Electronic Supplementary Information (ESI) for

Interfacial properties of POPC/GDO liquid crystalline nanoparticles deposited on anionic and cationic silica surfaces

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Dynamic Light Scattering (DLS)

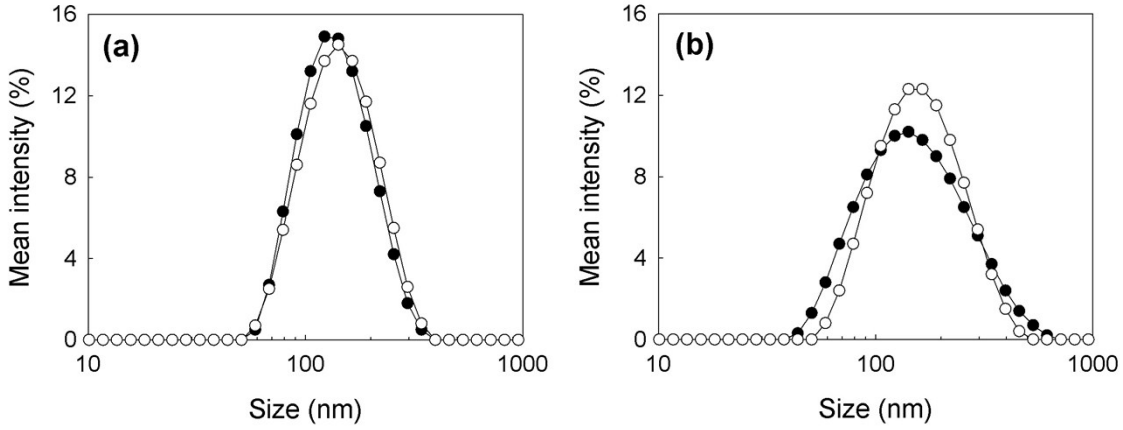

Figure S1. Size distributions of POPC/GDO/P80 LCNPs involving h-POPC (filled symbols) and d-POPC (open symbols) prepared at (a) 42.5/42.5/15 and (b) 40/40/20 compositions by weight, measured using DLS.

Small-Angle X-ray Diffraction (SAXD)

