

Supported lipid bilayers with encapsulated quantum dots (QDs) via liposome fusion: effect of QD size on bilayer formation and structure

Magdalena Wlodek,* Marta Kolasinska-Sojka,* Michal Szuwarzynski, Sami Kereiche, Lubomir Kovacik, Liangzhi Zhou, Luisa Islas, Piotr Warszynski and Wuge H. Briscoe*

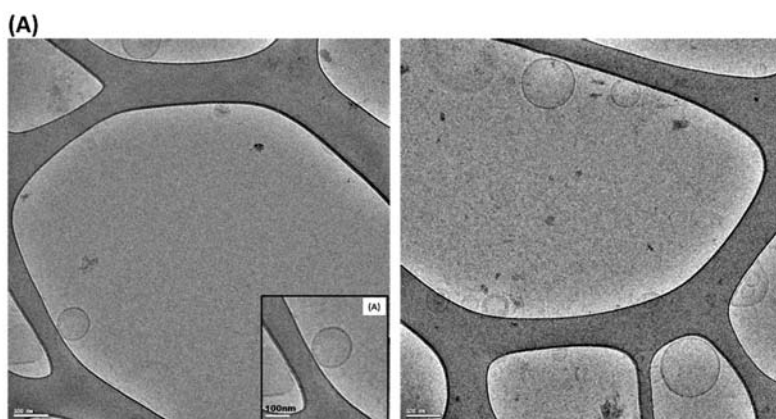
* E-mail: ncwlodek@cyf-kr.edu.pl (MW); nckolasi@cyf-kr.edu.pl (MKS);
wuge.briscoe@bristol.ac.uk (WHB)

Electronic Supporting Information

SI.1 The sample preparation and imaging details for cryo-TEM measurements.

The samples for cryo-TEM were prepared by applying a small 3 μ L drop of suspension onto a copper grid covered with a perforated carbon film forming woven-mesh-like openings of different sizes and shapes (the lacey carbon grids were #LC-200 Cu, Electron Microscopy Sciences, Hatfield, PA, USA). The grid was then glow discharged for 40 s with a 5 mA current prior to specimen application. Most of the samples were removed by blotting (Whatman no. 1 filter paper) for approximately 1 s, and the grid was immediately plunged into liquid ethane held at -183°C . The grid was then transferred without rewarming into the microscope. Images were recorded at the accelerating voltage of 120 kV and with magnifications ranging from $11500\times$ to $50000\times$ using a GatanUltraScan 1000 slow scan CCD camera in the low-dose imaging mode, with the electron dose not exceeding 1500 electrons per nm^2 . The magnifications resulted in final pixel size ranging from 0.9 to 0.2 nm, the typical value of under applied focus ranged between 0.5 to 2.5 μm . The applied blotting conditions resulted in the specimen thickness varying between 100 to ca. 300 nm.

SI.1.1 Cryo-TEM images.



