ELECTRONIC SUPPORTING INFORMATION

Tuneable interfacial surfactant aggregates mimic lyotropic phases and facilitate large scale nanopatterning

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Supplementary AFM height modulation images

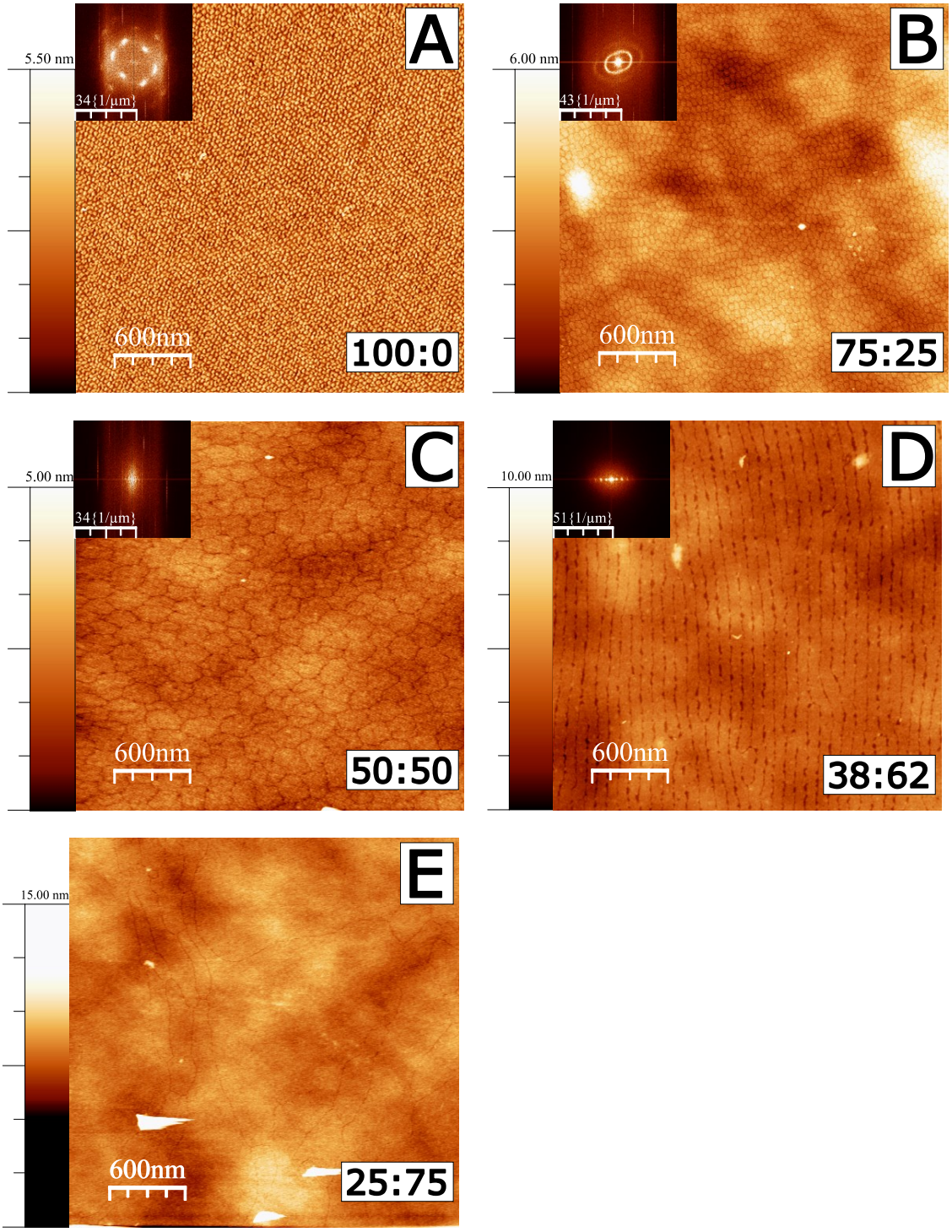

Figure S1. AFM height images of monolayers deposited at 20 mN m^{-1} on silicon wafers. Fractions in wt.% for 18-MEA:EA are shown in the bottom right for each deposition. A Fourier transform is shown as inset in the top left corner of each image, except for the 25:75 mixture where no correlated surface structure was observed. The minimum height on all scalebars is zero nanometre.