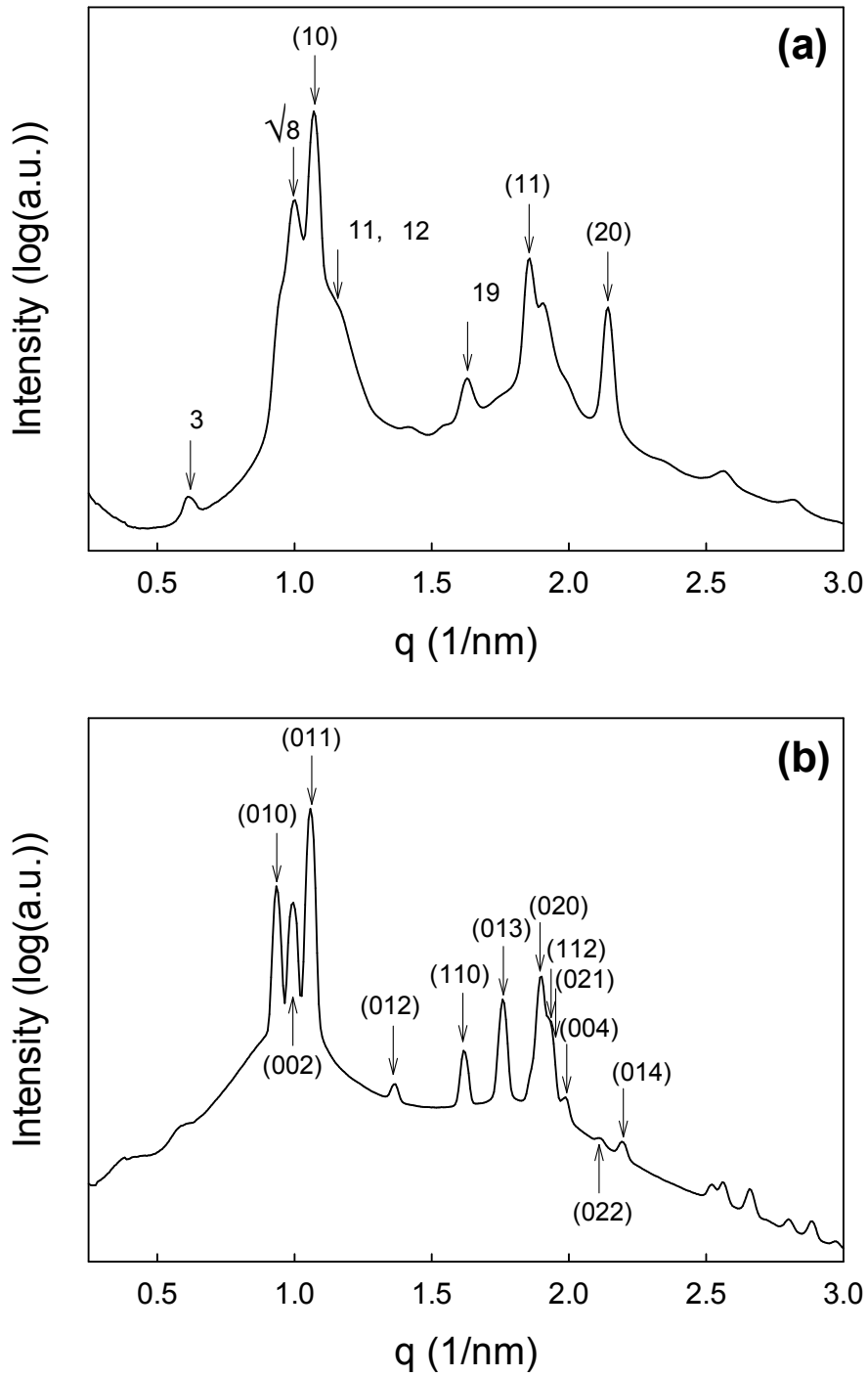

Figure S2. Indexed small angle X-ray diffractograms of the bulk POPC/GDO/P80 liquid crystalline phases prepared at equal POPC/GDO weight ratios in excess water at 25 °C: **(a)** a mixture of the reversed hexagonal (H_2) (10, 11, 20) and *Fd3m* micellar cubic (√3, √8, √11, √12,..., √19) phases prepared without P80, and **(b)** liquid crystalline phase with *p63/mmc* symmetry (010, 002, 011, 012, 110, 013, 020, 112, 021, 004, 022, 014) prepared at a lipid/P80 weight ratio of 95/5.

