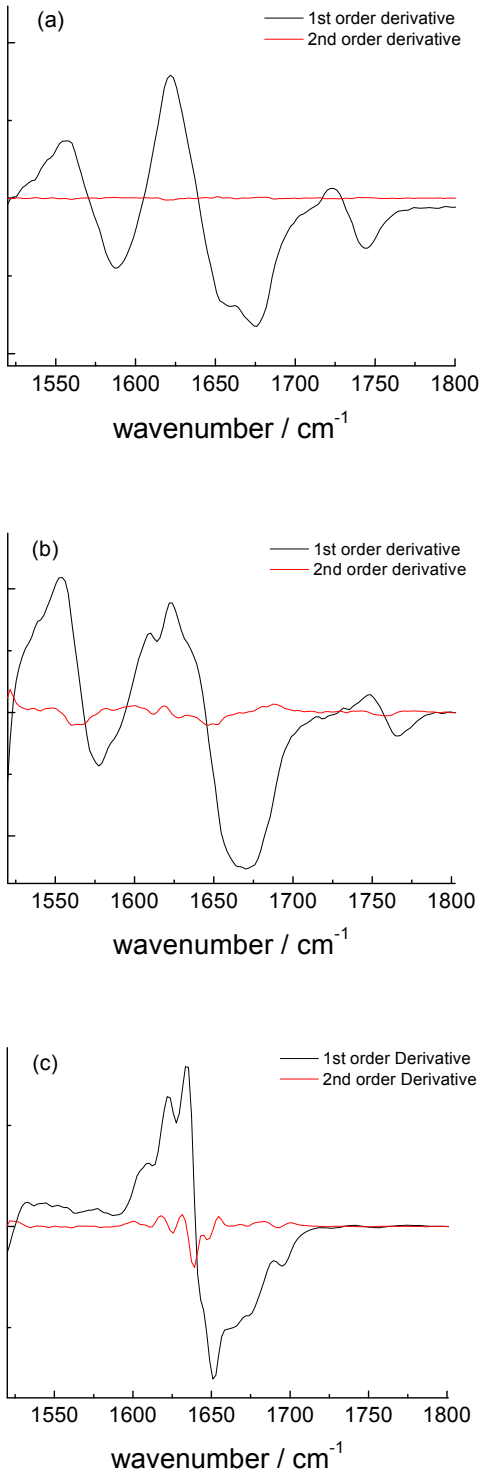
Electronic Supplementary Material (ESI) for Soft Matter

Supporting Information

Self-Assembly of Three Bacterially-Derived Bioactive Lipopeptides

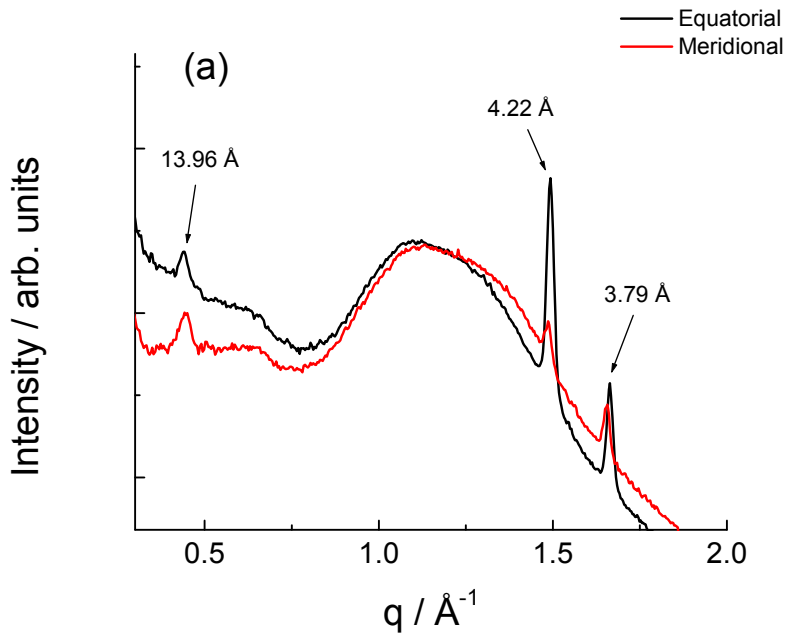
Ian W. Hamley,* Ashkan Dehsorkhi, Paula Jauregi, Jani Seitsonen, Janne Ruokolainen, François Coutte, Gabrielle Chataigné, Philippe Jacques