Langmuir isotherms

Langmuir isotherms presented in Figure S2 were collected during neutron reflectometry. Isotherms were collected on a D_2O subphase with 0.1 mM $CdCl_2$, 0.1 mM $NaHCO_3$, and buffered to pD 6.0. The barriers were compressed at 4.5 cm^2 min^{-1}. The isotherms represented by solid lines were collected at the same experimental beam time (DOI10.5291/ILL-DATA.9-10-1487), whereas the dashed line was collected at a separate occasion (DOI:10.5291/ILL-DATA.9-10-1515). The horizontal steps at constant surface pressure show isotherm stability during neutron reflectivity acquisition time of roughly 45 minutes.

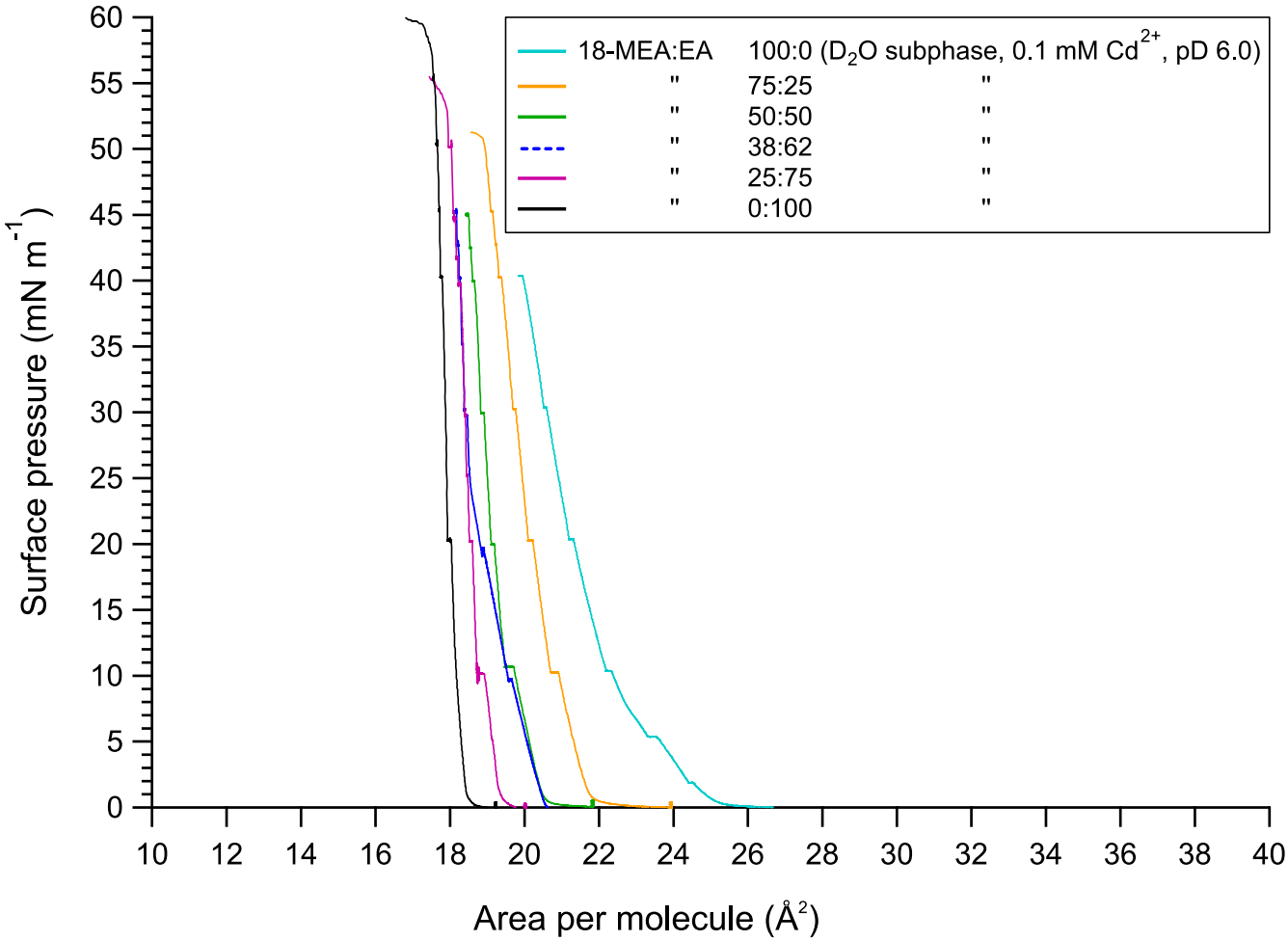

Figure S2. Langmuir isotherms collected during neutron reflectometry measurements. Solid line isotherms show collection at one experimental beam time, whereas the dashed line data is collected at a separate occasion.

AFM FT analysis

Domain sizes were analysed statistically analysed to determine characteristic length scales in AFM images. This was done by sector intensity integration of 2D FTs using a radial integration tool in the software ImageJ.[1] Integrations over different angles and regions of interest were performed to decouple intensity contributions due to particle elongation, as depicted for 18-MEA:EA 75:25 in Figure S3 (left), with the integrated intensity is shown versus inverse micrometres on the x-axis in Figure S3 (right). For clarity, the intensity has been arbitrarily shifted along the y-axis. Assuming a normal distribution of particle sizes, a gaussian function was used to fit the intensity peaks. Fitted results and corresponding characteristic sizes, attributed as domain diameters, are presented in Table S1 for 18-MEA:EA 100:0, 18-MEA:EA 75:25, 18-MEA:EA 50:50, and 18-MEA:EA 38:62. Assuming a Gaussian fluctuation around the mean spacing between neighbouring domains, the pair correlation decreases with distance.