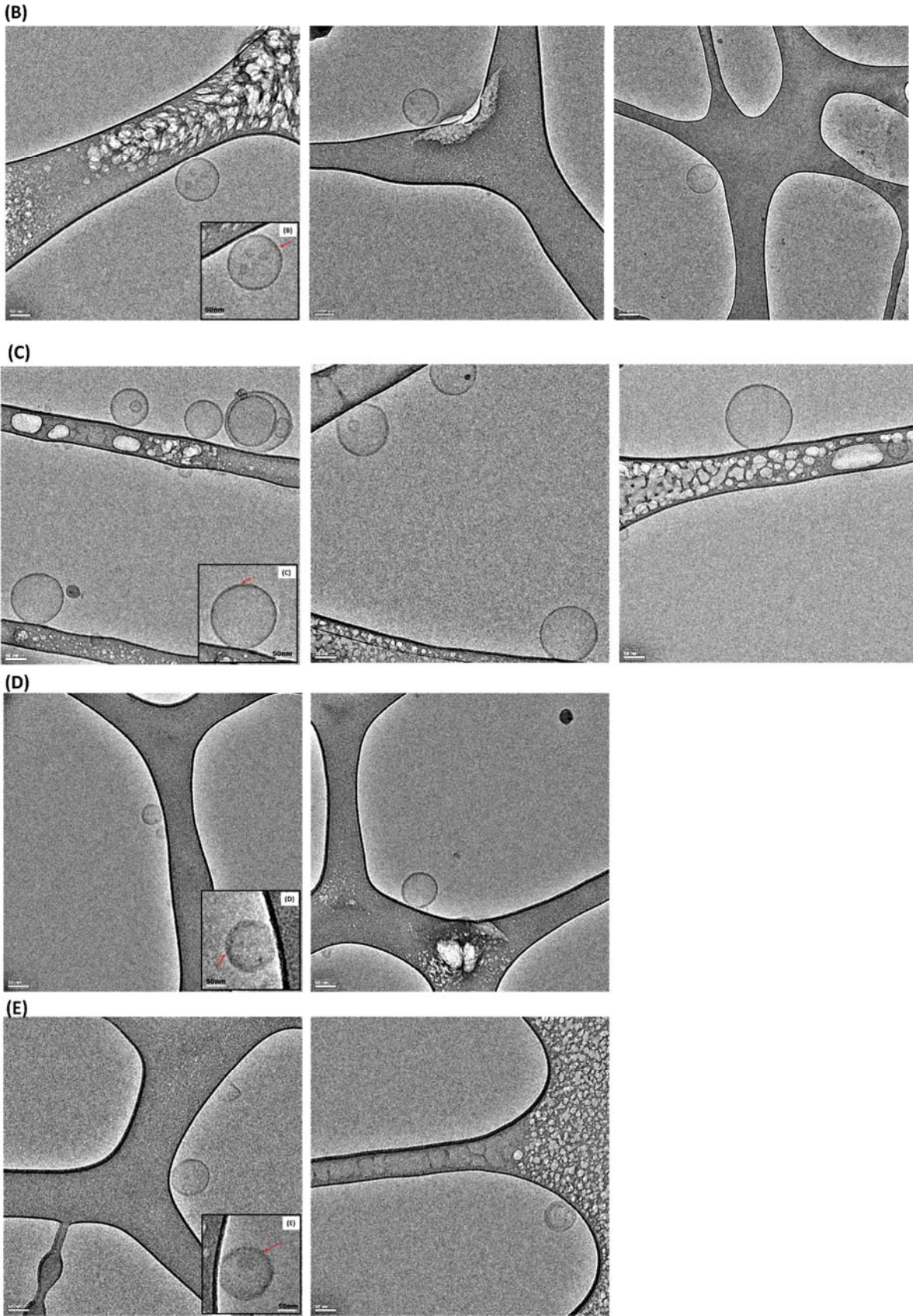


Figure S1. Cryo-TEM images of POPC/POPE liposomes without QDs (A) and with 2.7 nm (B); 3.8 nm (C); 4.9 nm (D); 5.4 nm (E) QDs. The inset images correspond to those used in the main text.

SL.2 DLS of POPC/POPE liposomes without QDs and with QDs.

The size distribution of (POPC/POPE SUV) and (POPC/POPE with QDs) aqueous liposome dispersions at 25°C was determined by the dynamic light scattering (DLS, Zetasizer Nano Series, Malvern Instruments) at scattering angle of 90°. The DLS results are presented in Table S1 and Figure S2.

Table S1. Hydrodynamic diameters and polydispersity index (PDI) of the dispersions of the POPC/POPE liposomes without (SUV) and with different sizes of CdS QDs from the DLS measurements.

System	Hydrodynamic diameter (nm)	PDI
POPC/POPE SUV	90.2±6.0	0.119
SUV- 2.7nm QDs	106.7±5.6	0.262
SUV- 3.8nm QDs	112.5±3.8	0.132
SUV-4.9nm QDs	108.4±4.3	0.154
SUV- 5.4nm QDs	115.5±4.0	0.201