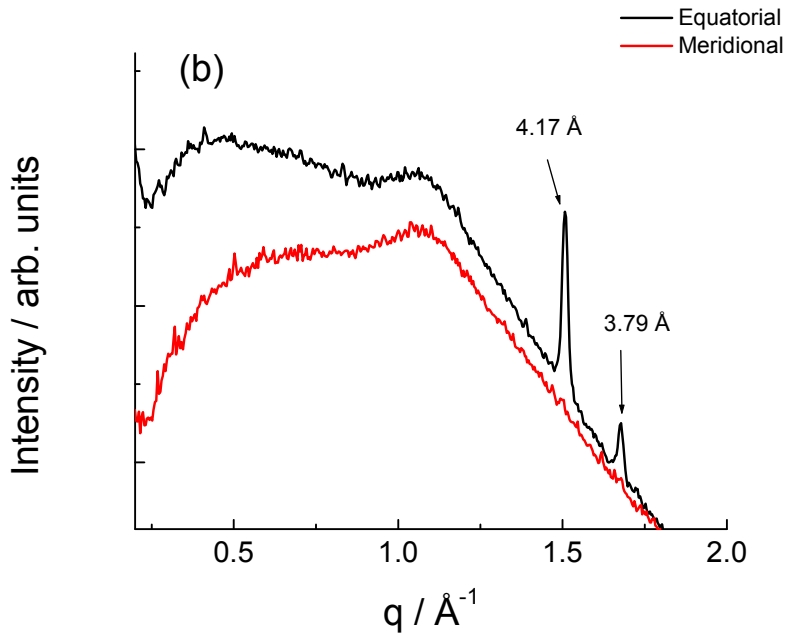
FTIR Derivative Spectra

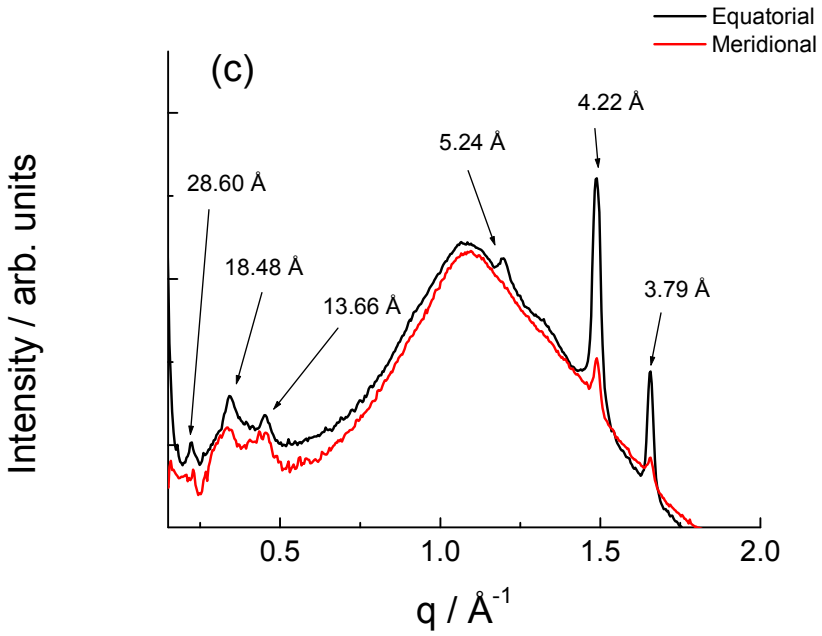


SI Fig.1. Derivative FTIR spectra corresponding to the data in Fig.1 for (a) Surfactin, (b) Plipastatin and (c) Mycosubtilin.