Ellipsometry

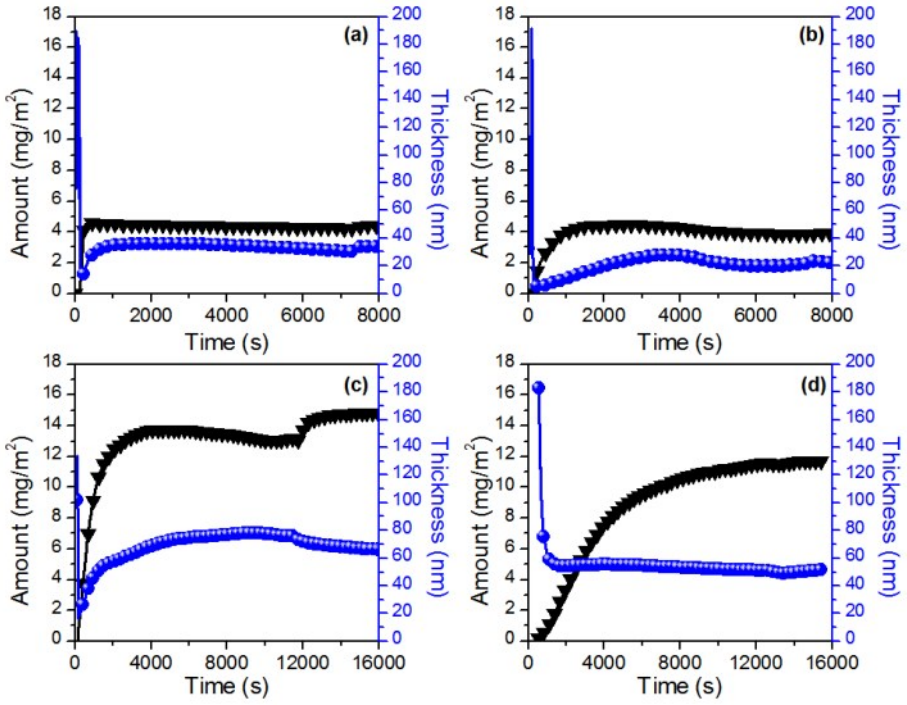

Figure S3. Adsorbed amount (▼) and layer thickness (●) as a function of time after the addition of 0.1 mg mL^{-1} of (a, c) d-POPC/GDO/P80 (42.5/42.5/15 weight ratio) and (b, d) h-POPC/GDO/P80 (42.5/42.5/15 weight ratio) LCNPs in pH 4 water on anionic (a, b) and cationic (c, d) silica surfaces, measured using *in situ* null ellipsometry. The data show that the d-POPC/GDO/P80 and h-POPC/GDO/P80 systems behave equivalently in terms of the plateau values of adsorbed amount and thickness of the formed layer.

Quartz Crystal Microbalance with Dissipation Monitoring (QCM-D)

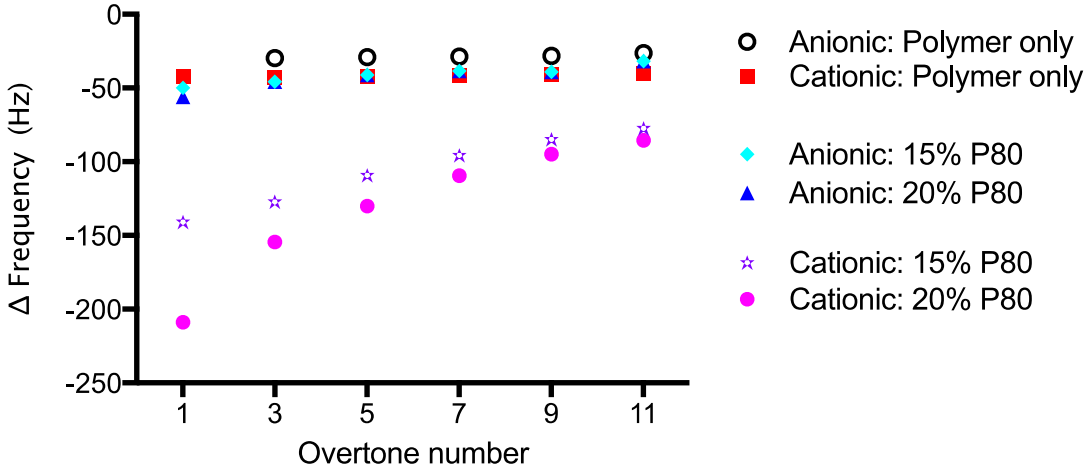

Figure S4. Frequency-dependence of the overtone number for the adsorption of LCNPs on anionic and cationic silica surfaces, measured using QCM-D. For P80, no dependence of the data on the overtone number could be found and hence the data could be evaluated by applying the Sauerbrey equation.