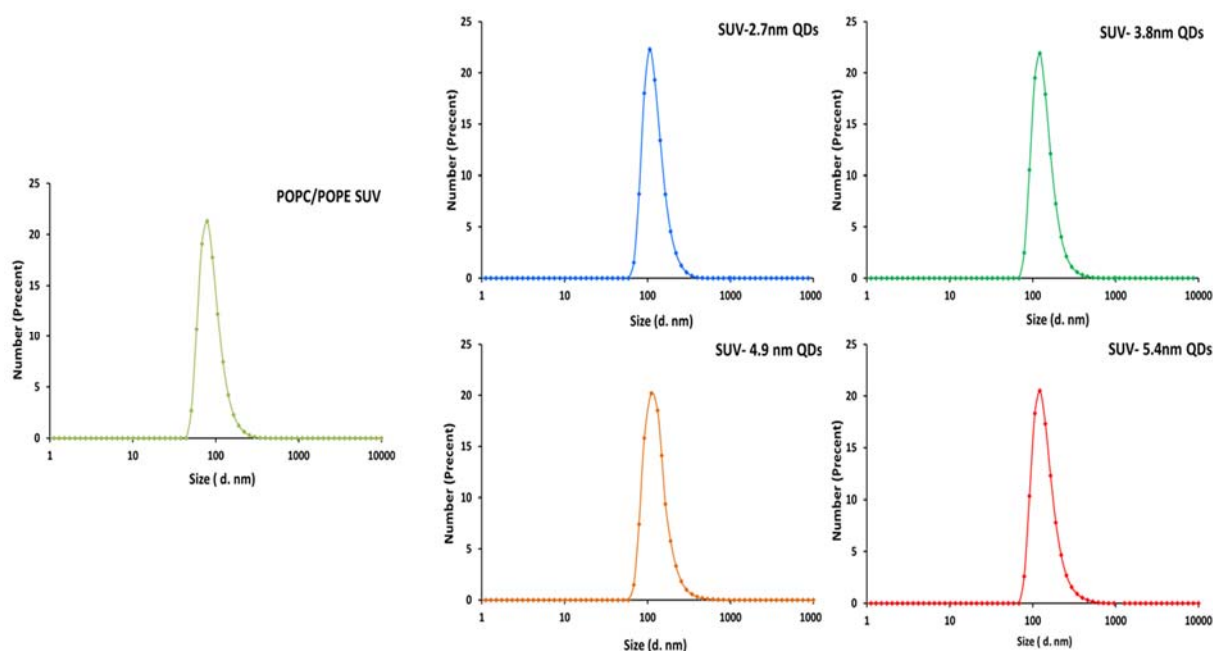


Figure S2. Average size distribution of POPC/POPE liposomes without and with QDs measured by DLS.

