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Supporting Information

Dendritic Domains with Hexagonal Symmetry Formed by X-Shaped Bolapolyphiles in Lipid Membranes

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Supporting Information

1. Synthesis of compounds B*n*-E*n,m*

1.1 General remarks

1,4-Dibromo-2,5-didodecyloxybenzene, 1,4-dibromo-2,5-dioctadecyloxybenzene,[1]4-(4-ethynylphenoxymethyl)-2,2-dimethyl-1,3-dioxolane (**2**),[2]4-triisopropylsilyloxybromobenzene,[3] 3,6,9,12,15,18,21-heptaoxadocosyl-*p*-toluenesulphonate,[4] 11,12-isopropylidenedioxy-3,6,9-trioxadodecan-1-ol[5] and $Pd[PPh_3]_4$ were prepared according to the mentioned literature procedures.
4-Bromophenylethynyltrimethylsilane, 4-iodophenylethynyltrimethylsilane, ethynyltrimethylsilane, *p*-toluenesulfonyl chloride and copper(I) iodide were used as obtained from Sigma-Aldrich. Pyridinium-4-toluensulphonate was used as obtained from Merck. Conformation of the structures and the purity of the compounds were obtained by ^{1}H-NMR spectroscopy, ^{13}C-NMR spectroscopy (*Varian* Gemini 2000 und Inova Unity 500) and mass spectrometry (*Bruker* HR-ESI-TOF). The purity was also checked by thin-layer chromatography (TLC, silica gel 60 F_{254}, *Merck*). Column chromatography was performed with silica gel 60 (0.063-0.2, *Merck*), flash-chromatography with silica gel 60 (0.040-0.063, *Merck*). Triethylamine was distilled from CaH_2 and stored over molecular sieve. DMF was stored over molecular sieve.

1.2 Synthesis of intermediates

4-[4-(4-Ethynylphenylethynyl)phenoxymethyl]-2,2-dimethyl-1,3-dioxolane 4a
Under an argon atmosphere a mixture of 4-bromophenylethynyltrimethylsilane (4.71 g, 22.3 mmol), 4-(4-ethynylphenoxymethyl)-2,2-dimethyl-1,3-dioxolane (5.18 g, 18.6 mmol), $Pd[PPh_3]_4$ (0.64 g, 1.1 mmol), copper(I) iodide (0.07 g, 0.74 mmol) and triethylamine (50 ml) is stirred under reflux for seven hours. After cooling, triethylamine is evaporated under reduced pressure and the residue is taken up in diethyl ether and water. The organic layer is separated and the water phase is extracted two times with diethyl ether. The combined organic layers are washed with saturated solution of sodium chloride, dried over sodium sulphate and evaporated under reduced pressure. The crude product TMS-**4a** is purified by flash-chromatography on silica gel (eluent: $CHCl_3$). Yield: 3.2 g (43 %); white crystalline solid; mp. 110-112 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.45 – 7.38 (m, 6H, Ar−*H*), 6.89 – 6.84 (m, 2H, Ar−*H*), 4.53 – 4.40 (m, 1H, C*H*), 4.15 (dd, *J* = 8.5, 6.4 Hz, 1H, OCH_2), 4.05 (dd, *J* = 9.5, 5.4 Hz, 1H, CH_2O), 3.94 (dd, *J* = 9.6, 5.8 Hz, 1H, CH_2O), 3.88 (dd, *J* = 8.5, 5.8 Hz, 1H, OCH_2), 1.44 (s, *J* = 23.5 Hz, 3H, CH_3), 1.38 (s, 3H, CH_3), 0.24 (s, 9H, $Si(CH_3)_3$).
A suspension of TMS-**4a** (3.2 g, 7.9 mmol), potassium carbonate (5.33 g, 39.5 mmol), methanol (50 ml) and dichloromethane (25 ml) is stirred for ten hours at room temperature. The reaction mixture is evaporated under reduced pressure and the residue is taken up in diethyl ether and water. The organic layer is separated and the water phase is extracted twice with diethyl ether. The combined organic layers are washed with a saturated solution of sodium chloride, dried over sodium sulphate and evaporated under reduced pressure. The crude product is used without further purification. Yield: 2.4 g (91.4 %); white crystalline solid; mp. 118-121 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.46 – 7.41 (m,