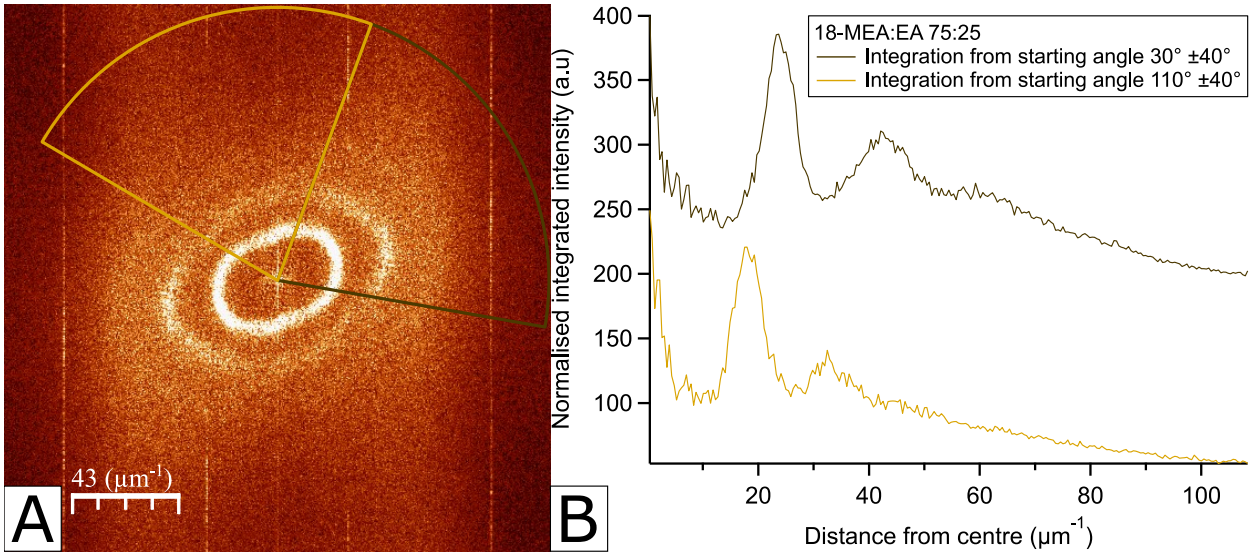

Figure S3. A 2D FT generated from AFM image of deposited monolayer of 18-MEA:EA 75:25 is shown in A (left) with two highlighted segments distinguishing semi-axis lengths in the deposited domains. Radial intensity integration over highlighted segments in A are shown in B (right) as a function of distance from FT centre.

Table S1. Fourier transform peaks fitted with a Gaussian function, corresponding to domain sizes in deposited monolayers. The integrated regions in column FT are given as a starting angle followed by the integration angle above and below this point. Zero degrees is defined as the positive x-axis with the origin in the centre of the FT image.

Sample	FT	max	centre distance (1/µm)	error (1/µm)	length (nm)	
18-MEA	45 deg 10	1	25.653	± 0.14	38.982	± 0.21
"	45 deg 10	2	49.095	± 0.23	42.658	± 0.41
"	n45 deg 45	1	32.371	± 0.13	30.892	± 0.12
"	n45 deg 45	2	60.604	± 0.33	35.420	± 0.41

Sample	FT	max	centre distance (1/µm)	error (1/µm)	length (nm)	
18-MEA:EA 75:25	30 deg 40	1	23.97	± 0.05	41.719	± 0.08
"	30 deg 40	2	42.787	± 0.10	53.143	± 0.29
"	30 deg 40	3	57.078	± 0.63	69.974	± 2.93
"	110 deg 40	1	18.198	± 0.06	54.951	± 0.19
"	110 deg 40	2	32.518	± 0.24	69.832	± 1.13

Sample	FT	max	centre distance (1/µm)	error (1/µm)	length (nm)	
18-MEA:EA 50:50	0 deg 60	1	6.068	± 0.04	164.799	± 1.10
"	0 deg 60	2	10.981	± 0.11	203.542	± 4.42

Sample	FT	max	centre distance (1/µm)	error (1/µm)	length (nm)	
18-MEA:EA 38:62	95 deg 15	1	18.152	± 0.23	55.090	± 0.69

AFM height image line profile

A deposited monolayer of neat 18-MEA is shown in Figure S4, with a line profile shown in black, as drawn over five fatty acid domains. The topography shows domain heights between 2 and 2.5 nm, which can be expected with the extended chain length of a C20 carbon chain, and close to the values found through x-ray reflectometry.

