On the Formation of Dendrimer/Nucleolipids Surface Films for Directed Self-Assembly

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Electronic Supplementary information

1. *Expression for β in the modelling of the QCM-D data using the Voigt model:*[1]

$$\beta = \xi_1 \frac{2\pi f \eta_{film} - i\mu_{film}}{2\pi f} \frac{1-\alpha\exp\left(2\xi_1 d_{film}\right)}{1+\alpha\exp\left(2\xi_1 d_{film}\right)} \quad (1)$$

$$\alpha = \frac{\frac{\xi_1}{\xi_2}\frac{2\pi f \eta_{film} - i\mu_{film}}{2\pi f \eta_{liquid}} + 1}{\frac{\xi_1}{\xi_2}\frac{2\pi f \eta_{film} - i\mu_{film}}{2\pi f \eta_{liquid}} - 1} \quad (2)$$

$$\xi_1 = \sqrt{-\frac{(2\pi f)^2 \rho_{film}}{\mu_{film} + i2\pi\eta_{film}}} \quad (3)$$

$$\xi_2 = \sqrt{i\frac{2\pi f \rho_{liquid}}{\eta_{liquid}}} \quad (4)$$

where f represents the fundamental frequency, η the viscosity, μ the elastic modulus and ρ the density.

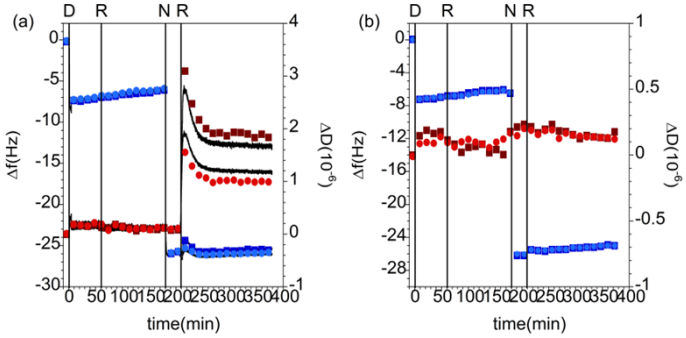
2. *Characterization of the SiO_2 layer from the NR experiments*

SI Table 1. Parameters obtained from the modeling of the NR profiles of the bare silica layer.

d (Å)	δ_1 (Å)	δ_2 (Å)	$v_{solvent}$ ± 0.03	Experiment
12.5 ± 0.5	3.9 ± 0.9	4.5 ± 0.5	0.37	Addition of hDLPA to pre-adsorbed PAMAM
8.9 ± 0.3	2.3 ± 0.9	2.4 ± 0.5	0.15	Addition of hDLPU to pre-adsorbed PAMAM
6.2 ± 0.5	1 ± 1	2 ± 1	0.21	Addition of dDLPA to pre-adsorbed PAMAM
8.8 ± 0.5	1 ± 1	3 ± 1	0.31	Addition of dDLPU to pre-adsorbed PAMAM
8.2 ± 0.5	2.7 ± 0.9	2.8 ± 0.7	0.24	Addition of hDLPA to pre-adsorbed PAMAM in 10 mM Tris-HCl buffer.
11.0 ± 0.6	1 ± 1	4.3 ± 0.8	0.38	Adsorption of PAMAM/hDLPA mixture in 10 mM Tris-HCl buffer
6.6 ± 0.3	2.1 ± 0.5	1 ± 1	0.26	Adsorption of PAMAM/hDLPU mixture
5.0 ± 0.4	1.0 ± 0.9	1 ± 1	0.29	Adsorption of PAMAM/dDLPU mixture
9.3 ± 0.4	3.6 ± 0.5	3.8 ± 0.6	0.33	Addition of PolyU to PAMAM/hDLPA layers

