

Supplementary Information

Table S1. Fit parameters for [PEI/PSS]₃-PEI-dPSS-PEI measured in bulk H₂O. Experiments were performed at pH7.0, pH 2.5, and pH 7.0 restored.

pH	Bottom stratum thickness [Å]	Bottom stratum SLD x 10 ⁶ [Å ⁻²]	Top stratum thickness [Å]	Top stratum SLD x 10 ⁶ [Å ⁻²]	Roughness of the film-air interface [Å]	Total thickness [Å]
7.0	42.0±0.2	0.37±0.01	197.0±0.2	0.83±0.01	14.8±0.8	239±0.4
2.5	25.0±0.3	0.07±0.01	208.0±0.4	0.39±0.01	4.0±3.7*	233±0.7
7.0 - restored	25.0±0.2	0.50±0.01	205.0±0.3	0.90±0.01	4.1±2.6*	230±0.5

* Due to the limited Q_z-range of the NR data and significant number of parameters of the models used in data refinement, some error values of the roughness parameters are substantial.

Table S2. Fit parameters for PEM ([PEI-PSS]₃-PEI), PEM+DPPE at pH 7.0, PEM+DPPE at pH 3.0, and PEM+DPPE after pH was restored back to 7.0. D₂O was used as a subphase.

	PEM: 7-layered	PEM + DPPE: pH 7	PEM + DPPE: pH 3	PEM + DPPE: pH 7 return
Bottom strata Thickness [Å]/ SLD/Roughness	102.0±0.4/ 3.20±0.01/ 8.1±1.0	70.0±0.5/ 3.60±0.01/ 3.0±2.3*	107.0±0.7/ 3.70±0.01/ 4.0±2.7*	64.0±0.3/ 3.60±0.01/ 3.0±1.5
Top strata Thickness [Å]/ SLD/Roughness	64.0±0.5/ 3.00±0.01/ 5.0±6.4*	77.0±0.4/ 3.30±0.01/ 3.0±6.5*	42.0±0.7/ 3.30±0.01/ 4.0±2.9*	79.0±0.3/ 3.30±0.01/ 3.0±4.5*
Total thickness of PEM [Å]	166±0.9	147±0.9	149±1.4	143±0.6
Hydrated headgroup region Thickness [Å]/ SLD/Roughness	---	23.0±0.3/ 4.30±0.02/ 10.0±0.6	---	20.0±0.2/ 4.50±0.01/ 10.0±0.4
Tail region of lipid bilayer Thickness [Å]/ SLD/Roughness	---	48.0±0.1/ 0.26±0.01/ 10.0±0.2	---	49.0±0.1/ 0.56±0.01/ 10.0±0.1
χ ²	7.97	2.37	2.06	5.57

* Due to the limited Q_z-range of the NR data and significant number of parameters of the models used in data refinement, some error values of the roughness parameters are substantial.

Table S3. Fit parameters for PEM ([PEI-PSS]₃-PEI-dPSS-PEI), PEM+dDPPC at pH 7.0, PEM+dDPPC at pH 3.0, and PEM+dDPPC after pH restored back to 7.0.