X-ray Diffraction Profiles





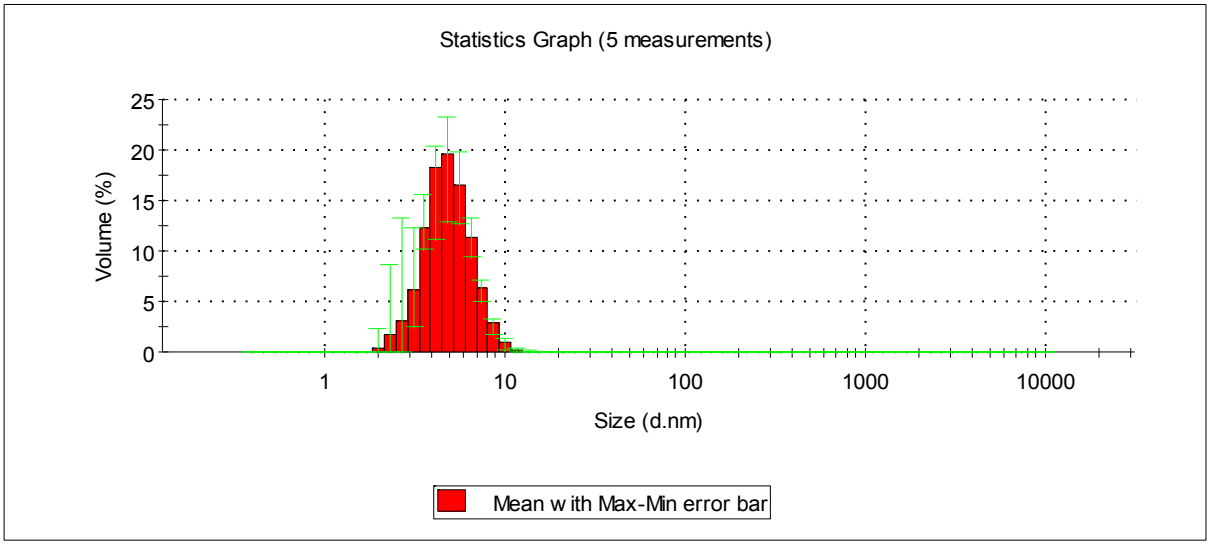


SI Fig.2. XRD profiles obtained by sector integration of the patterns in Fig.5. (a) Surfactin, (b) Plipastatin, (d) Mycosubtilin.

Pictures of Samples

SI Fig.3. Images of 1 wt% samples from L to R: surfactin, mycosubtilin and plipastatin.

Dynamic Light Scattering Results



SI Fig.4. Size distribution obtained from dynamic light scattering for plipastatin, 500mg/L in Tris buffer 50 mM pH 8.5.

Details of SAXS models

The SAXS data was modelled using the software SASfit.[1]

(i) For spherical micelles, model "spherical shell i" with Gaussian polydispersity in radius. This implementation of a spherical shell is parametrised with an outer radius R and an inner radius R_{in}. The scattering contrast relative to the matrix of the core is $\mu\Delta\eta$ and the one of the shell $\Delta\eta$:

$$I(q) = (K(q,R,\Delta\eta) - K(q,R_{in},\Delta\eta(1-\mu)))^2 , \quad (1)$$

with

$$K(q,R,\Delta\eta) = \frac{4}{3}\pi r^3 \Delta\eta .3\frac{\sin qR - qR\cos qR}{(qR)^3} . \quad (2)$$

For surfactin, the fitted parameters were: Gaussian height N = 0.31, width σ = 0.53, R=2.02, R_{in} =0.97, μ =-2.97, $\Delta\eta$ = 0.93, constant background BG=9.8. Length parameters are in nm, contrast terms are in arbitrary units.

For plipastatin, the fitted parameters were: Gaussian height N = 0.77, width σ = 0.55, R=2.04, R_{in} =1.41 , μ =-0.74, $\Delta\eta$ = 1.04, constant background BG=8. Length parameters are in nm, contrast terms are in arbitrary units.

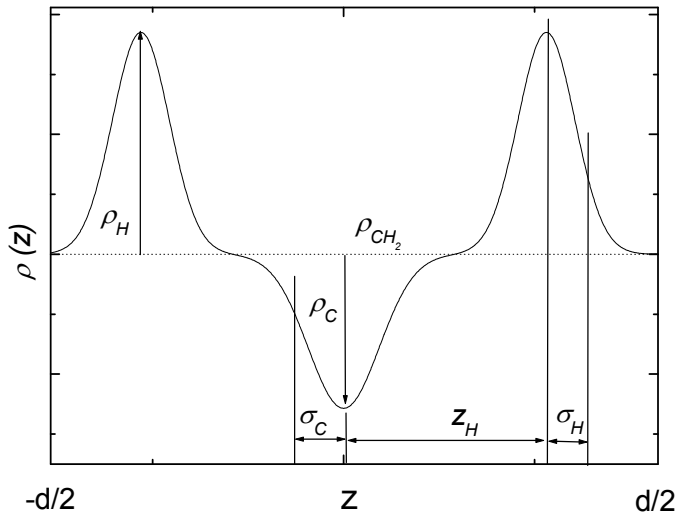
For plipastatin, the fitted parameters were Gaussian height N = 1, width σ = 0.24, R=2.79, ν =0.61, μ =-0.81, $\Delta\eta$ = 0.053, constant background BG=0.05

(ii) For tape structures, the SAXS data shows structure factor peaks from a bilayer. A model comprising a bilayer Gaussian form factor (used to represent the scattering from lipid bilayers) was combined with a Caillé structure factor for a lamellar system: The SAXS intensity from a finite stack of unoriented bilayers can formally be written, within the monodisperse approximation, as:

$$I(q) \propto \left\langle F^2(q) S(q) \right\rangle \tag{3}$$

where $F^2(q)$ is form factor, and $S(q)$ is the interference or structure factor, which tends to unity for weakly interacting systems.

The electron density profile of the form factor is shown in SI Scheme 1.



SI Scheme 1. Gaussian model of the electron density profile used to describe *F(q)* in Equation 3.

