Electronic Supplementary Material (ESI) for Soft Matter.

Supporting Information

Structural Behaviour and Gene Delivery in Complexes Formed Between DNA and Arginine-Containing Peptide Amphiphiles

Emerson R. da Silva[a,b]*, Gary Cooney[c], Ian W. Hamley[d], Wendel A. Alves[a], Shannon Lee[c], Brendan F. O'Connor[c], Mehedi Reza[e], Janne Ruokolainen[e] and Dermot Walls[c]

[a]*Centro de Ciências Naturais e Humanas, Universidade Federal do ABC, Santo André-SP, 09210-580, Brazil*
[b]*Instituto de Física, Universidade Federal de Alagoas, Maceió-AL, 57072-900, Brazil*
[c]*School of Biotechnology and National Centre for Sensor Research, Dublin City University, Dublin 9, Ireland*
[d]*Department of Chemistry, University of Reading,Whiteknights, RG6 6AD, United Kingdom*
[e]*Department of Applied Physics, Aalto University School of Science, P.O. Box 15100, FI-00076, Finland*

SAXS MODELING:

SAXS curves from single-phase formulations – i.e., containing only DNA or peptides – have been fitted using models available on the library of SASFit program.[1] Data from RFL_4FR nanostructures have been described according to the Gaussian bilayer form factor proposed by Pabst et al.[2] plus a flat background:

$$I_{bil}(q) = \frac{N_{bil}}{q^2} \times \left[\sqrt{2\pi}\,\sigma_{core}\, b_{core} \exp\left(-q\frac{t^2 \sigma_{core}^{\,2}}{2} \right) + 2\sqrt{2\pi}\,\sigma_{out}\, b_{out} \exp\left(-\frac{q^{2\sigma_{out}^{\,2}}}{2} \right) cos \right.$$

The model consists in the summation of three Gaussian functions: one to describe the hydrophobic core of the bilayer and other two Gaussians to account for polar heads at both sides of the membrane. In the case of the current work, where one

has bolaamphiphile monolayers, the system is equivalent to bilayers made up from single-headed amphiphiles – i.e., a hydrophobic central core flanked by two polar heads. In this case, the effective cross-section thickness of the sheets has been considered to be as the sum of head-to-head distance plus the full width at half maximum of Gaussian describing the polar regions:

$$d_B = t + 2\sigma_{out}\sqrt{2ln2} \qquad (Eq\ S3)$$

Scattering profiles either from DNA chains or from rod-like lipopeptide micelles have been properly fitted using a cylinder shell form factor given by:[3]

$$I_{tubes}(q) = Bkg + \left[\frac{2Si(qL)}{qL} - \left(\frac{\sin\left(\frac{qL}{2}\right)}{\frac{qL}{2}}\right)\right]$$

$$\times \left(\frac{2J_1(qR)}{qR}(\eta_{core} - \eta_{shell})R^2L\pi + \frac{2J_1(q(R+\Delta R))}{q(R+\Delta R)}(\eta_{shell} - \eta_{solv})(R + \Delta R)^2L\pi\right)^2 \quad (Eq.S2)$$

The resulting fitting parameters were as it follows:

Gaussian bilayer form factor								
Sample	**N_{bil}**	**σ_{out} (nm)**	**bout**	**σ_{core} (nm)**	**b_{core}**	***T* (nm)**	**d_B (nm)**	**Bkg**
RFL_4FR	3.3×10^{-13}	0.38	1.83	1.35	0.17	2.1	2.99	0.79

Cylinder shell form factor								
Sample	**N_{cyl}**	**R (nm)**	**ΔR (nm)**	**L (nm)**	**η_{core}**	**η_{shell}**	**η_{solv}**	**Bkg**
DNA rods	1.4×10^{-4}	0.98	0.40	51.9	-7.1	-2.4	0	0.43
Plasmid	8.1×10^{-4}	1.1	0.47	145	-4.8	-1.5	0	0.47
PRW-C16	7.6×10^{-10}	1.33	1.61	187.4	-1.30	0.99	0	0.002

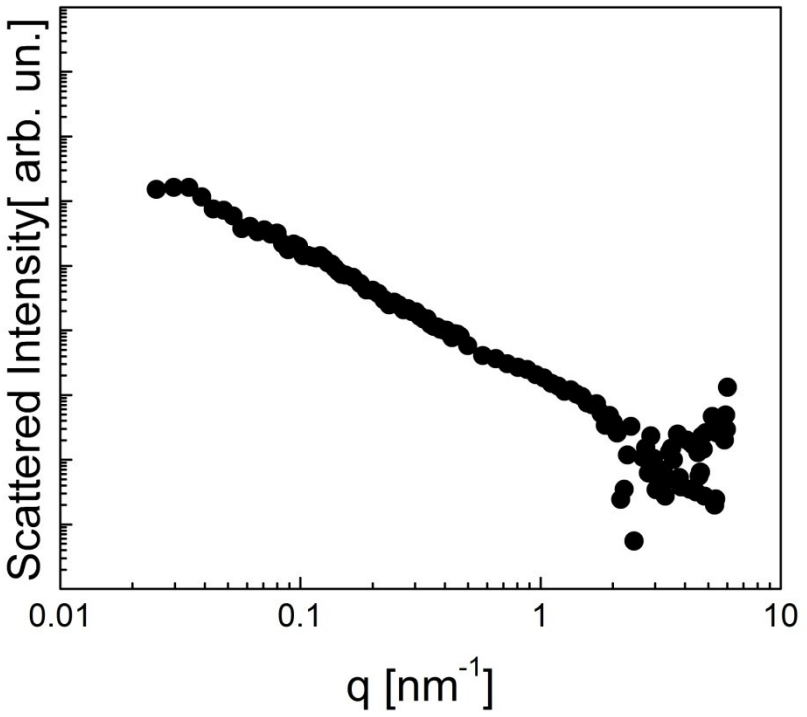

Figure S1: Small-angle neutron scattering data from DNA fragments dissolved into D_2O at 6 mg/ml.

