

Supporting Information

Testing the Triple Network Structure of the Cubic $Im\bar{3}m$ (I) Phase by Isomorphous Replacement and Model Refinement

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Synthesis

Synthesis of methyl 3,4,5-tris(dodecyloxy)benzoate (1)

1-Bromo-dodecane (5.0 g, 20 mmol) was added to a suspension of methyl 3,4,5-tris(hydroxy)benzoate (1.0 g, 5.5 mmol), K₂CO₃ (14 g, 80 mmol), KI (0.4 g, 2.4 mmol) and 4Å molecular sieves in dry butanone (100 ml), and the mixture was heated under reflux for 3 days. The reaction mixture was filtered and the butanone distilled off. The crude product was purified by column chromatography (SiO₂, CH₂Cl₂/hexane = 8/2) yielded white powder (2.6 g, 3.8 mmol, 70 %). ¹H-NMR (400MHz, CDCl₃) δ = 0.88 (t, 9 H, CH₂-CH₃), 1.29 (m, 54 H, -(CH₂)₉-CH₃), 1.79 (m, 6 H, CH₂-CH₂-CH₂-O), 3.88 (s, 3 H, COO-CH₃), 4.00 (m, 6 H, CH₂-O), 7.24 (s, 2 H, CH_{ar}).

Synthesis of 3,4,5-tris(dodecyloxy)benzoic acid (2)

Compound **1** (2.6 g, 3.8 mmol) was dissolved in THF (8 ml) and methanol (50 ml). A solution of KOH (1.8 g, 30 mmol) in water (10 ml) was then added drop-wise to the mixture with stirring. The mixture was stirred at room temperature overnight, followed by reflux for 4 hours. The solvents were evaporated and ice/water (30 ml) was added to the residue. The mixture was acidified with HCl conc. until pH = 3 and the product was filtered off, washed with water and in the end with hexane (2.5 g, 3.7 mmol, 98 %). ¹H-NMR (400 MHz, CDCl₃) δ = 0.87 (t, 9 H, CH₂-CH₃), 1.29 (m, 54 H, -(CH₂)₉-CH₃), 1.75 (m, 6 H, CH₂-CH₂-CH₂-O), 3.98 (m, 6 H, CH₂-O), 7.27 (s, 2 H, CH_{ar}).

Synthesis of methyl 4-(undec-10-enyloxy)benzoate (3)

11-bromo-1-undecene (9.0 g, 40 mmol) was added to a suspension of methyl 4-hydroxy benzoate (5.1 g, 33 mmol), K₂CO₃ (25 g, 0.2 mol), KI (0.8 g, 5.2 mmol) and 4Å molecular sieves in dry butanone (150 ml), and the mixture was heated under

reflux for 1 day. The reaction mixture was filtered and the butanone distilled off. The crude product was purified by recrystallization from hexane to yield white powder (9.8 g, 31 mmol, 94 %); (SiO₂, DCM/hexane = 8/2; R_f = 0.5). ¹H-NMR (400 MHz, CDCl₃) δ = 1.29 (m, 10 H, -(CH₂)₅-CH₂-CH=CH₂), 1.43 (m, 2 H, -CH₂-CH₂-CH₂-O), 1.76 (q, 2 H, -CH₂-CH₂-O), 2.04 (m, 2 H, CH₂-CH=CH₂), 3.88 (s, 3 H, COO-CH₃), 4.06 (t, 2 H, CH₂-O), 4.97 (m, 2 H, CH=CH₂), 5.80 (m, 1 H, CH=CH₂), 6.90 (dd, 2 H, CH_{ar}), 7.98 (dd, 2 H, CH_{ar}).

Synthesis of 4-(undec-10-eneoxy)benzoic acid (4).

Compound **2** (6.1 g, 20 mmol) was dissolved in THF (25 ml) and methanol (140 ml). A solution of KOH (6.7 g, 0.12 mol) in water (20 ml) was then added drop-wise to the mixture with stirring. The mixture was stirred at room temperature overnight, followed by reflux for 2 hours. The solvents were evaporated and ice/water (90 ml) was added to the residue. The mixture was acidified with HCl conc. until pH = 3 and the product was filtered off, washed with water and in the end with hexane (5.9 g, 19.6 mmol, 98 %). ¹H-NMR (400 MHz, DMSO-D₆) δ = 1.35 (m, 12 H, -(CH₂)₆-CH₂-CH=CH₂), 1.74 (q, 2 H, -CH₂-CH₂-O), 2.04 (m, 2 H, CH₂-CH=CH₂), 4.01 (t, 2 H, CH₂-O), 4.99 (m, 2 H, CH=CH₂), 5.83 (m, 1 H, CH=CH₂), 6.86 (dd, 2 H, CH_{ar}), 7.87 (dd, 2 H, CH_{ar}).

