Electronic Supplementary Information

Interfacial properties of lipid sponge-like nanoparticles and the role of stabilizer on particle structure and surface interactions

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SANS modelling:

The core-shell sphere model is described as follows (from SASView models[1,2]):

$$P(q) = \frac{scale}{V_s}\left[3V_c(\rho_c - \rho_s)\frac{[\sin(qr_c) - qr_c cos(qr_c)]}{(qr_c)^3} + 3V_c(\rho_c - \rho_{solv})\frac{[\sin(qr_s) - qrcos(qr_s)]}{(qr_s)^3}\right]^2 + background$$

where scale is a scale factor, V_s is the volume of the outer shell, V_c is the volume of the core, r_s is the radius of the shell, r_c is the radius of the core, ρ_c is the scattering length density of the core, ρ_s is the scattering length density of the shell and ρ_{solv} is the scattering length density of the solvent.

SANS results: Table S1 shows the estimated solvent fractions and SLD corrected by the solvent values of the core and the shell of L_3-NP, obtained by comparing two isotopic solvent contrasts.

Table S1	dP80			hP80		
Estimated values of	D_2O and H_2O	H_2O and 1:4	D_2O and 1:4	D_2O and H_2O	H_2O and 1:4	D_2O and 1:4
Hydration Core (%)	55.7	55.5	56.3	58.6	58.4	59.6
Hydration Shell (%)	90.7	90.8	90.2	89.5	89.5	89.5
SLD Core ($Å^{-2}$) 10^{-6} lipid/P80 mixture	1.04	1.03	0.97	0.32	0.31	0.18
SLD Shell ($Å^{-2}$) 10^{-6} lipid/P80 mixture	3.38	3.43	3.53	0.58	0.58	0.57

$$SLD_{core-Fitting1} = SLD_{core}\cdot(1-x) + SlD_{solvent1}\cdot x \rightarrow SLD_{core} = \frac{SLD_{core-Fitting1} - SlD_{solvent1}\cdot x}{(1-x)} \quad (1)$$

$$SLD_{core-Fitting2} = SLD_{core}\cdot(1-x) + SlD_{solvent2}\cdot x \rightarrow SLD_{core} = \frac{SLD_{core-Fitting2} - SlD_{solvent2}\cdot x}{(1-x)} \quad (2)$$

If we assume that SLD_{core} and volume fraction of the solvent (x) is equal for both solvent contrast (1 and 2):

$$x = \frac{SLD_{core-Fitting1} - SLD_{core-Fitting2}}{SlD_{solvent1} - SlD_{solvent2}}$$

QCM-D theory

Voigt viscoelastic model:[3]

This model takes into account the effects of coupled water or solvent used and the adsorbed film is represented by a complex shear modulus according to:

$$G = G' + iG'' = \mu_f + i2\pi f\eta_f = \mu_f\left(1 + i2\pi f\tau_f\right)$$

where μ_f is the elastic shear modulus, η_f the shear viscosity, f the oscillation frequency, and τ_f the characteristic relaxation time of the film. The frequency and dissipation changes are then correlated to the viscoelastic properties of the film as

$$\Delta f = \frac{Im(\beta)}{2\pi t_q \rho_q}$$

and

$$\Delta D = -\frac{Re(\beta)}{\pi f t_q \rho_q}$$

where β relies on the thickness (t) and density (ρ = 0.984 g·cm^{-3}) of the film, and on the bulk-liquid density (0.997 g·cm^{-3}) and viscosity (0.9 mPa·s).

β expression for QCM-D data analysis:

$$\beta = \xi_1 \frac{2\pi f\eta_f - i\mu_f}{2\pi f} \frac{1 - \alpha\exp\left(2\xi_1 d_f\right)}{1 + \alpha\exp\left(2\xi_1 d_f\right)},$$

$$\alpha = \frac{\frac{\xi_1}{\xi_2}\frac{2\pi f\eta_f - i\mu_f}{2\pi f\eta_l} + 1}{\frac{\xi_1}{\xi_2}\frac{2\pi f\eta_f - i\mu_f}{2\pi f\eta_l} - 1},$$

$$\xi_1 = \sqrt{-\frac{(2\pi f)^2\rho_f}{\mu_f - i2\pi\eta_f}}, \xi_2 = \sqrt{\frac{2\pi f\rho_l}{\eta_l}}$$

where f is the oscillation frequency, η is the shear viscosity,μ is the elastic shear modulus and ρ the density.

QCM results

QCM fitting: Figure S1 depicts the viscosity and shear values obtained from fitting the QCM-D data in Figure 3 to the Voigt viscoelastic model.