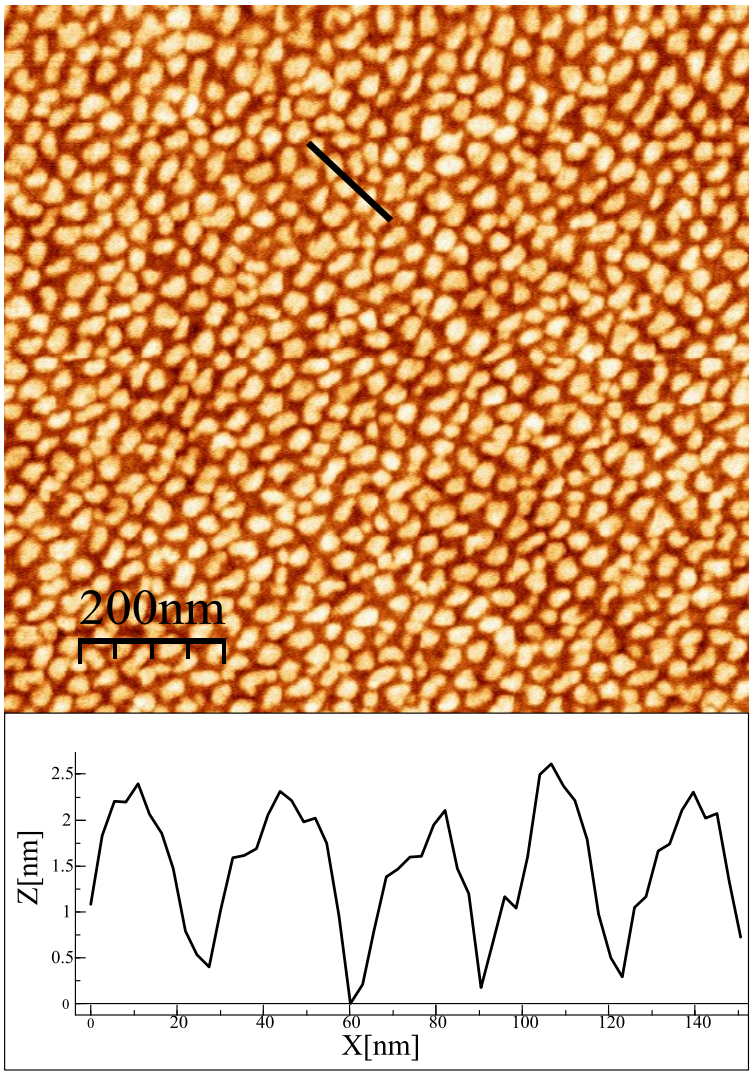

Figure S4. AFM height image of monolayer of neat 18-MEA deposited on a silicon wafer, and a corresponding topographic profile of the line segment drawn in black.

Reflectivity fitting procedure

Specular X-ray reflectivity (XRR) was acquired for EA and 18-MEA, from which values for headgroup and tail thicknesses were extracted from fitting and later employed in the fitting of NR data, as the neutron probe is inherently insensitive to a hydrocarbon chain. Additionally, the water content of the headgroup region and the degree of dissociation of the carboxylate moiety were determined via XRR.

X-ray fitting

In the fitting procedure, the fatty acid layer was divided into two slabs, one consisting of the aliphatic chain, and the other consisting of the headgroup, its associated metal counter ion, and any water required to fill empty space. The aliphatic tail is in contact with air fronting and the carboxylic acid headgroup is in contact with a water backing. The thicknesses and scattering length densities (SLD) of the headgroup and tail layers were loosely constrained fitting parameters. The interfacial roughness of each layer was fixed to be equal during the fit*. A Monte Carlo analysis option in Motofit was used to visualise co-dependency between fitting parameters in 1250 individual fits. The constrained parameters did not reach their boundary conditions. Normally the fitting parameters for tail layer thickness and SLD clustered and an initial estimate was determined as a mean value from this group. Subsequently, the values for each fitted pair of head group thickness and SLD were used separately to calculate the volume of water in the headgroup layer, as demonstrated in route 1 and route 2 below.

Route 1. The SLD of the headgroup was defined as a summation of all scattering contributions from the headgroup layer, normalised by their volume ratios:

$$\mathrm{SLD} = \frac{b_{Cd}V_{Cd} + b_{COO}V_{COO} + b_{H_2O}V_{H_2O}}{\left(V_{Cd} + V_{COO} + V_{H_2O}\right)^2} \rightarrow \left\{ \begin{array}{l} b_{Cd}V_{Cd} = p \\ b_{COO}V_{COO} = q \\ p + q = p_q \\ V_{Cd} + V_{COO} = c \end{array} \right\} \rightarrow$$

$$\mathrm{SLD} = \frac{p_q + b_{H_2O}V_{H_2O}}{c^2 + 2cV_{H_2O} + V_{H_2O}^2} \rightarrow$$