Synthesis of 4'-hydroxybiphenyl-4-yl 4-(undec-10-eneoxy)benzoate (5)

4-(Undec-10-eneoxy)benzoic acid (14.5 g, 0.05 mol), 4,4'-dihydroxybiphenyl (20.5 g, 0.11 mol) and 4-(dimethylamino)pyridine (DMAP) (1.2 g, 0.01 mol) was dissolved in dry tetrahydrofuran (THF) (300 ml) and N,N'-dicyclohexylcarbodiimide (DCC) (12.4 g, 0.06 mol) was added. After stirring for 18 h at room temperature the reaction mixture was filtered, the precipitate was washed with CH₂Cl₂ and the solvents distilled off. The residue was dissolved in hot ethanol under reflux and after cooling to r.t. the suspension was filtered. The crude product was purified by column chromatography (SiO₂; CH₂Cl₂/hexane = 8/2 first spot, and then CH₂Cl₂/Ether = 5/5-second spot). This yielded a white powder (8.3 g, 17.5 mmol, 35 %). ¹H-NMR (400 MHz, CDCl₃) δ = 1.31 (m, 10 H, CH₂-CH₂-CH₂), 1.47 (m, 2 H, CH₂-CH₂-CH₂-O), 1.82 (q, 2 H, CH₂-CH₂-O), 2.04 (m, 2 H, -CH₂-CH=CH₂), 4.04 (t, 2 H, CH₂-O), 4.95 (m, 2 H,

CH=CH₂), 5.80 (m, 1 H, CH=CH₂), 6.87 (m, 2 H, CH_{ar}), 6.97 (m, 2 H, CH_{ar}), 7.24 (m, 2 H, CH_{ar}), 7.44 (m, 2 H, CH_{ar}), 7.55 (m, 2 H, CH_{ar}), 8.16 (m, 2 H, CH_{ar}).

Synthesis of 4'-(4-(undec-10-enyloxy)benzoyloxy)biphenyl-4-yl 3,4,5-tris(dodecyloxy)benzoate (6)

Compound **2** (8.7 g, 13 mmol) was dissolved in dry toluene (70 ml) under nitrogen; thionyl chloride (18 ml, 0.26 mol) was added and the solution was heated to 80 °C for 3 h, the reaction being completed after heating for 45 min at reflux. The thionyl chloride and toluene were distilled off under nitrogen. A solution of compound **5** (5.9 g, 13 mmol) and dry pyridine (20 ml, 0.25 mol) in toluene (30 ml) was added to the residue. This reaction mixture was heated at 80 °C for 18 h and the reaction completed after reflux for 1 h. Ice-water (150 ml) and ether was then added; the phases were separated and the organic layer extracted with ether (3 x 100 ml). The combined organic layers were dried over MgSO₄ and the solvents distilled off. The crude product was purified by column chromatography (SiO₂; CH₂Cl₂/Hexane = 8/2, R_f = 0.6) yielded white powder (11.4 g, 10.2 mmol, 79 %). C₇₃H₁₁₀O₈; M = 1115.6; **A.E.**: Calc.: C 78.59 %, H 9.94 %; Exp.: C 78.70 %, H 10.00 %; ¹H-NMR (400 MHz, CDCl₃) δ = 0.88 (t, 9 H, -CH₂-CH₃), 1.26-1.51 (m, 66 H, (-CH₂), 1.80 (m, 8 H, -CH₂-CH₂-O-), 2.05 (m, 2 H, -CH₂-CH=CH₂), 4.05 (m, 8 H, -CH₂-O-), 4.97 (m, 2 H, -CH=CH₂), 5.81 (m, 1 H, -CH=CH₂), 6.98 (m, 2 H, CH_{ar}), 7.28 (m, 4 H, CH_{ar}), 7.43 (s, 2 H, CH_{ar}), 7.62 (m, 4 H, CH_{ar}), 8.17 (m, 2 H, CH_{ar}).