6H, Ar−*H*), 6.90 – 6.84 (m, 2H, Ar−*H*), 4.52 – 4.41 (m, 1H, C*H*), 4.15 (dd, *J* = 8.5, 6.4 Hz, 1H, OCH_2), 4.05 (dd, *J* = 9.5, 5.4 Hz, 1H, CH_2O), 3.95 (dd, *J* = 9.5, 5.8 Hz, 1H, CH_2O), 3.89 (dd, *J* = 8.5, 5.8 Hz, 1H, OCH_2), 3.14 (s, 1H, C≡C*H*), 1.45 (d, *J* = 0.5 Hz, 3H, CH_3), 1.39 (d, *J* = 0.5 Hz, 3H, CH_3)

1,4-Bis{4-[4-(2,2-dimethyl-1,3-dioxolane-4-ylmethoxy)phenylethynyl]phenyl-ethynyl}-2,5-didodecyloxybenzene 6a (*n* = 12)

Under an argon atmosphere a mixture of **4a** (660 mg (1.99 mmol), 1,4-dibromo-2,5-didodecyloxybenzene (500 mg, 0.83 mmol), $Pd[PPh_3]_4$ (29 mg, 3 mol-%) and copper(I) iodide (3 mg, 2 mol-%) in triethylamine (30 ml) is stirred under reflux for ten hours. After cooling, triethylamine is evaporated under reduced pressure and the residue is taken up in chloroform and water. The organic layer is separated and the water layer is extracted two times with chloroform. The combined organic layers are washed with a saturated solution of sodium chloride, dried over sodium sulphate and evaporated under reduced pressure. The crude product is purified by column chromatography on silica gel (eluent: dichloromethane) and crystallized from dichloromethane/diethyl ether. Yield: 513 mg (55.8 %); light yellow crystalline solid, mp. 152-154 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.40 (m, 12H, Ar−*H*), 6.99 (s, 2H, Ar−*H*), 6.92 – 6.84 (m, 4H, Ar−*H*), 4.52 – 4.41 (m, 2H, C*H*), 4.16 (dd, *J* = 8.5, 6.4 Hz, 2H, OCH_2), 4.06 (dd, *J* = 9.6, 5.4 Hz, 2H, CH_2O), 4.02 (t, *J* = 6.4 Hz, 4H, OCH_2CH$_2$), 3.98 – 3.93 (m, 2H, CH_2O), 3.90 (dd, *J* = 8.5, 5.8 Hz, 2H, OCH_2), 1.87-1.80 (m, 4H, OCH$_2$CH_2), 1.57-1.49 (m, 4H, OCH$_2$CH$_2$CH_2), 1.45 (s, 6H, CH_3), 1.40 (s, 6H, CH_3), 1.40-1.20 (m, 32H, OCH$_2$CH$_2$CH$_2$(CH_2)$_8$), 0.87-0.84 (m, 6H, CH_3)

1,4-Bis{4-[4-(2,2-dimethyl-1,3-dioxolane-4-ylmethoxy)phenylethynyl]phenyl-ethynyl}-2,5-dioctadecyloxybenzene 6a (*n* = 18)