$$c^2 + 2cV_{H_2O} + V_{H_2O}^2 = \frac{p_q + b_{H_2O}V_{H_2O}}{\mathrm{SLD}}$$

$$V_{H_2O}^2 = \frac{b_{H_2O}V_{H_2O}}{SLD} - \frac{2cV_{H_2O}SLD}{SLD} + \frac{p_q}{SLD} - c^2$$

$$V_{H_2O}^2 = V_{H_2O}\left(\frac{b_{H_2O} - 2cSLD}{SLD}\right) - c^2 + \frac{p_q}{SLD}$$

$$V_{H_2O}^2 + V_{H_2O}\left(\frac{2cSLD - b_{H_2O}}{SLD}\right) + c^2 - \frac{p_q}{SLD} = 0$$

$$V_{H_2O} = \frac{\left(\frac{2cSLD - b_{H_2O}}{SLD}\right) \pm \sqrt{\left(\frac{2cSLD - b_{H_2O}}{SLD}\right)^2 - 4\left(c^2 - \frac{p_q}{SLD}\right)}}{2}$$

where *b* is the scattering length determined by the product of the classical electron radius (28.179 $\times 10^{-6}$ Å) and the number of electrons in the compound.

Route 2. It is assumed that for every aliphatic chain in the monolayer, there is a corresponding headgroup. To avoid empty space in the applied slab model, it is also assumed that the headgroup will cover the projected area of its corresponding aliphatic chain. If this projected area is larger than the actual headgroup, this space has to be filled with solvent molecules, in this case water. The total volume of the headgroup layer can thus be described as the sum of the carboxylic acid moiety (and possible counter ions) and solvent contributions:

$$a_t l_{HG} = V_{tot} = V_{H_2O} + V_{head}$$
$$V_{H_2O} = a_t l_{HG} - V_{head}$$

where a_t is the area of the tail calculated by the initial fitting parameters, described above.

When the results for Route 1 and Route 2 intercept, the amount of water in the headgroup layer is determined, and a value for the total headgroup volume can be calculated. This value has to be correlated to the number of electrons in the headgroup layer, which is predominantly determined by the degree of dissociation of the monolayer. For the determination of the degree of dissociation, it is assumed that one Cd-ion is bound to each dissociated carboxylate group. The newly determined SLD and thickness parameters for the headgroup can then be inserted in Motofit and fixed while the tail thickness and SLD are fitted. These fitted parameters are used to find new values for the water volume and degree of dissociation. This iterative process is continued until the there is no change in tail thickness and SLD, as well as the headgroup water volume and degree of dissociation.

*the fitting procedure was performed for a range of interfacial roughnesses, fixed and equal for the three interfaces. The interfacial roughness affects the fit the most at higher q_z and only varied within 0.5 Å for each surface pressure

Neutron fitting

As well in the neutron fitting, the headgroup and aliphatic chains were divided into separate layers, with the same orientation as described above, although with the headgroup in contact with a D_2O instead of H_2O backing. The headgroup and tail thicknesses, and the headgroup SLD for the different fatty acid ratios were determined as linear combinations of values extracted from the X-ray fitting procedure for 18-MEA and EA. A tail group SLD of -0.36×10^{-6} $Å^{-2}$ was determined from bulk crystalline EA, assumed to correspond to a well-packed monolayer. The tail group SLD was fitted between 0 and -0.36×10^{-6} $Å^{-2}$ to accommodate for molecular tilt and incomplete monolayer coverage at low surface pressures. This can be expected, as the monolayer is still patchy before isotherm lift-off, and part of the neutron beam might hit the liquid expanded phase, rather than the tilted condensed. At each interface (air–tails, tails–headgroup, and headgroups–water), a roughness parameter is added to account for capillary wave roughness in addition to texturing of the monolayer (and the underlaying water). The roughness parameter is the only parameter used to fit the data. This parameter is constrained to be identical for the three interfaces.

Supplementary X-ray and neutron reflectivity data

XRR data and appurtenant fits modelled by the fitting procedure described above, are presented in Figure S5 for 18-MEA (left) and EA (right). Resultant fitting parameters are presented for 18-MEA and EA in Table S2 and Table S3, respectively.