Synthesis of 4'-(4-(11-mercaptoundecyloxy)benzoyloxy)biphenyl-4-yl 3,4,5-tris(dodecyloxy)benzoate (7)

A stirred solution of **6** (1.56 g, 1.4 mmol), triphenylsilanethiol (0.47 g, 1.6 mmol) and AIBN (0.06 g, 0.4 mmol) in benzene (4 ml) was warmed until reflux. After 2 days the mixture was cooled to room temperature. Trifluoroacetic acid (TFA) (0.54 ml, 7 mmol) was added and allowed to react 30 min. The solvent was removed give crude product which was purified by column chromatography (Si₂O; CH₂Cl₂/hexane = 7/3, R_f = 0.59) yielded white powder (0.5 g, 0.45 mmol, 32 %). C₇₃H₁₁₂O₈S; M = 1149.7; Elemental analysis: Calc.: C 76.26 %, H 9.82 %, S 2.79 %; Exp.: C 76.50 %, H 9.90 %, S 2.73 %; ¹H-NMR (400 MHz, CDCl₃) δ = 0.88 (t, 9 H, -CH₂-CH₃), 1.29-1.48 (m, 69 H, -CH₂-; -SH), 1.54 (m, 2 H, -CH₂-CH₂-SH), 1.82 (m, 8 H, -CH₂-CH₂-O-), 2.53

(m, 2 H, $-CH_2-SH$), 4.05 (m, 8 H, $-CH_2-O$), 6.98 (d, 2 H, CH_{ar}), 7.28 (m, 4 H, CH_{ar}), 7.43 (s, 2 H, CH_{ar}), 7.63 (d, 4 H, CH_{ar}), 8.1 (d, 2 H, CH_{ar}).

Synthesis of 4'-(4-(11-(1,1,3,3,3-pentamethyldisiloxanyl) undecyloxy) benzoyloxy) biphenyl-4-yl 3,4,5-tris(dodecyloxy)benzoate (8)

A solution of toluene (15 ml), compound **6** (0.67 g, 0.6 mmol), and 7 drops of Karstedt's catalyst dissolved in xylene was prepared. The solution was gently aerated for 20 s, and then pentamethyldisiloxane (1.18 ml, 6 mmol) was added at room temperature. After 30 min. a spatula tip of triphenylphosphane was added to convert the catalyst into the less reactive triphenylphosphane complex, and the solution was concentrated under reduced pressure. The crude product was purified by column chromatography (Si_2O ; ethyl acetate/hexane = 1/9) and yielded a white product (0.6 g, 0.5 mmol, 82 %). $C_{78}H_{126}O_9Si_2$; M = 1264.02; Elemental analysis.: Calc.: C 74.12 %, H 10.05 %; Exp.: C 73.97 %, H 9.95 %; ^1H-NMR (400 MHz, $CDCl_3$) δ = 0.0014 (s, 15 H, Si- CH_3), 0.45 (m, 2 H, $-CH_2-Si-O$), 0.82 (t, 9 H, $-CH_2-CH_3$), 1.12-1.48 (m, 70 H, $(-CH_2-)$), 1.74 (m, 8 H, $-CH_2-CH_2-O-$), 3.99 (m, 8 H, $-CH_2-O-$), 6.91 (d, 2 H, CH_{ar}), 7.22 (m, 4 H, CH_{ar}), 7.36 (s, 2 H, CH_{ar}), 7.56 (d, 4 H, CH_{ar}), 8.1 (d, 2 H, CH_{ar}).

See Scheme 1 in the main text.