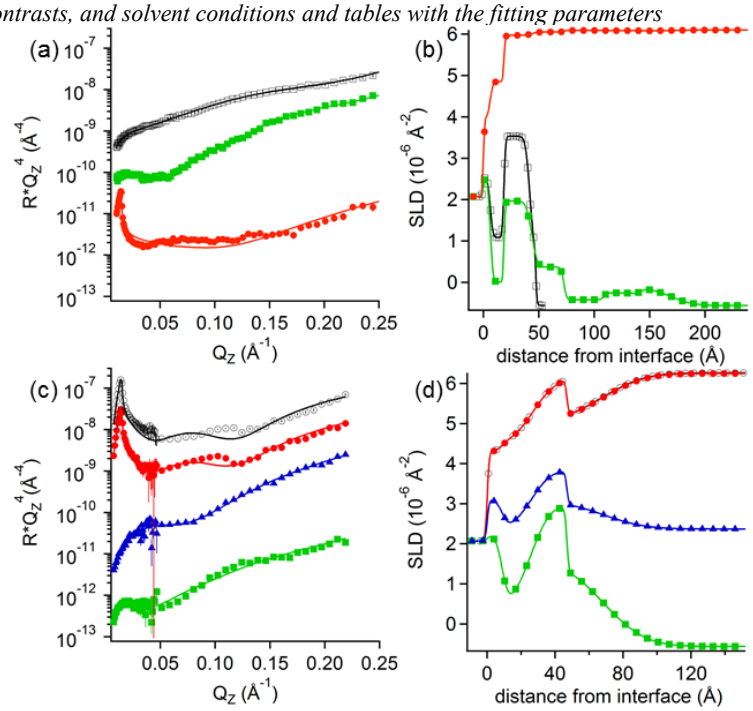
d represents the thickness of the SiO_2 layer, δ_1 the roughness between the silica layer and the silicon crystal, δ_2 the roughness between the layer and the bulk and $v_{solvent}$ the volume fraction of solvent. The measurements were done in 10 mM NaCl unless otherwise stated.

3. *QCM-D data from the interactions of DLPNs with preadsorbed layers of PAMAM in 10 mM Tris-HCl pH 7.6 buffer*



SI Figure 1. Changes of frequency (Δf, closed symbols) and dissipation (ΔD, open symbols) as a function of time for the adsorption of (a) PAMAM/DLPA and (b) PAMAM/DLPU mixtures on silica. The mixtures had a bulk composition of 50 ppm PAMAM-G4 with 0.1 mM DLPN (squares and circles) and 0.5 mM DLPN (diamonds and triangles) in 10 mM Tris-HCl pH 7.6 buffer. The data correspond to the overtones 3 (squares and diamonds) and 5 (circles and triangles). The vertical lines correspond to: (i) injection of dendrimer (D), (ii) rinsing with solvent (R), (iii) injection of nucleolipid (N) and (iv) final rinse with solvent (R).

4. *Neutron reflectivity profiles with the respective models from the interactions of DLPNs with preadsorbed PAMAM in different contrasts, and solvent conditions and tables with the fitting parameters*



SI Figure 2. (a,c) Neutron reflectivity profiles and (b,d) SLD profiles as a function of the distance from the Si interface for the adsorption of (a,b) dDLPA and (c,d) dDLPU to PAMAM-G4 monolayers on silica. The data correspond to the rinses with D_2O (red circles), cmSi (blue triangles) and H_2O (green squares). The reflectivity before rinsing with pure solvent is also plotted in black open symbols. Note that in (a) the DLPA was injected in H_2O and in (b) the DLPU was injected in D_2O. The concentration of DLPNs was 0.1 mM and the solvent was 10 mM NaCl. The lines correspond to the calculated reflectivity profiles from the fitted model. The data in (a,b) are offset in the y-axis for clarity. The data in (a) are reproduced from previous work.[2] The data in (a) were recorded using INTER and in (b) using MARIA.

SI Table 2. Parameters obtained from the modeling of the NR profiles for the adsorption of dDLPU onto a pre-adsorbed PAMAM-G4 monolayer on silica after rinsing with 10 mM NaCl.