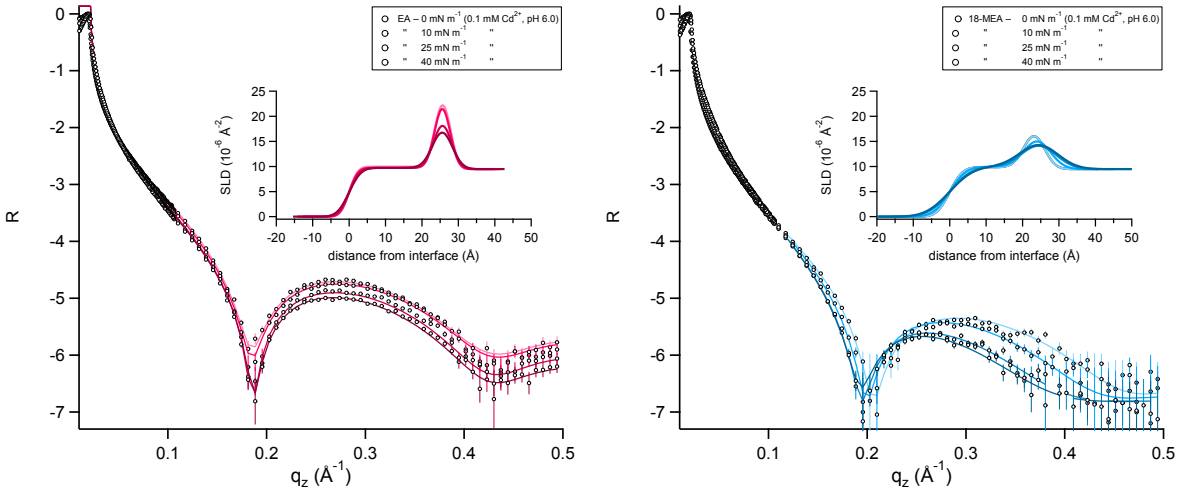

Figure S5. Normalised specular X-ray reflectivity data for EA (left) and 18-MEA (right), and appurtenant fits are represented as filled circles and lines, respectively. Reflectivity was collected at increasing surface pressure, as indicated by the darkening colour gradient of data and fits. Insets show SLD profiles as a function of distance from water interface.

Supplementary NR data and appurtenant fits modelled by the two-layer model described above, are presented in Figure S6 for 18-MEA:EA 75:25 (left) and 18-MEA:EA 38:62 (right). Resultant fitting parameters using the two-layer model are presented in Table S4–Table S8 for NR data sets presented here as well as in the main article.