The form factor was modelled as for a lipid bilayer, based on a sum of Gaussian functions to represent the electron density profile. The details of the model are given elsewhere.[2] The model assumes an electron density profile comprising Gaussians for the headgroups on either side of the bilayer and another Gaussian for the hydrocarbon chain. SI Scheme 1 shows a scheme of the electron density distribution along the lamellar normal and illustrates the parameters in the model. The total form factor, is taken as the contributions from the headgroup $F_H(q)$ and the hydrocarbon chain $F_c(q)$:

$$F(q) = 2F_H(q) + F_C(q) \tag{4}$$

where

$$F_H(q) = \sqrt{2\pi}\sigma_H\rho_H \exp(-\frac{\sigma_H^2 q^2}{2})\cos(qz_H) \tag{5}$$

and

$$F_C(q) = \sqrt{2\pi}\sigma_C\rho_C \exp(-\frac{\sigma_C^2 q^2}{2}). \tag{6}$$

The fitting parameters of the model in Equations 5 and 6 are the electron densities of the headgroup (ρ_H), the thickness z_H, the electron density of the hydrocarbon chains (ρ_C), the standard deviation of the position of the Gaussian peak z_H (σ_H) and the standard deviation of the position of the Gaussian peak at z_C (σ_C) (Scheme 1). The midpoint of the bilayer is defined as z = 0. In our model we assumed a Gaussian

distribution of inter-headgroup thicknesses z_H, with an associated degree of polydispersity Δ_H.

To model the structure factor, *S(q)* in Equation 3, we used the modified Caillé theory appropriate for lamellar systems.[3] It corresponds to a multilayer structure influenced by thermal fluctuations. Details of the model are given elsewhere.[2, 4] Briefly, *S(q)* is described by

$$S(q) = N_{diff} + \sum_{N_k=N-2\sigma}^{N+2\sigma} x_K S_K \quad , \tag{7}$$

where N is the total number of layers within a scattering domain and N_{diff} accounts for a diffuse background, due to a number of uncorrelated bilayers in *S(q)*, x_k is the weight of the structure factor S_k,[4] and S_k is given by[3]:

$$S_K = N_K + 2\sum_{m=1}^{N_K-1} (N_K - m)\cos(mqd)e^{-\left(\frac{2}{2\pi}\right)^2 q^2\eta\gamma}(\pi m)^{-\left(\frac{\omega}{2\pi}\right)^2 q^2\eta} \tag{8}$$

γ is the Euler constant in Equation 6, d is the layer spacing, and

$$\eta = \pi k_B T / 2d^2 (BK_c)^{1/2} \tag{9}$$

is the Caillé parameter which is a measure for the bilayer fluctuations and depends on the bilayer rigidity K_c and the bulk modulus of compression B.

The fitting parameters in Equations 7-9 are N, d, η and N_{diff}.

For mycosubtilin, fitting the data required addition of terms corresponding to two tape thicknesses: a thicker multi-layer stack to account for the structure factor peak (with associated form factor) and a second term for a single bilayer (with no associated structure factor):

$$I(q) = w_1 F_1^2(q) + w_2 F_2^2(q) S_2(q) . \qquad (10)$$

Here w_1 and w_2 are weighting factors. The terms in $F_1(q)$, $F_2(q)$, $S_2(q)$ are defined in Equations (4) – (9).

The fit parameters were as follows (lengths in nm, contrast terms in arbitrary units):
For the first term, w_1 = 6.22, $t = 2z_H$ = 9.09 with Gaussian polydispersity σ = 0.31, ρ_H = 0.0024 , σ_H = 0.319, ρ_c = 0.00094, σ_C = 0.67, D = 300 (fixed) and for the structure factor N=12, d = 5.4, η = 0.0005 and N_{diff} = 200.

For the second term, w_2 = 6.22, $t = 2z_H$ = 4.00 with Gaussian polydispersity σ = 0.62, ρ_H = 0.144 , σ_H = 0.139, ρ_c = 0.00015, σ_C = 1.87, D = 300 (fixed)

References

1. http://Kur.Web.Psi.Ch/Sans1/Sanssoft/Sasfit.Html. In 2013.
2. Pabst, G.; Rappolt, M.; Amenitsch, H.; Laggner, P., Structural Information from Multilamellar Liposomes at Full Hydration: Full Q-Range Fitting with High Quality X-Ray Data. *Phys. Rev. E* **2000,** 62, 4000.
3. Caillé, A., X-Ray Scattering by Smectic-a Crystals. *C.R. Hebd. Seances Acad. Sci. (Paris) B* **1972,** 274, 891.
4. Zhang, R. T.; Suter, R. M.; Nagle, J. F., Theory of the Structure Factor of Lipid Bilayers. *Phys. Rev. E* **1994,** 50, 5047.