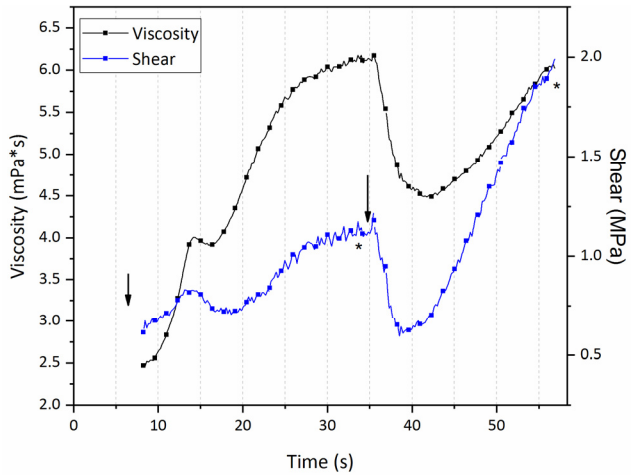

Figure S1. Viscosity and shear values obtained from the Voigt viscoelastic model fit. Arrows indicate addition of L_3-NPs and rinsing processes.

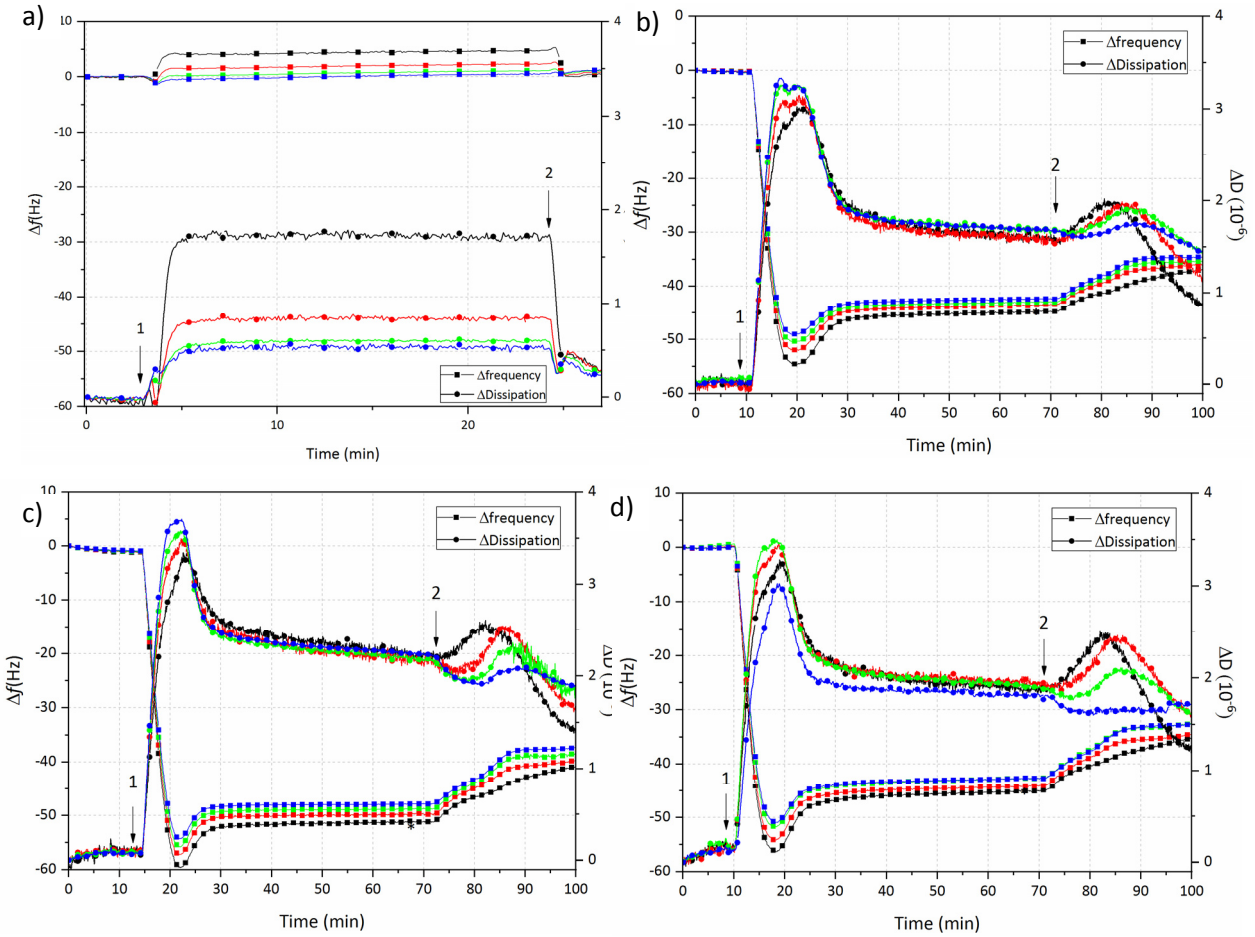

Figure S2. Adsoprtion of 0.1mg/ml of L_3-NPs on bare hydrophilic silica a) In water with no salt, b) 10mM citrate buffer pH=4 and no salt, c) 10mM citrate buffer pH=5.5 and no salt and d) 10mM citrate buffer pH=5.5 and 150mM NaCl. Number 1 and 2 indicate injection of sample and rinsing with corresponding solvent, respectively. Asterisk display when the pump was stopped. Experimental is depicted for four different overtones.

Neutron reflectometry results: 5-layer model

Neutron reflectometry data was also fitted using a 5-layer model (Figure S3 and Table S2). This model consists of the same 4-layers described on the paper with the addition of a solvent layer between the silica surface and the lipid film. As a result of adding this extra layer, the head group thickness is reduced and it is closer to the head group size expected for DGMO and GMO-50 rather than the one from P80. In addition, the head group layer became much less hydrated. This can be explained because some of the solvent in the head group layer from the 4-layer model is now found in the solvent layer and hence, the head group hydration is diminished. It can be noticed that the SLD value of the head group is lower, while the SLD value of the hydrocarbon tail is higher than the 4-layer model. The resulting reflectivity curve could be averaging these two values and that is why one compensates the other. It should be although noted that the highly