DSC Thermograms

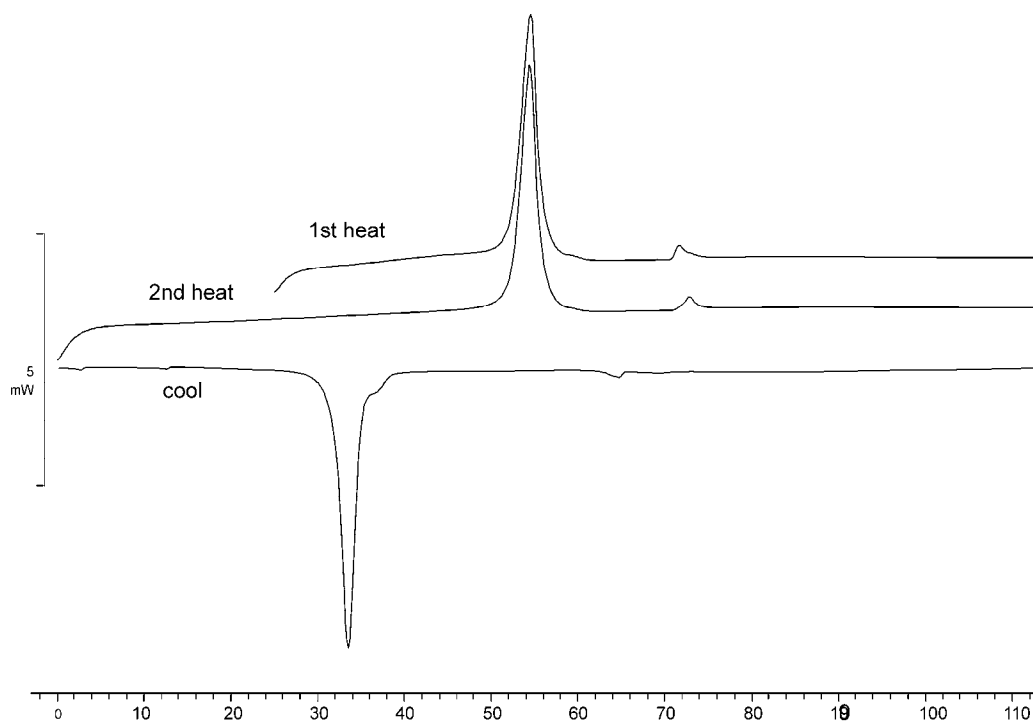


Figure S 1 DSC thermograms of compound 6.

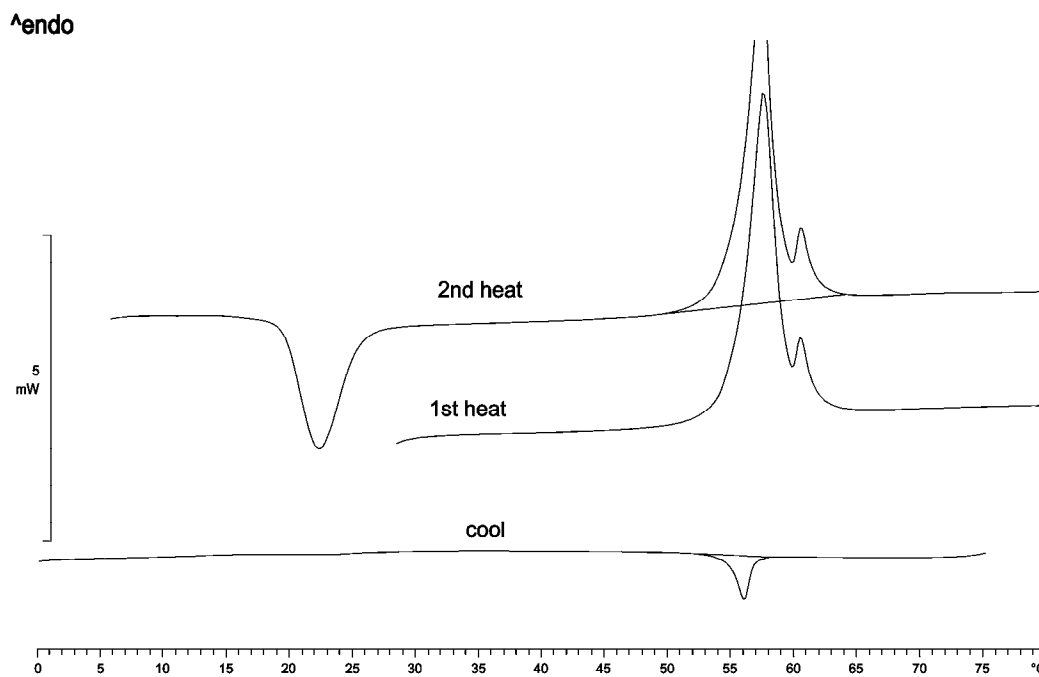


Figure S 2 DSC thermograms of compound 8.