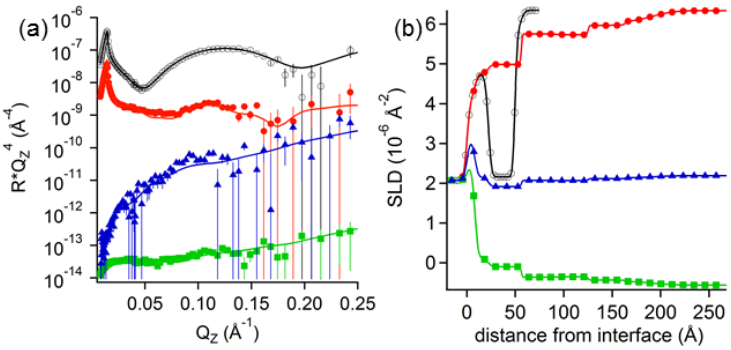
Layer	d_i (Å)	δ (Å)	$v_{\text{PAMAM-G4}}$	$v_{\text{DLPU heads}}$	$v_{\text{DLU tails}}$
2	17.4 ± 0.1	9.8 ± 0.8	0.42 ± 0.01	0.05 ± 0.02	0
3	20.7 ± 0.5	1 ± 1	0	0.11 ± 0.08	0.39 ± 0.06
4	21 ± 1	19.8 ± 0.7	0	0.59 ± 0.03	0

Layer 1 is the SiO_2 layer. d_i represents the thickness of the layer i, δ is the roughness between the layer i and the layer i+1 (or the bulk) and v the volume fraction of the different components. Note that although the volume fraction of the DLPU heads is very high in the last layer, the roughness is high as well and therefore there is a higher uncertainty.

SI Table 3. Parameters obtained from the modeling of the NR profiles for the adsorption of dDLPA onto a pre-adsorbed PAMAM-G4 monolayer on silica after rinsing with 10 mM NaCl.

Layer	d_i (Å)	δ (Å)	$v_{PAMAM-G4}$	$v_{DLPA} \pm 0.01$
2	12.4 ± 0.4	1 ± 4	0.32 ± 0.02	0
3	25.0 ± 0.7	4 ± 2	0	0.42
4	29 ± 1	2 ± 5	0	0.16
5	36 ± 3	2 ± 1	0	0.02
6	34 ± 3	3 ± 1	0	0.05
7	27 ± 3	16 ± 3	0	0.07

The parameters are explained in the footnote of Table S2.



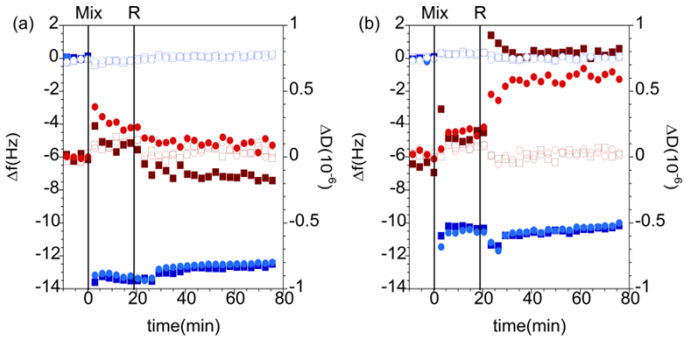
SI Figure 3. (a) Neutron reflectivity profiles and (b) SLD profiles as a function of the distance from the Si interface for the adsorption of hDLPA to PAMAM-G4 monolayers on silica in 10 mM Tris-HCl ph 7.6 buffer. The data corresponds to the rinses with D_2O (red circles), cmSi (blue triangles) and H_2O (green squares). The reflectivity in D_2O before rinsing with pure solvent is also plotted (black open circles). The concentration of DLPA was 0.1 mM. The lines correspond to the calculated reflectivity profiles from the fitted model. The data in (a) are offset in the y-axis for clarity. Data reproduced from previous work.[2] The data were recorded using FIGARO.

SI Table 4. Parameters obtained from the modeling of the NR profiles for the adsorption of hDLPA onto a pre-adsorbed PAMAM-G4 monolayer on silica after rinsing with 10 mM Tris-HCl buffer.

Layer	d_i (Å)	δ (Å) ± 1	$v_{PAMAM-G4}$	$v_{DLPA} \pm 0.01$
2	13.9 ± 0.2	3	0.38 ± 0.01	0
3	34 ± 1	1	0	0.28
4	35 ± 3	4	0	0.12
5	34 ± 3	1	0	0.23
6	38 ± 7	1	0	0.08
7	28 ± 9	18	0	0.06

The parameters are explained in the footnote of Table S2.