Synthesized according to the procedures given above, but starting from 1,4-dibromo-2,5-dioctadecyloxybenzene (310 mg, 0.40 mmol), yield: 93 mg (18.4 %), light yellow crystalline solid, mp. 153-155 °C, ^{1}H-NMR ($CDCl_3$, 400 MHz) δ = 7.51-7.45 (m, 12H, Ar−*H*), 7.01 (s, 2H, Ar−*H*), 6.90 (d, ^3J = 8.8 Hz, 4H, Ar−*H*), 4.52-4.46 (m, 2H, OC*H*), 4.20-4.16 (m, 2H, OCH_2), 4.10-4.02 (m, 6H, CH_2O, OCH_2CH$_2$), 3.99-3.95 (m, 2H, CH_2O), 3.93-3.89 (m, 2H, OCH_2), 1.89-1.82 (m, 4H, OCH$_2$CH_2), 1.63-1.50 (m, 4H, OCH$_2$CH$_2$CH_2), 1.47 (s, 6H, CH_3), 1.41 (s, 6H, CH_3), 1.41-1.25 (m, 56H, OCH$_2$CH$_2$CH$_2$(CH_2)$_{14}$), 0.89-0.86 (m, 6H, CH_3)

4-Ethynylphenoxytriisopropylsilane 3

Synthesized according to the procedures given for **4a**, but starting from 4-triisopropylsilyloxybromobenzene (19.8 g, 0.06 mol) and ethynyltrimethylsilane (7.3 g, 0.07 mol), the crude product is purified by column chromatography on silica gel (eluent: petrol ether), yield: 5.9 g (36 %), colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.23 (m, 2H, Ar-*H*), 6.73 – 6.68 (m, 2H, Ar-*H*), 2.88 (s, 1H, C≡C*H*), 1.20 – 1.07 (m, 3H, SiC*H*), 1.02 – 0.93 (m, 18H, CHCH_3)

4-(4-Ethynylphenylethynyl)phenoxytriisopropylsilane 4b

Under an argon atmosphere a mixture of **3** (3.2 g, 11.7 mmol), 4-iodophenylethynyltrimethylsilane (3.5 g, 11.7 mmol), $Pd[PPh_3]_4$ (0.3 g, 0.26 mmol), copper(I) iodide (0.03 g, 0.17 mmol) and triethylamine (100 ml) is stirred at room temperature for seven hours. Triethylamine is evaporated under reduced pressure and the residue is taken up in diethyl ether and water. The organic layer is separated and the water phase is extracted two times with diethyl ether. The combined organic layers

are washed with saturated solution of sodium chloride, dried over sodium sulphate and evaporated under reduced pressure. The crude 4-(4-triisopropylsilyloxyphenylethynyl)trimethylsilyl-ethynylbenzene (TMS-**4b**) is purified by column chromatography on silica gel (eluent: *n*-hexane). Yield: 4.5 g (87 %), colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.34 (m, 6H, Ar-*H*), 6.89 – 6.75 (m, 2H, Ar-*H*), 1.33 – 1.17 (m, 3H, SiC*H*), 1.17 – 1.04 (m, 18H, CHCH_3), 0.23 (s, 9H, SiCH_3).
Desilylation of TMS-**4b** (4.5 g, 10.1 mmol) was performed according to the procedures given for TMS-**4a**, using shorter reaction time (2 h); the crude product is purified by column chromatography on silica gel (eluent: *n*-hexane), Yield: 1.3 g (34 %), colorless crystalline solid, mp. 35-38 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (s, 4H, Ar-*H*), 7.42 – 7.36 (m, 2H, Ar-*H*), 6.88 – 6.82 (m, 2H, Ar-*H*), 3.16 (s, 1H, C≡C*H*), 1.33 – 1.20 (m, 3H, SiC*H*), 1.13 – 1.06 (m, 18H, CHCH_3)

2,5-Didodecyloxy-1,4-bis[4-(4-triisopropylsilyloxyphenylethynyl)phenyl-ethynyl]benzene <u>6b</u>
Synthesized according to the procedures given for **6a**, but starting from **4b** (650 mg, 1.74 mmol) and 1,4-dibromo-2,5-didodecyloxybenzene (437 mg, 0.72 mmol); the crude product is purified by column chromatography on silica gel (eluent: *n*-hexane/$CHCl_3$ 3:1 → 2:1 V/V), Yield: 510 mg (59 %), light yellow crystalline solid, mp. 97-100 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (s, 4H, Ar-*H*), 7.42 – 7.36 (m, 2H, Ar-*H*), 6.88 – 6.82 (m, 2H, Ar-*H*), 3.16 (s, 1H, C≡C*H*), 1.33 – 1.20 (m, 3H, SiC*H*), 1.13 – 1.06 (m, 18H, CHCH_3)