Table S1 Measured and calculated X-ray lattice spacings

Index (hkl)	Compound 6 T = 70 °C, a = 168 Å		Compound 7 T = 100 °C, a = 181 Å	
	Experimental	Calculated	Experimental	Calculated
	(Å)	(Å)	(Å)	(Å)
(310)	53.0	53.1	56.6	57.1
(222)	48.3	48.5	51.9	52.1
(321)	44.9	44.9	48.2	48.2
(400)	41.9	42.0	45.2	45.1
(411)	39.5	39.6	42.7	42.5
(330)				
(420)	37.5	37.6	40.4	40.4
(422)	34.3	34.3	-	-
(431)	33.0	32.9	35.5	35.4
(510)				

Principle of electron density map reconstruction

The electron density of a liquid crystal in the unit cell $\rho(x,y,z)$ is related to the structure factor $F(hkl)$ by Fourier transformation:

$$\rho(x, y, z) = \frac{1}{V} \sum_{hkl} F(hkl) \exp[-2\pi i(hx + ky + lz)]$$

$F(hkl)$ is in turn related to the intensity of the (hkl) reflection $I(hkl)$ as

$$I(hkl) = \text{const.} \times |F(hkl)|^2$$

Thus the electron density $\rho(x,y,z)$ can be reconstructed from the intensities of x-ray reflections $I(hkl)$ using the general formula:

$$\rho(x, y, z) = \frac{1}{\text{const.}} \sum_{hkl} \sqrt{I(hkl)} \exp[-2\pi i(hx + ky + lz) + i\phi_{hkl}]$$

Here ϕ_{hkl} is the phase angle of the structure factor $F(hkl)$.

The diffraction intensities of the current phase, measured from the powder diffraction pattern of compounds **6** and **9** are provided in Table 2 of the main text.