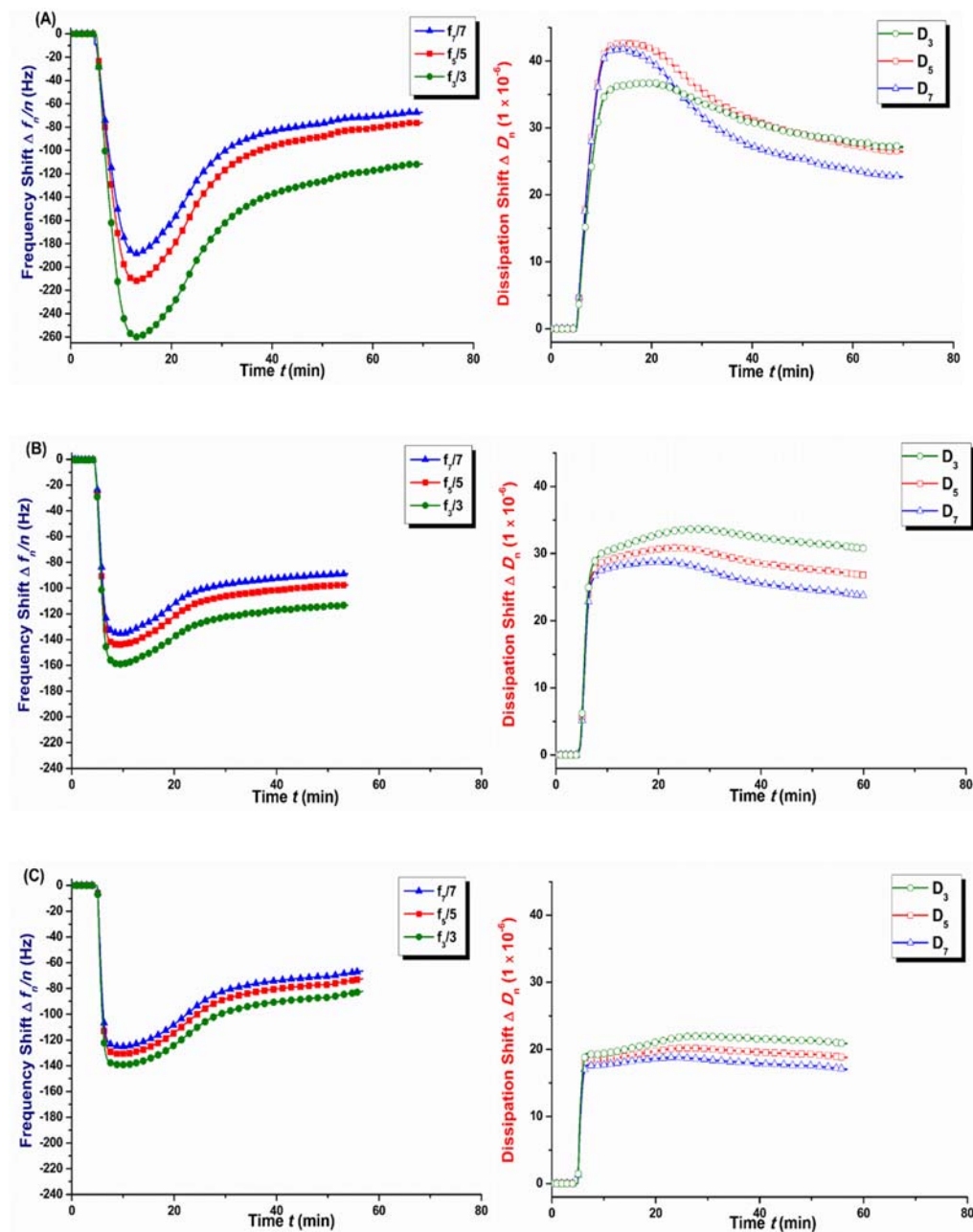
SL.3 Fluorimetric analysis.

The fluorescence emission spectra of POPC/POPE liposomes with the QDs adsorbed on PEI monolayer after 3h incubation were measured with spectrofluorimeter, and compared with that of the POPC/POPE liposomes with QDs in solutions.

Table S2. The wavelengths of fluorescence emission spectra of POPC/POPE SUV-QDs and POPC/POPE SUV-QDs deposited on PEI monolayer.

CdS diameter d (nm)	Wavelength λ (nm)	
	<i>SUV-QDs</i>	<i>PEI/SUV-QDs</i>
2.7	391	392
3.8	415	418
4.9	444	445
5.4	467	467

SI.4 QCM-D measurements.