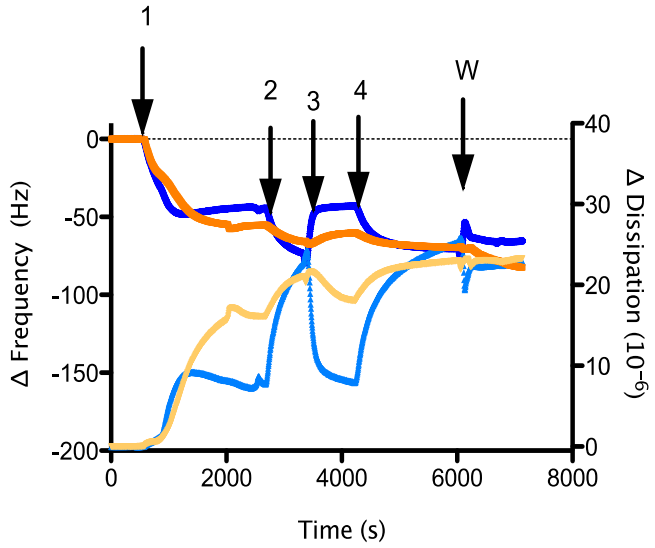

Figure S5. Simultaneous response in frequency and dissipation as a function of time after additions of POPC:GDO:P80 (42.5:42.5:15; 0.1 mg mL^{-1}; dark blue for F and light blue for D) and POPC:GDO:P80 (40:40:20; 0.1 mg mL^{-1}; dark orange for F and light orange for D) on cationic silica surfaces, measured using QCM-D. Overtone 7 is shown. Black arrows indicate (1) the first injection of LCNPs, (2) end of that injection, (3) second injection of LCNPs, (4) end of that injection, and (w) rinsing with water (pH adjusted). It can be seen that continuous flow suppressed the full adsorption of particles while ending the flow resulted in re-adsorption.