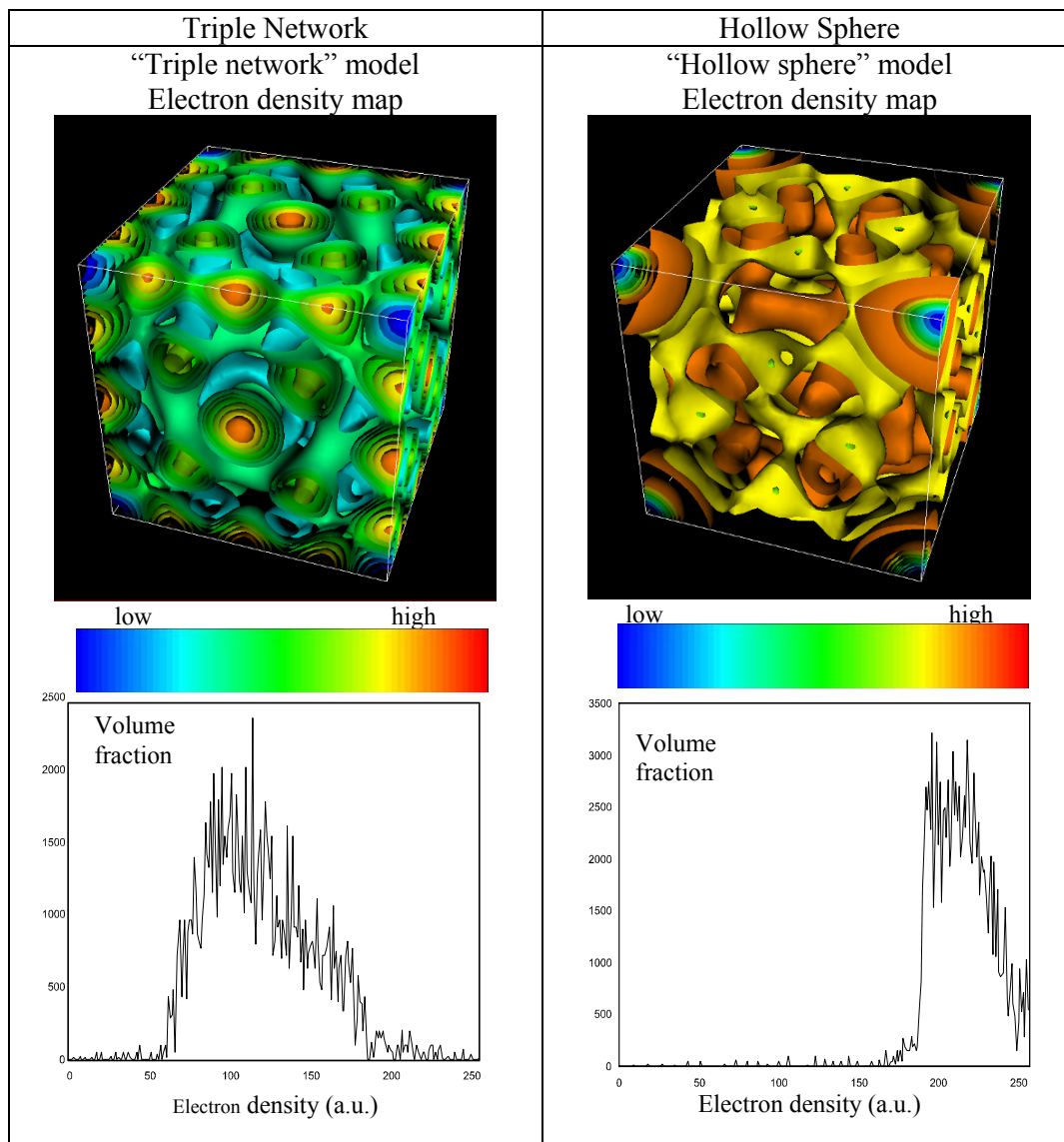


Figure S3. Comparison of reconstructed electron density maps for phase combinations which give rise to triple network (left column) and hollow sphere (right column) models. Multiple isosurfaces at regular intervals were used to visualise the distribution of high and low density regions in the two maps. Distribution of volume over electron density levels is shown below in the form of histogram for each phase combination. The histogram on the left shows a hint of the expected double maximum, the larger lower-density one and the smaller higher density shoulder, associated, respectively, with the aliphatic and aromatic regions. The histogram of the right has a long thin low-density tail corresponding to the unexplainable deep density minima at the corners and in the body centre of the unit cell. Note that the electron density scale is in arbitrary units and the scales in two maps are not normalized relative to each other.

Calculation of the number of molecules in the cross-section of a cylinder

a) Hexagonal columnar phase

Compound **8**: recorded at 58°C, parameter of the 2-d hexagonal unit cell $a = 45 \text{ \AA}$,
unit cell area: $1.754 \times 10^3 \text{ \AA}^2$; 1 column per unit cell.

Molecular weight 1264.03.

Volume of a 4.5 Å thick slice: $7.891 \times 10^3 \text{ \AA}^3$

Molecules per slice: $7891 \times 6.02 / 1264.03 / 10 = 3.8$

b) Cubic $\text{Im}\bar{3}\text{m}$ (I) phase

Compound **6**:

$a = 168.0 \text{ \AA}$ (70 °C), unit cell volume: $4.742 \times 10^6 \text{ \AA}^3$.

molecular weight 1115.67.

Molecules in the unit cell: $4.742 \times 10^6 \times 6.02 / 1115.67 / 10 = 2559$

Compound **7**:

Unit cell parameter $a = 180.3 \text{ \AA}$, unit cell volume: $5.861 \times 10^6 \text{ \AA}^3$.

molecular weight 1149.75

Molecules in the unit cell: $5.861 \times 10^6 \times 6.02 / 1149.75 / 10 = 3069$

Length of outer and inner (“octahedral”) networks each, according to the model:

$a/2 * 3 + a/2/\text{sqrt}(2) * 12 = 5.74 a$

For compound **6**: $5.74 \times 168 = 964 \text{ \AA}$

For compound **7**: $5.74 \times 180 = 1034 \text{ \AA}$

Length of middle network:

$0.183 a * 72 = 13.176 a$

For compound **7**: $13.176 \times 180 = 2371 \text{ \AA}$

For compound **6**: $13.176 \times 168 = 2214 \text{ \AA}$

Combined length of all networks: compound **6**: 4142 Å; compound **7**: 4439 Å.

Average number of molecules per 4.5Å slice of a network segment:

Compound **6**: $4142/4.5 = 920$ layers, each has $2559 / 920 = 2.8$ molecules

Compound **7**: $4439/4.5 = 986$ layers, each has $3069 / 986 = 3.1$ molecules