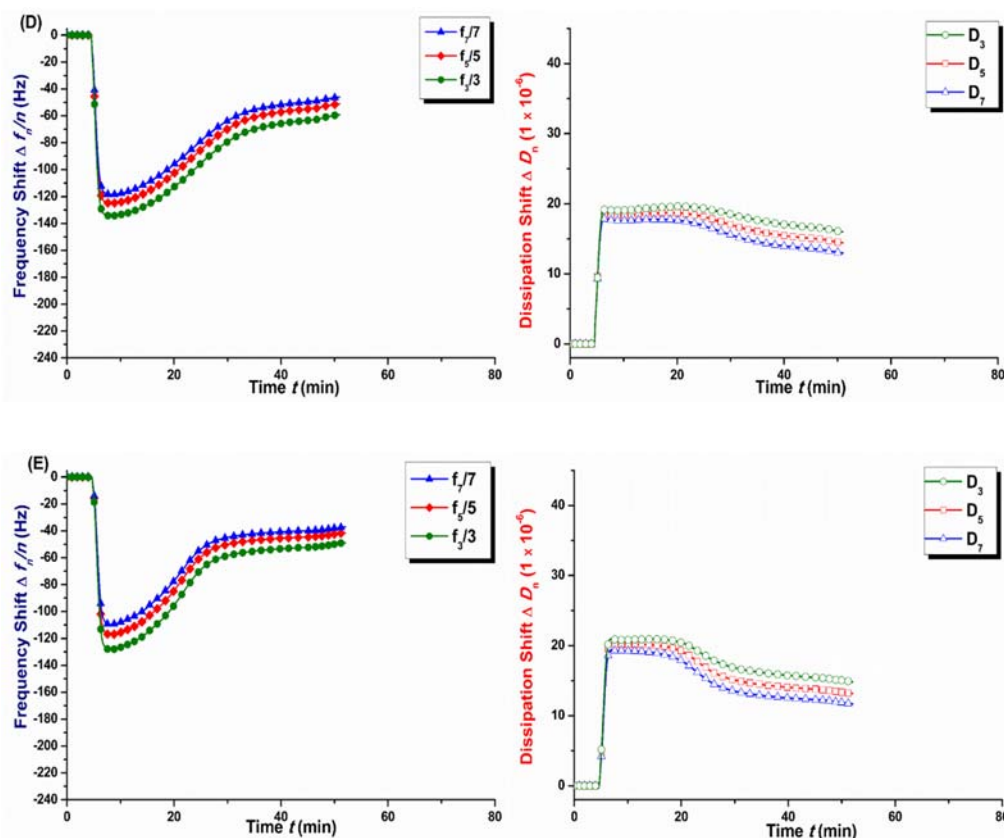


Figure S3. Frequency (Left) and dissipation (Right) shifts upon the deposition of POPE/POPE liposomes without (A) and with 2.7 nm (B); 3.8 nm (C); 4.9 nm (D); 5.4 nm (E) QDs. Overtones 3rd, 5th and 7th are shown for each experiment.

SI.5 Fitting parameters for XRR data.

The best fitting parameters, i.e. thickness, scattering length density (SLD) and roughness to the experimental data are summarized in Tables S2 - S6. The fit was based on six slab model, which is shown in Figure S4 and represents: (1) the outer headgroup layer to the superphase, (2) the outer hydrocarbon chain layer, (3) the inner hydrocarbon chain layer, (4) the inner headgroup layer, (5) polyethylenimine layer and (6) silicon oxide layer.

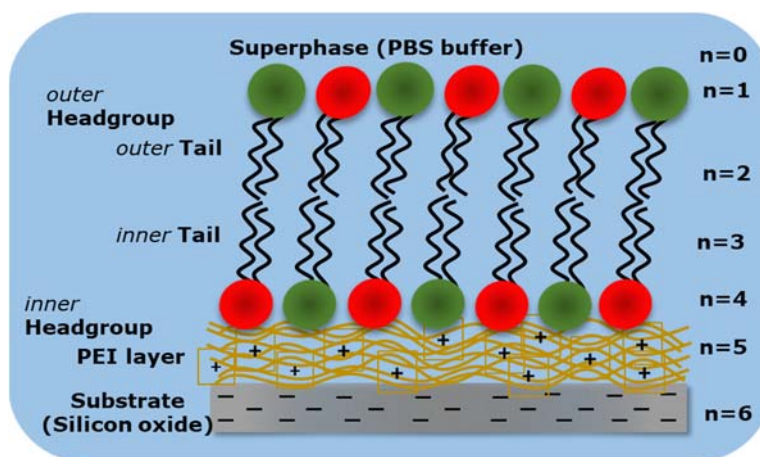


Figure S4. Schematic representation of six slab model used for fitting experimental data.

Table S3. Parameters obtained from fitting XRR data for POPC/POPE on PEI monolayer at 3h incubation.

Layer	Thickness (Å)	SLD (10^{-6}Å^{-2})	Roughness (Å)
oHead	6.40	9.50	2.74
oChain	11.79	6.66	1.75
iChain	10.55	6.58	1.79
iHead	5.00	9.74	2.79
PEI-layer	9.00	9.67	1.65
SiO₂	5.82	18.70	2.99

$$Thickness_{SLBs} = 33.74 \text{ Å}$$

Table S4. Parameters obtained from fitting XRR data for POPC/POPE with 2.7 nm QDs on PEI monolayer at 3h incubation.