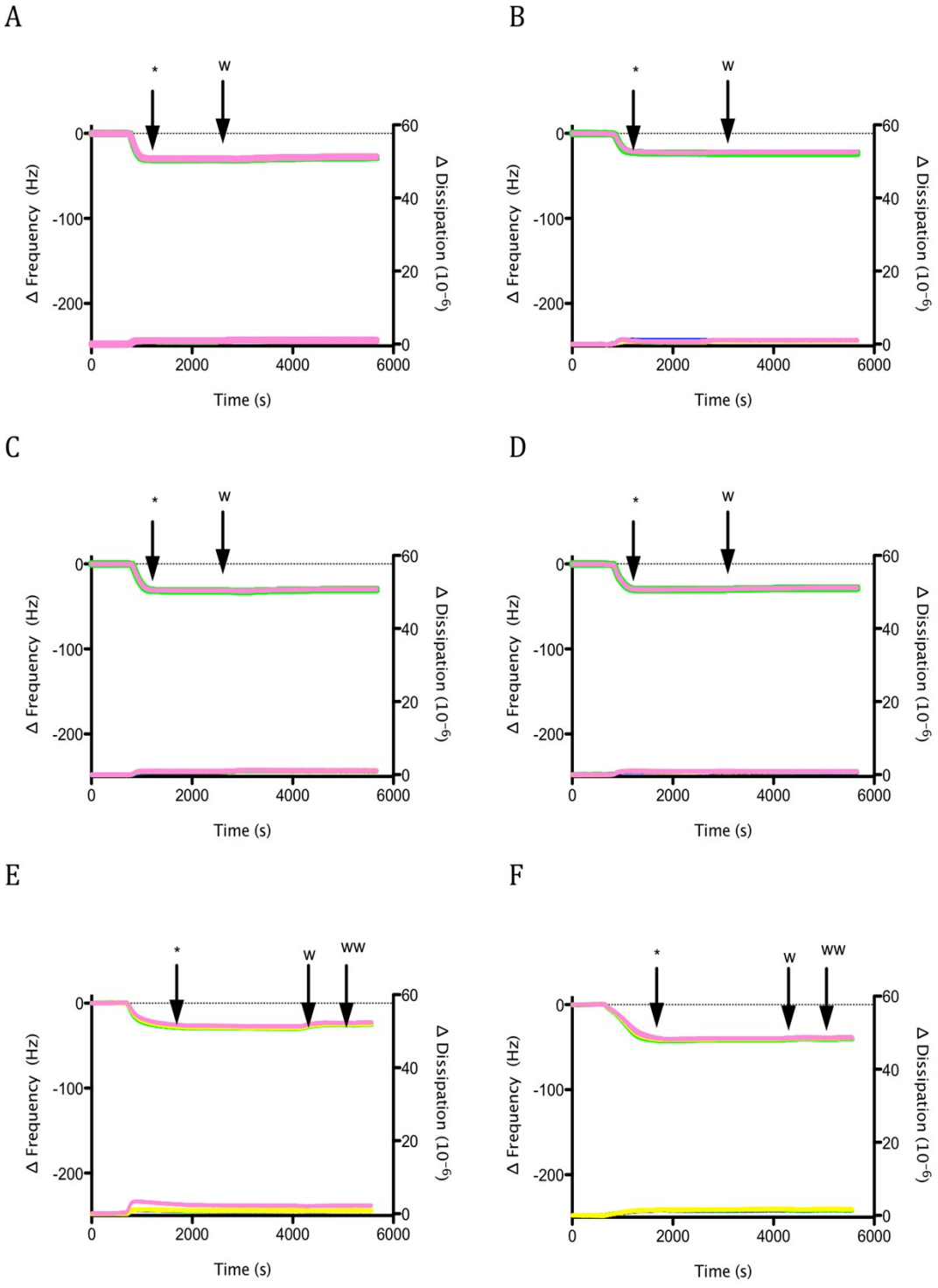

Figure S6. Simultaneous response in frequency and dissipation as a function of time after the addition of pure P80 polymer (0.02 mg mL^{-1}) on (A) anionic and (B) cationic silica surfaces, measured using QCM-D. Overtones 3 (blue), 5 (green), 7 (orange), 9 (yellow) and 11 (pink) are shown. Black arrows indicate the end of injections of LCNPs (*), rinsing with water (w) and a second rinsing with water (ww). Reproducibility was tested by repeating the experiments on (C, E) anionic and (D, F) cationic silica surfaces. The layer thicknesses in all cases were calculated using the Sauerbrey equation as around 3–5 nm.

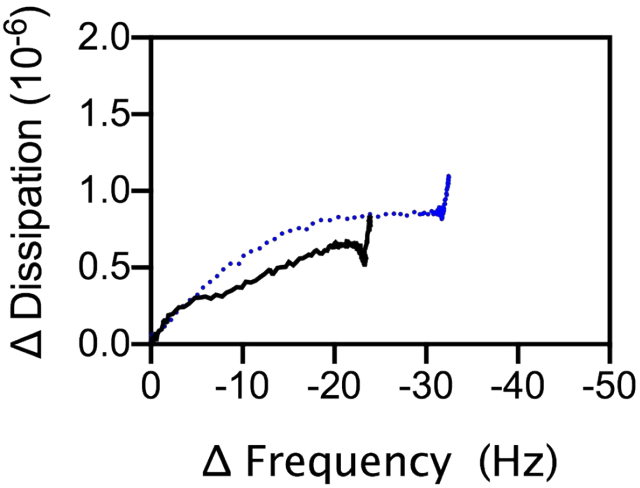

Figure S7. Plot of the frequency with respect to the dissipation for the adsorption of pure P80 polymer (0.02 mg mL^{-1}) on anionic (blue) and cationic (black) silica surfaces, measured using QCM-D. Overtone 7 is shown.

Neutron Reflectometry (NR)

Four different anionic and cationic silica substrates were used in the NR experiment. The thickness and roughness of the SiO_2 and APTES layers and the penetration of solvent into them were determined from the reflectivity data (Figure S8 A and B). As can be seen, the data differ slightly among the four different anionic silica substrates (Figure S8A) while the reflectivity profiles from the four different cationic silica substrates (Figure S8B) are more similar. As listed in Table S1, slightly different models were thus used for the different anionic silica substrates in the study of the adsorbed LCNP layers. A single model was used to describe the APTES layer for all the cationic silica substrates, as specified in Table S2.