12-Bromo-3,6,9-trioxadodecane-1,2-diol
11,12-Isopropylidenedioxy-3,6,9-trioxadodecan-1-ol (1.16 g, 4.64 mmol) and sodium hydroxide (0.27 g, 6.96 mmol) are solved in a mixture of water and THF (5 ml/ 20ml) and cooled to 0 °C. Afterwards, *p*-toluenesulfonyl chloride (1.00 g, 5.10 mmol), solved in THF (10 ml), is added, temperature must not exceed 5 °C, and the solution is stirred at 0 °C for three hours. Subsequent, the reaction mixture is poured into ice water (20 ml) and extracted three times with methylene chloride. The combined organic layers are washed with water, saturated solution of sodium hydrogen carbonate and sodium chloride, dried over sodium sulphate and evaporated under reduced pressure. The crude product (1.76 g, 4.35 mmol) and lithium bromide (1.13 g, 13.0 mmol) are solved in acetone (50 ml) and refluxed for five hours. The suspension is cooled to room temperature and the solvent is evaporated under reduced pressure. The residue is taken up in water and methylene chloride and the phases are separated. The aqueous phase is extracted three times with methylene chloride, the combined organic layers are dried over sodium sulphate and the solvent is evaporated under reduced pressure. The crude product is purified by column chromatography on silica gel (eluent: $CHCl_3$:MeOH 9:1 V/V), Yield: 630 mg (46%), colorless oil, ^{1}H-NMR (400 MHz, $CDCl_3$,): δ = 3.86 (m, 1H, $CH_2CHOHCH_2$), 3.80 (t, *J* = 6.3 Hz, 2 H, CH_2OCH_2), 3.73 – 3.51 (m, 12 H, OCH_2CH_2O), 3.47 (t, *J* = 6.3 Hz, 2H, $BrCH_2$), 3.24 (s, 1 H, CH_2OH), 2.57 (s, 1 H, $CH_2CHOHCH_2$), MS: *m/z* $[M+H+Na]^+$ 311.10 (calc. 311.14)

2.3 Compounds B*n*-E*n,m*

<u>B12</u>: A mixture of **6a** with *n* = 12 (513 mg, 0.46 mmol), pyridinium-4-toluenesulphonate (23 mg, 0.46mmol), methanol (5 ml) and THF (40 ml) is stirred at 60 °C for five days. The reaction is monitored by TLC. After the reaction is finished, the solvent is removed under reduced pressure and the residue is taken up in a small amount of THF. The pyridinium-4-toluensulphonate is filtered off

and the solution is evaporated under reduced pressure. The crude product is purified by column chromatography on silica gel (eluent: ethyl acetate) and recrystallized from THF/methanol. Yield: 230 mg (48.6 %), light yellow crystalline solid, cr 177 Col 181 iso (*T*/ °C), ^{1}H NMR (400 MHz, THF-d8) δ = 7.48 (s, 8H, Ar−*H*), 7.43 (m, 4H, Ar−*H*), 7.08 (s, 2H, Ar−*H*), 6.95 (m, 4H, Ar−*H*), 4.17 (d, *J* = 5.1 Hz, 2H, CHO*H*), 4.09 – 4.02 (m, 6H, OC*H*$_2$CH$_2$), 3.96 (dd, *J* = 9.5, 6.1 Hz, 2H), 3.92 – 3.85 (m, 2H, C*H*), 3.74 (dd, *J* = 5.8 Hz, 2H, CH$_2$O*H*), 3.65 – 3.49 (m, 4H), 1.91 – 1.79 (m, 4H, OCH$_2$C*H*$_2$), 1.65 – 1.53 (m, 4H, OCH$_2$CH$_2$C*H*$_2$), 1.48 – 1.18 (m, 32H, OCH$_2$CH$_2$CH$_2$(C*H*$_2$)$_8$), 0.88 (t, *J* = 6.7 Hz, 6H, C*H*$_3$); ^{13}C-NMR (CDCl$_3$, 126 MHz) δ = 158.59, 153.72, 133.20, 131. 49, 131.37, 123.36, 123.03, 116.92, 115.93, 114.64, 114.02 (Ar-*C*), 94.77, 91.13, 88.23, 87.83 (*C*≡*C*), 70.28, 69.69, 69.25, 63.58 (O*C*H$_2$, O*C*H), 31.94, 29.72, 29.69, 29.67, 29.65, 29.46, 29.38, 26.12, 22.71, 14.13 (*C*H$_2$, *C*H$_3$); HR-MS: m/z [*M*+Cl]$^-$ 1061.5708 (calc. 1061.5693)