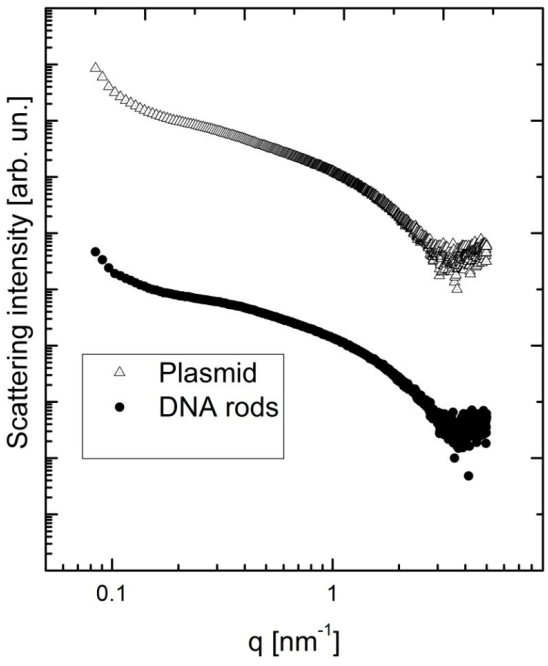

Figure S2: SAXS profiles from solutions containing plasmid DNA (open symbols) and sonicated calf-thymus DNA fragments. Scattering is quite similar indicating small variations at e same local structure.

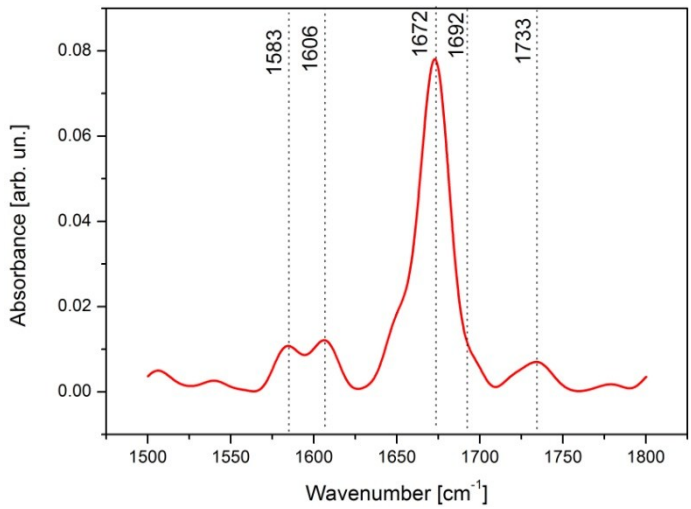

Figure S3: FTIR spectra from solution containing PRW-C_{16} at 10 mg/ml concentration into D_2O. The presence of a strong peak at 1672 cm^{-1} is indicative of TFA counterions, whereas β-sheet formation between tripeptide headgroups could be tentatively assigned to the small shoulder at 1692 cm^{-1}.

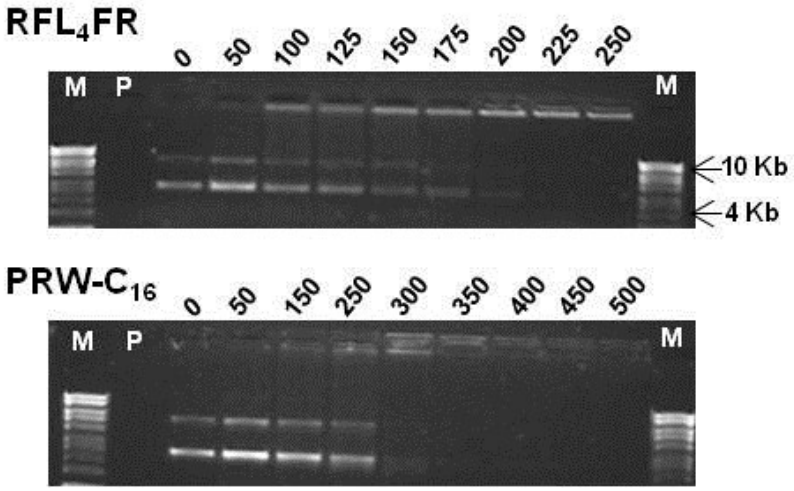

Figure S4: RF_4FR and PRW-C_{16} can form complexes with plasmid DNA. Complex formation between pEGFP-N1 (100 ng) and various peptides was assessed by agarose

gel electrophoresis. The names and quantities of the peptides used are indicated (in nanograms) above each gel image. Lane P contains the corresponding peptide only (100 ng each). Lanes M show DNA size markers and the location of two bands are shown in kilobase pairs (kb) on the right hand side of the topmost gel.

ADITIONAL REFERENCES:

1. Bressler, I.; Kohlbrecher, J.; Thunemann, A. F., SASfit: a tool for small-angle scattering data analysis using a library of analytical expressions. *Journal of Applied Crystallography* **2015,** 48, (5), 1587-1598.
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 Stat Phys Plasmas Fluids Relat Interdiscip Topics* **2000,** 62, (3 Pt B), 4000-9.
3. Pedersen, J. S., Analysis of small-angle scattering data from colloids and polymer solutions: modeling and least-squares fitting. *Advances in Colloid and Interface Science* **1997,** 70, (0), 171-210.