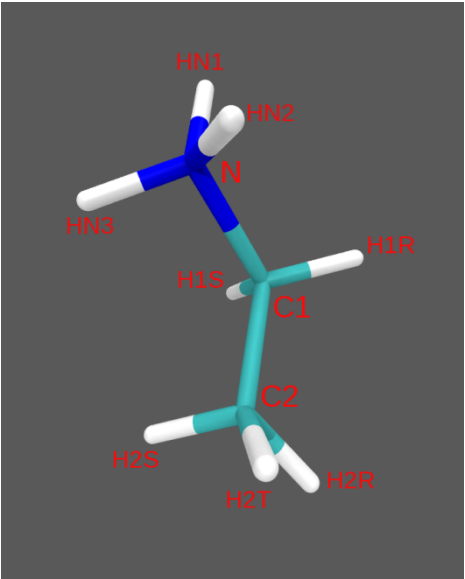
	pH 7	pH 7 +dDPPC	pH 3 +dDPPC	pH 7 return +dDPPC
Bottom strata Thickness [Å]/sld/R	42.0±0.2/ 0.37±0.01/ 6.0±0.1	40.0±0.1/ -0.37±0.01/ 6.3±0.1	38.0±0.2/ -0.49±0.01/ 6.0±0.1	42.0±0.1/ -0.16±0.01/ 5.0±0.1
Top strata Thickness [Å]/sld/R	197.0±0.2/ 0.83±0.01/ 14.8±0.8	183.0±0.1/ 0.99±0.01/ 4.1±0.8	191.0±0.4/ 0.44±0.01/ 4.1±0.9	184.0±0.1/ 0.92±0.01/ 3.5±0.7
Top + Bottom [Å]	239±0.4	223±0.2	229±0.6	226±0.2
Hydrated lipid headgroup region Thickness [Å]/sld/R	--	11.0±0.1/ 0.88±0.03/ 5.2±7.1*	--	15.0±0.1/ 0.61±0.02/ 7.8±2.5
Lipid bilayer Thickness [Å]/sld/R	--	47.0±0.1/ 1.95±0.01/ 14.6±0.5	--	48.0±0.1/ 1.88±0.01/ 14.4±0.3
χ ²	1.39	6.71	2.42	8.23

*Due to the limited Qz-range of the NR data and significant number of parameters of the models used in data refinement, some error values of the roughness parameters are substantial.

For Tables S2 and S3, the SLD values are given in x 10⁶ Å⁻² units.

Table S4. Coulombic charges on the protonated ethylamine (CH₃CH₂NH₃⁺). The “atom types” corresponds to Charm c36 force field in Gromacs-4.5.1

Atom No.	Atom Name	Atom Type	Atom Charge
1	N	NH3L	-0.3
2	HN1	HCL	0.33
3	HN2	HCL	0.33
4	HN3	HCL	0.33
5	C1	CTLS	0.13
6	H1R	HAL2	0.09
7	H1S	HAL2	0.09
8	C2	CTL3	-0.27
9	H2R	HAL3	0.09
10	H2S	HAL3	0.09
11	H2T	HALS	0.09



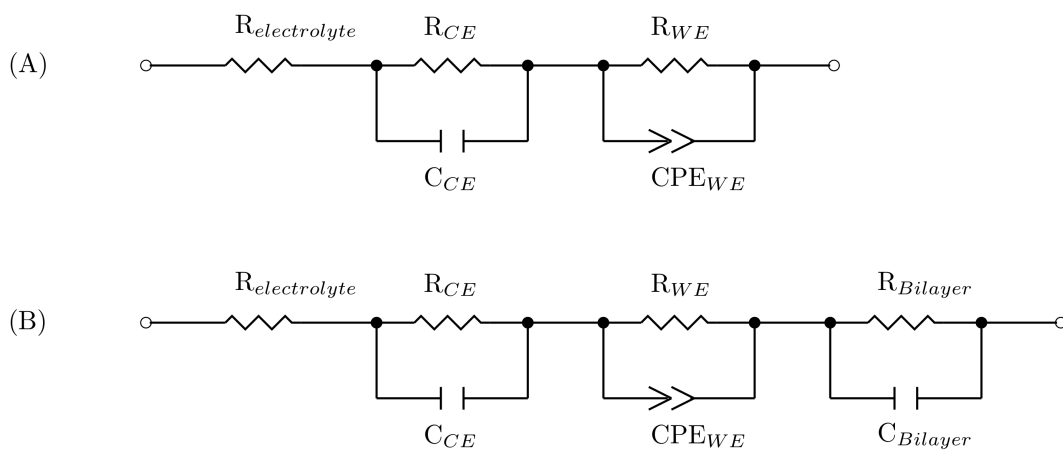


Figure. S1: Equivalent electrical circuits employed to model the EIS data. (A) was used for CrAu + Thiol + PEM at pH7, pH3 and CrAu + Thiol + PEM + DPPE-Bilayer at pH3, (B) for CrAu + Thiol + PEM + DPPE-Bilayer at pH7.