B18: Synthesized according to the procedures given for **B12**, but starting from **6a** with *n* = 18 (93 mg, 0.073 mmol), Yield: 20 mg (23 %), light yellow crystalline solid, cr 158 (Col$_{hex}$/*p*6*mm* 156) iso (*T*/ °C), ^{1}H-NMR (500 MHz, THF-d8): δ = 7.48 (s, 8H, Ar−*H*), 7.43 (m, 4H, Ar−*H*), 7.08 (s, 2H, Ar−*H*), 6.95 (m, 4H, Ar−*H*), 4.17 (d, *J* = 5.1 Hz, 2H, CHO*H*), 4.14 – 4.01 (m, 6H, OC*H*$_2$CH$_2$), 3.95 (dd, *J* = 9.5, 6.1 Hz, 2H), 3.92 – 3.84 (m, 2H, C*H*), 3.73 (dd, *J* = 5.8 Hz, 2H, CH$_2$O*H*), 3.64 – 3.51 (m, 4H), 1.90 – 1.80 (m, 4H, OCH$_2$C*H*$_2$), 1.63 – 1.53 (m, 4H, OCH$_2$CH$_2$C*H*$_2$), 1.46 – 1.20 (m, 56H, OCH$_2$CH$_2$CH$_2$(C*H*$_2$)$_{14}$), 0.88 (t, *J* = 6.9 Hz, 6H, C*H*$_3$); ^{13}C-NMR (CDCl$_3$, 126 MHz) δ = 158.59, 153.72, 133.20, 131.49, 131.37, 123.36, 123.03, 116.93, 115.94, 114.64, 114.02 (Ar-*C*), 94.77, 91.13, 88.23, 87.83 (*C*≡*C*), 70.29, 69.69, 69.24, 63.58 (O*C*H$_2$, O*C*H), 31.94, 29.72, 29.69, 29.65, 29.45, 29.49, 29.38, 26.11, 22.70, 14.13 (*C*H$_2$, *C*H$_3$); HR-MS: m/z [*M*+Cl]$^-$ 1229.7588 (calc. 1229.7571)

C12: 6b (510 mg, 0.43 mmol) is solved in THF (10 ml), tetrabutylammoniumfluorid (0.2 ml of 1 M solution in THF, 0.17 mmol) is added and the solution was stirred at room temperature for two hours. After the reaction is finished, the solution is diluted with methylene chloride and water. The organic layer is separated and the aqueous layer is extracted two times with methylene chloride. The combined organic layers are washed with brine, dried over sodium sulphate and evaporated under reduced pressure. The crude product is purified by column chromatography on silica gel (eluent: CHCl$_3$/MeOH 10:0 → 10:0.05 V/V) and crystallized from chloroform. Yield: 277 mg (74 %), light yellow crystalline solid, mp. 184-188 °C, ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.49 – 7.44 (m, 8H, Ar-*H*), 7.43 – 7.39 (m, 4H, Ar-*H*), 6.99 (s, 2H, Ar-*H*), 6.84 – 6.76 (m, 4H, Ar-*H*), 4.83 (s, 2H, O*H*), 4.02 (t, *J* = 6.5 Hz, 4H, OC*H*$_2$), 1.85 – 1.81 (m, 4H, OCH$_2$*CH*$_2$), 1.56 – 1.45 (m, 4H, OCH$_2$CH$_2$*CH*$_2$), 1.40 – 1.17 (m, 32H, OCH$_2$CH$_2$CH$_2$(*CH*$_2$)$_8$), 0.85 (t, *J* = 6.3 Hz, 6H, CH$_2$C*H*$_3$); HR-MS: m/z [*M*+Cl]$^-$ 913.4984 (calc. 913.4957)