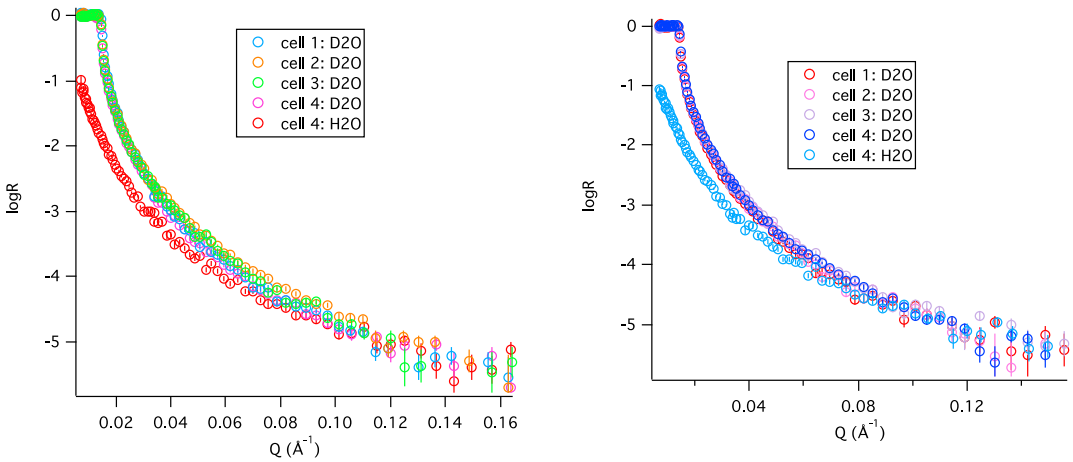

Figure S8. Reflectivity profiles of clean (A) anionic and (B) cationic silica substrates, measured using NR.

Table S1. Parameters used for the optical layer model fit to the NR data recorded of clean anionic silica substrates.

Substrate	Thickness (Å)	Solvent (vol%)	Roughness (Å)
1	15	7	3/8
2	10	7	3/3
3	12	7	4/6
4	15	7	3/8

Table S2. Parameters used for the optical layer model fit to the NR data recorded of clean cationic silica substrates (i.e. APTES-functionalized).

Layer	Thickness (Å)	Solvent (vol%)	Roughness (Å)
SiO_2	15	7	3/3
APTES	7	43	3/3

An aqueous solution of pure P80 polymer (0.02 mg mL^{-1}) was injected into solid/liquid interface cells for NR to monitor its adsorption to anionic and cationic silica surfaces. The neutron reflectivity profiles measured immediately after injection and after rinsing with D_2O and cmSi are shown in Figure S9. The changes in reflectivity show clearly that P80 adsorbs to both types of surface but a single isotropic layer cannot be used to fit the data. This result confirms that P80 alone does not form a thin uniform layer. One possible scenario is that micelles are adsorbed intact to the surface. Three layers were used to represent adsorbed micelles, as sketched in Figure S10, and the parameters of the model fit are listed in Table S3. The total thickness of the adsorbed material is 63 and 74 Å on anionic and cationic silica surfaces, respectively, which coincides relatively well with the expected diameter of P80 micelles in H_2O (previously reported to ~70 Å).[1] However, several other models (with ambiguous physical meaning) can be fitted to the data if three layers are used.

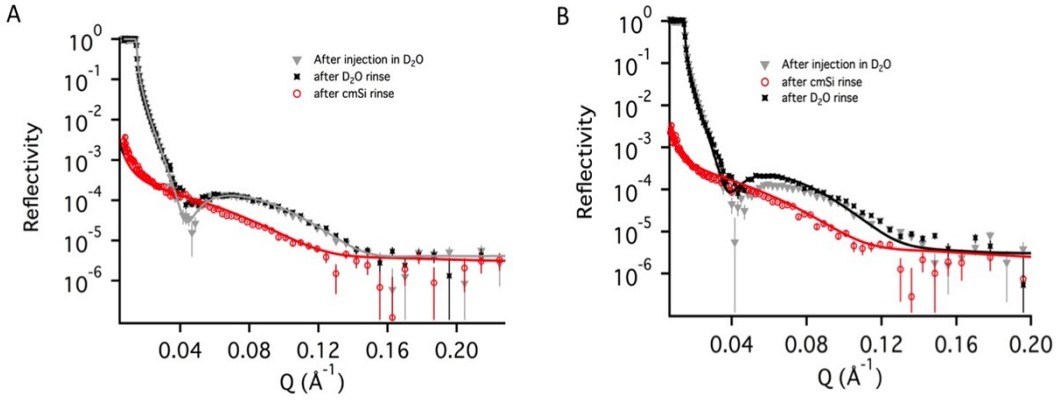

Figure S9. Reflectivity profiles after injection of 0.02 mg mL^{-1} polymer P80 and after rinsing with cmSi and D_2O on (A) anionic and (B) cationic silica surfaces, measured using NR.

Table S3. Model fits for the P80 polymer data in Figure S8.