5. *QCM-D data from the interactions of premixed PAMAM/DLPN samples with hydrophilic silica in 10 mM Tris-HCl pH 7.6 buffer*



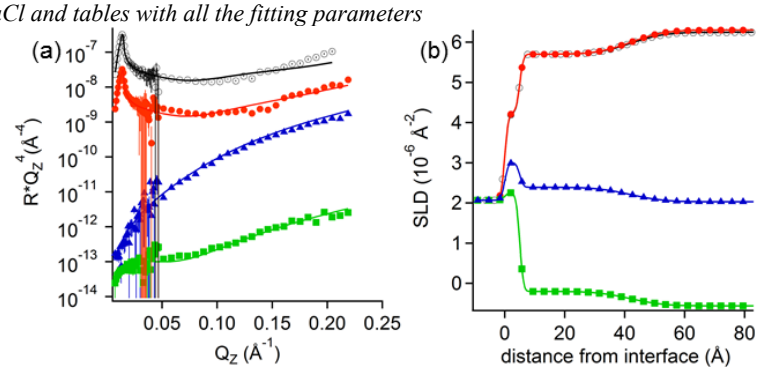
SI Figure 4. Changes of frequency (Δf, blue symbols) and dissipation (ΔD, red symbols) as a function of time for the adsorption of (a) PAMAM-G4/DLPA and (b) PAMAM-G4/DLPU mixtures on silica. The mixtures had a bulk composition of 50 ppm PAMAM-G4 and 0.1 mM DLPN (positively charged complexes, closed symbols) or 0.5 mM DLPN (negatively charged complexes, open symbols). The solvent was 10 mM Tris-HCl pH 7.6 buffer. The data corresponds to the overtones 3 (squares) and 5 (circles). The vertical lines correspond to: (i) injection of dendrimer/nucleolipid mixture (Mix) and (ii) rinsing with solvent (R).

SI Table 6. Interfacial wet mass, Δm, obtained by QCM-D for the interactions of premixed (1) PAMAM-G4/DLPA and (2) PAMAM-G4/DLPU with hydrophilic silica in Tris-HCl buffer. The mixtures had a bulk composition of 50 ppm PAMAM-G4 and 0.1 mM DLPN.[a]

Process	Δm (mg m^{-2})[1]	Δm (mg m^{-2})[2]
PAMAM-G4/DLPN mixture	2.3 ± 0.1	1.8 ± 0.1
Tris-HCl Buffer	2.2 ± 0.1	1.8 ± 0.1

[a] The interfacial wet mass values were calculated using the Sauerbrey equation.

6. *Neutron Reflectivity profiles with the respective models from the adsorption of PAMAM/dDLPU mixtures on silica in 10 mM NaCl and tables with all the fitting parameters*



SI Figure 5. (a) Neutron reflectivity profiles and (b) SLD profiles as a function of the distance from the Si interface for the adsorption of PAMAM/DLPU mixtures on silica with 0.1 mM DLPU. The isotopic contrasts were dDLPN after rinsing with D_2O (red circles), cmSi (blue triangles) and H_2O (green squares) and the data before rinsing in D_2O (black open circles). The solvent was 10 mM NaCl. The lines correspond to the calculated reflectivity profiles from the fitted model. The data in (a) are offset in the y-axis for clarity. Data recorded using MARIA.

SI Table 7. Parameters obtained from the modeling of the NR profiles of the adsorption of a PAMAM/dDLPU mixture with positively charged aggregates onto silica

Layer	d_i (Å)	δ (Å)	$\nu_{PAMAM-G4}$	ν_{DLPA}
2	37 ± 3	9 ± 9	0.13 ± 0.06	0.06 ± 0.03

The parameters are explained in the footnote of Table S2.

References

1. F. Höök, B. Kasemo, T. Nylander, C. Fant, K. Sott and H. Elwing, *Anal. Chem.*, 2001, **73**, 5796-5804.
2. M. Yanez Arteta, D. Berti, C. Montis, R. A. Campbell, L. A. Clifton, M. W. A. Skoda, O. Soltwedel, P. Baglioni and T. Nylander, *Soft Matter*, 2014, **10**, 8401-8405.