D12/3: A suspension of **C12** (70 mg, 0.079 mmol), 12-bromo-3,6,9-trioxadodecane-1,2-diol (50 mg, 0.175 mmol) and potassium carbonate (110 mg, 0.79 mmol) in DMF (30 ml) is stirred at 80 °C for eight hours. After cooling, water is added and the water layer is extracted three times with ethyl acetate. The combined organic layers are washed three times with saturated solution of lithium chloride, dried over sodium sulphate and the solvent is evaporated under reduced pressure. The crude product is purified by column chromatography on silica gel (eluent: CHCl$_3$/MeOH 10:0.3 V/V). Yield: 52 mg (51 %), light yellow crystalline solid, mp. 131 °C, ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.50 – 7.40 (m, 12H, Ar-*H*), 6.99 (s, 2H, Ar-*H*), 6.93 – 6.84 (m, 4H, Ar-*H*), 4.19 – 4.13 (m, 4H), 4.02 (t, *J* =

6.4 Hz, 4H, OCH_2CH$_2$CH$_2$), 3.90 – 3.80 (m, 6H), 3.74 – 3.58 (m, 22H), 3.56 (dd, *J* = 10.1, 6.3 Hz, 2H), 1.88 – 1.78 (m, 4H, OCH$_2$CH_2CH$_2$), 1.56 – 1.46 (m, 4H, OCH$_2$CH$_2$CH_2), 1.42 – 1.16 (m, 32H, OCH$_2$CH$_2$CH$_2$(CH_2)$_8$), 0.85 (t, *J* = 6.9 Hz, 6H, CH$_2$CH_3); HR-MS: *m/z* [*M*+Cl]$^-$ 1325.7209 (calc. 1325.7266)

E12/7: Synthesized according to the procedures given for **D12/3**, starting from **C12** (50 mg, 0.057 mmol) and 3,6,9,12,15,18,21-heptaoxadocosyl-*p*-toluenesulphonate (62 mg, 0.125 mmol). Yield: 31 mg (36 %), light yellow crystalline solid, mp. 87 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.39 (m, 12H, Ar-*H*), 6.99 (s, 2H, Ar-*H*), 6.90 – 6.84 (m, 4H, Ar-*H*), 4.18 – 4.09 (m, 4H), 4.02 (t, *J* = 6.4 Hz, 4H, OCH_2CH$_2$CH$_2$), 3.90 – 3.82 (m, 4H), 3.75 – 3.69 (m, 4H), 3.69 – 3.56 (m, 40H), 3.56 – 3.49 (m, 4H), 3.36 (s, 6H, OCH_3), 1.89 – 1.79 (m, 4H, OCH$_2$CH_2CH$_2$), 1.59 – 1.44 (m, 4H, OCH$_2$CH$_2$CH_2), 1.42 – 1.16 (m, 32H, OCH$_2$CH$_2$CH$_2$(CH_2)$_8$), 0.85 (t, *J* = 6.8 Hz, 6H, CH$_2$CH_3); HR-MS: *m/z* [*M*+Li]$^+$ 1529.9450 (calc. 1529.9414).