Layer	Thickness (Å) SiO_2/APTES	SLD (10^{-6} Å^{-2}) SiO_2/APTES	Solvent (%) SiO_2/APTES	Roughness (Å)
1	15/17	1.13	80/75	8/7
2	33/38	0.35/0.45	42/45	8/7
3	15/17	1.13	80/75	8/7

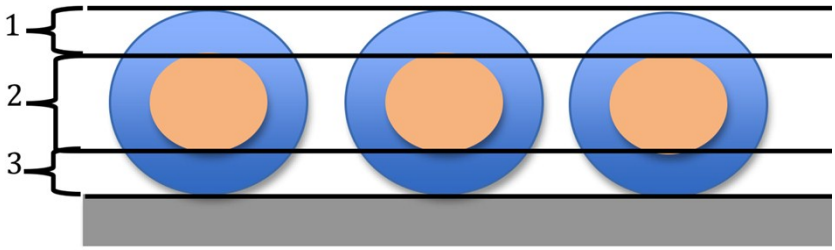

Figure S10. Schematic illustration of the model for adsorbed intact micelles on the surface. Three isotropic layers are used to represent the micelles.

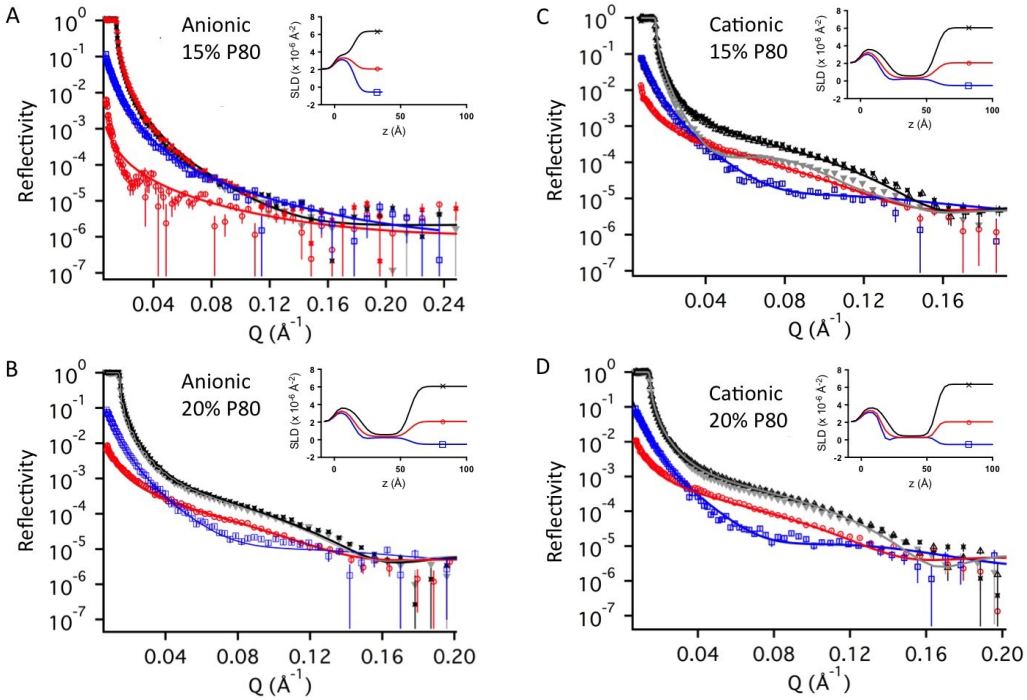

Figure S11. Reflectivity profiles after the exposure to anionic silica of (A) 42.5/42.5/15 POPC/GDO/P80 and (B) 40/40/20 POPC/GDO/P80 LCNPs containing h-POPC, and after the exposure to cationic silica of (C) 42.5/42.5/15 POPC/GDO/P80 and (D) 40/40/20 POPC/GDO/P80 LCNPs containing h-POPC, measured using NR. Data in D_2O (black markers) and after subsequent rinses with D_2O (grey markers), cmSi (red circle markers) and H_2O (blue markers) are shown. Data of the bare anionic silica surface are shown in panel (A) for comparison (red cross markers). The solid lines shown correspond to best fits of the optical layer models using the parameters listed in Tables 4–7 of the main text. The SLD profiles are shown in the inset.