Layer	Thickness (Å)	SLD (10^{-6}Å^{-2})	Roughness (Å)
oHead	8.76	9.60	2.69
oChain	18.65	9.93	3.21
iChain	10.63	9.68	4.03
iHead	5.10	9.51	2.78
PEI-layer	9.25	9.51	1.39
SiO₂	5.62	18.70	1.03

$$Thickness_{SLBs} = 43.14 \text{ Å}$$

Table S5. Parameters obtained from fitting XRR data for POPC/POPE with 3.8 nm QDs on PEI monolayer at 3h incubation.

Layer	Thickness (Å)	SLD (10^{-6}Å^{-2})	Roughness (Å)
oHead	8.35	9.82	2.91
oChain	17.81	9.50	3.72
iChain	19.24	9.01	2.40
iHead	6.34	9.51	2.95
PEI-layer	9.30	9.66	1.08
SiO₂	8.17	18.70	2.00

$$Thickness_{SLBs} = 51.74 \text{ Å}$$

Table S6. Parameters obtained from fitting of XRR data for POPC/POPE with 4.9 nm QDs on PEI monolayer at 3h incubation.

Layer	Thickness (Å)	SLD (10^{-6}Å^{-2})	Roughness (Å)
oHead	9.11	10.05	5.97
oChain	15.98	9.37	8.57
iChain	11.37	9.66	4.49
iHead	7.32	9.58	3.92
PEI-layer	11.92	9.67	1.20
SiO ₂	5.48	18.70	2.55

$$\text{Thickness}_{SLBs} = 43.78 \text{ Å}$$

Table S7. Parameters obtained from fits of XRR data for POPC/POPE with 5.4 nm QDs on PEI monolayer at 3h incubation.

Layer	Thickness (Å)	SLD (10^{-6}Å^{-2})	Roughness (Å)
oHead	9.08	10.13	7.99
oChain	19.63	10.32	3.54
iChain	12.02	10.22	5.44
iHead	8.18	10.16	4.78
PEI-layer	9.56	9.55	1.08
SiO ₂	5.10	18.70	1.42

$$\text{Thickness}_{SLBs} = 48.91 \text{ Å}$$

SI.6 Characterization of PEI monolayer.

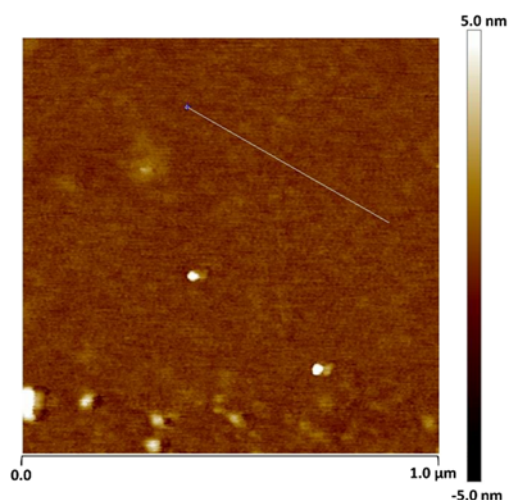


Figure S5. AFM image obtained for PEI monolayer.

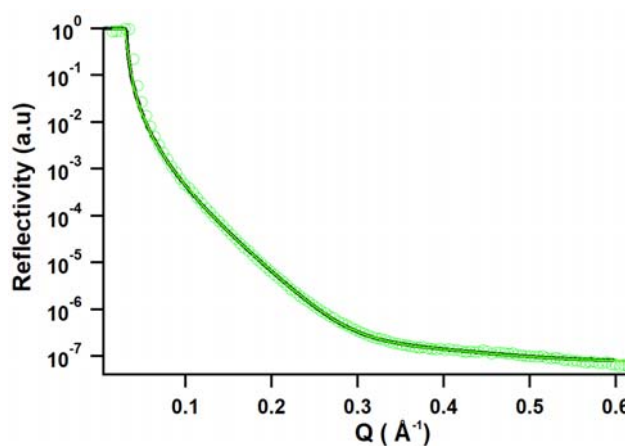


Figure S6. X-ray reflectivity experimental curve with fit for PEI monolayer.

Fitting the XRR curve shows that the PEI layer was 0.91 nm in thickness with a 60.8 % surface coverage and 0.45 nm interfacial roughness.