2. Estimation of the number of molecules in the B12-rich domains

For the estimations the following assumptions were made, see Fig. S1:

- The cross sectional area required by each **B12** molecule (cross sections of the aromatic core of the bolapolyphile + the attached lateral alkyl chains a_b) and each lipid molecule (cross sectional area of two alkyl chains, a_l) is $a_b \sim a_l \sim a \sim 0.4$ nm^2.
- The (inverse) total area ratio *r* of the lipids (A_l) to the total area of bolaamphiphiles and lipids ($A_{b+l} = A_b+A_l$) given an experimental number ratio n_b:n_l = 1:3 is
  $$r = (A_b+A_l)/A_l = (1+1.5)/1.5 = 1.667,$$
  considering that 2 lipids are located on top of each other ($A_b = a\, n_b$; $A_l = a\, n_l/2$).
- In the honeycomb walls the aromatic cores adopt some preferred face-to-face packing, so that the aromatic cores have an extension along *d* of ~ 0.55 nm and a distance between the faces of about ~ 0.36 nm.
- As average diameter of the alkyl chains ~0.45 nm is used.
- Along $2d_b$ there is one aromatic core and on average one alkyl chain (each alkyl chain covers one half of the aromatic core, i.e. on average there is one aromatic core and one alkyl chain arranged side-by side), which means that $2d_b \sim 0.55 + 0.45 \sim 1.0$ nm
- The relation of the area of the lipids (A_l) and the total area of bolaamphiphiles plus lipids ($A_{b+l} = A_b+A_l$) to the dimensions d_l and $d_{b+l} = d_l + d_b$ (using $d^2 = 3^{1/2} A$ for an equilateral triangle) is $(A_b+A_l)/A_l = r = (d_l + d_b)^2/d_l^2$. This quadratic equation is easily solved, given d_b = 0.5 nm and *r* = 1.667:
  $$d_l = d_b/(r\text{-}1) + [\ (d_b/(r\text{-}1))^2 + d_b^2/(r\text{-}1)\ ]^{1/2} = 1.72 \text{ nm}$$
- With $A_l = d_l^2\, 3^{-1/2} = 1.71$ nm^2, we finally obtain the number of lipid molecules per cell via
  $$\boldsymbol{N_l} = 6\times2\times A_l/a_l \approx \mathbf{50}$$
- The length of the equilateral triangle $c_{b+l} = (4/3)^{1/2}\, d_{b+l} = 2.56$ nm. From this we estimate
  $\boldsymbol{N_b}$ = 2.56 nm/0.36 nm ≈ **7 B12** molecules per honeycomb wall.

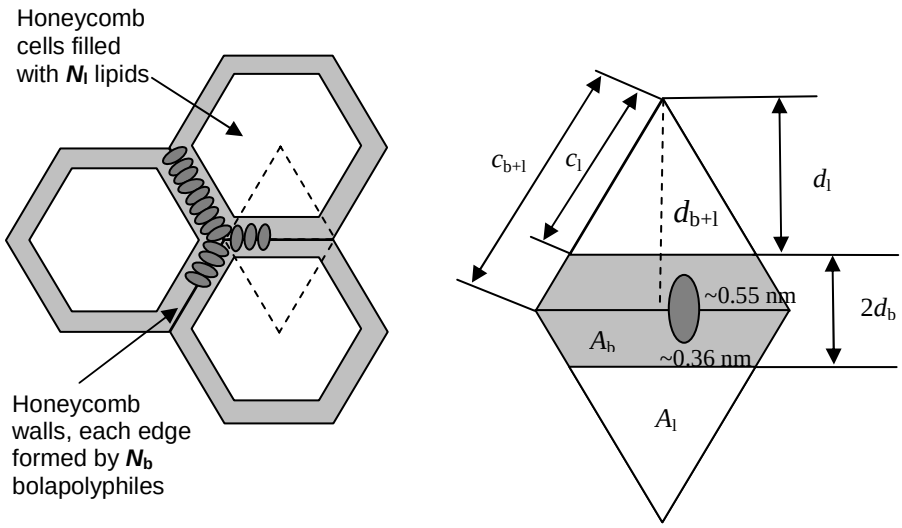

Figure S1. Model showing the organization of bolapolyphiles (**B12**) in the hexagonal honeycomb (cut perpendicular to the membrane normal) and definition of the parameters used for the estimation of the cell size.

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