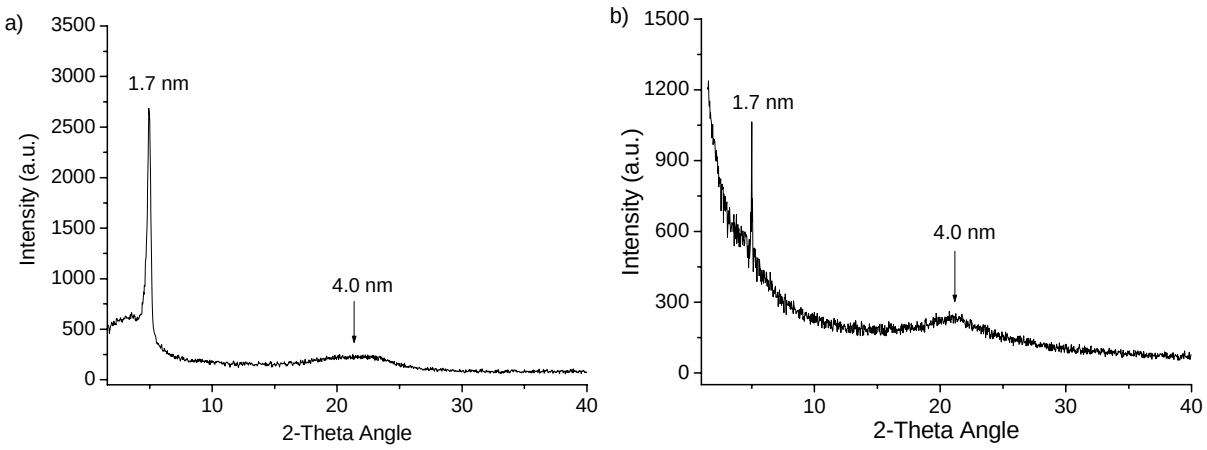


Fig. S8. The XRD profiles of the aggregates of a) **1a** and b) **1b**. The samples were prepared by evaporating their chloroform solutions of 3.0 mM.

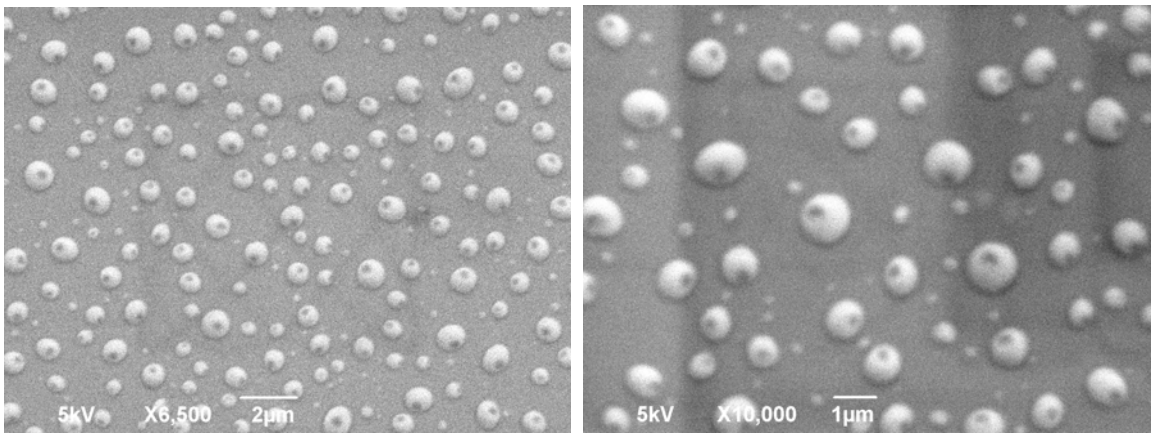


Fig. S9. SEM images of **1b**, obtained by evaporation of its chloroform solution (0.3 mM) on mica.