hydrated head group film in the 4-layer model makes this layer very little sensible to changes in head group SLD. The rest of the parameters are quite similar to the ones obtained with the 4-layer model and the total adsorbed mass was calculated to be very close as well (340 ng/cm^2). Therefore, most of the discussion regarding the 4-layer model can be also applied here, although the χ^2 values very slightly better for the other model.

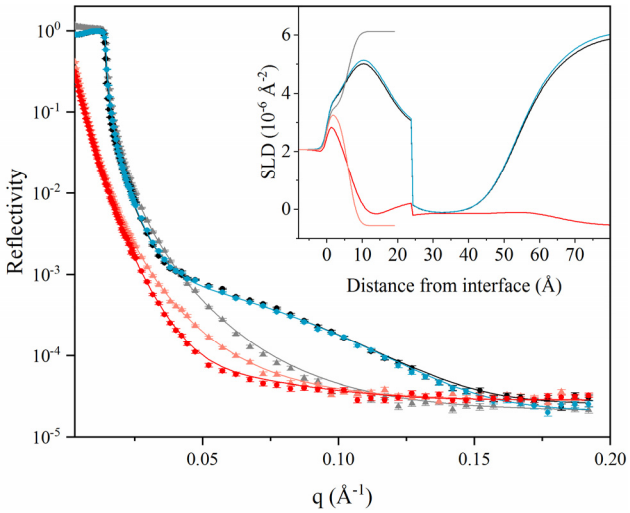

Figure S3. Neutron reflectivity curves as a function of momentum transfer (q) before addition of L_3-NPs (grey for D_2O and light red for H_2O), after adsoprtion of L_3 NPs in deuterated buffer (black) and after rinsing with deuterated (blue) and protonated water (red). Experimental and fitted data are depicted as dots and solic line respectively. Embedded plot show the scattering length density (SLD) values as a function of distance from the interface obtained from the fitting.

Table S2. Parameters used to fit the neutron reflectometry data displayed on Figure S3 with a 5-layer model.

	Thickness (Å)	SLD (10^{-6} Å^{-2})	Solvent (vol%)	Roughness (Å)
1.SiO_2	6 ± 1	3.41	1.4 ± 4.5	0.9 ± 3.2
2.Solvent layer	9.7 ± 2.7	same as solvent	100	3.9 ± 3.1
3.Lipid head	8.3 ± 3.3	0.8 ± 0.3	38 ± 10	6.2 ± 2
4.Lipid tail	28.1 ± 3.4	-0.13 ± 0.09	0.004 ± 4	0.06 ± 5
5.Lipid head	8.3 ± 3.3	0.8 ± 0.3	38 ± 10	6.2 ± 2

References

1 SasView, https://www.sasview.org/, (accessed July 2018).

2 A. Guinier and G. Fournet, Small-angle scattering of X-rays, John Wiley and Sons, New York, 1955.

3 F. Höök, B. Kasemo, T. Nylander, C. Fant, K. Sott and H. Elwing, Anal. Chem., 2001, 73, 5796–5804.