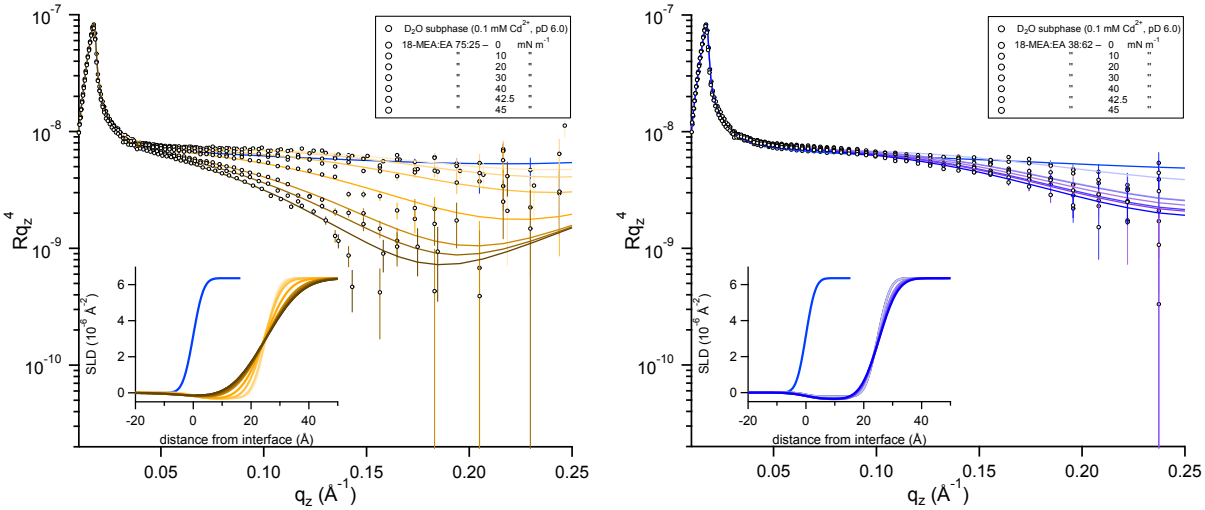

Figure S6. Specular neutron reflectometry data for 18-MEA:EA 75:25 (left) and 18-MEA:EA 38:62 (right), and appurtenant fits are represented as filled circles and lines, respectively. Reflectometry was collected at increasing surface pressure, indicated by the darkening colour gradient of data and fits. Insets show SLD profiles as a function of distance from water interface. The smaller blue markers and dashed lines represent a reference measurement on a neat D_2O-buffer subphase.

X-ray and neutron fitting results

XRR 18-MEA:EA 100:0

Table S2. X-ray reflectivity fitting parameters for 18-MEA.

Model parameter	0 mN m-1	10 mN m-1	25 mN m-1	40 mN m-1		free D_2O surface	
thickness tail (Å)	21.64	22.47	22.89	22.85			
thickness headgroup (Å)	3.13	3.20	3.36	3.46			
SLD tail (x10^{-6} Å^2)	9.85	9.96	9.96	9.96			
SLD headgroup (x10^{-6} Å^2)	24.76	25.04	25.46	27.16			
SLD backing (x10^{-6} Å^2)	9.47	9.47	9.47	9.47		9.47	
# water in headgroup	0.46	0.47	0.48	0.53			
roughness tail (Å)	2.80	3.60	4.70	5.30			
roughness headgroup (Å)	2.80	3.60	4.70	5.30			
roughness backing (Å)	2.80	3.60	4.70	5.30		2.20	
area per molecule (Å^2)	20.23	19.74	18.90	18.94		**BACKGROUND**	**SCALE**
degree of dissociation	0.62	0.60	0.63	0.77		1.50E-07	1.00

XRR 18-MEA:EA 0:100

Table S3. X-ray reflectivity fitting parameters for EA.

Model parameter	0 mN m-1	10 mN m-1	25 mN m-1	40 mN m-1		free D_2O surface	
thickness tail (Å)	23.83	23.85	23.96	23.91			
thickness headgroup (Å)	3.71	3.53	3.41	3.38			
SLD tail (x10^{-6} Å^2)	9.96	9.72	9.72	9.72			
SLD headgroup (x10^{-6} Å^2)	28.27	27.86	25.23	24.33			
SLD backing (x10^{-6} Å^2)	9.47	9.47	9.47	9.47		9.47	
# water in headgroup	0.57	0.54	0.47	0.45			
roughness tail (Å)	1.90	1.90	2.30	2.60			
roughness headgroup (Å)	1.90	1.90	2.30	2.60			
roughness backing (Å)	1.90	1.90	2.30	2.60		2.20	
area per molecule (Å^2)	18.17	18.60	18.50	18.55		BACKGROUND	SCALE
degree of dissociation	0.86	0.81	0.62	0.59		1.50E-07	1.37

NR 18-MEA:EA 100:0

Table S4. Neutron reflectivity fitting parameters for 18-MEA.

Model parameter	0 mN m^{-1}	10 mN m^{-1}	20 mN m^{-1}	25 mN m^{-1}	30 mN m^{-1}	35 mN m^{-1}	40 mN m^{-1}	42.5 mN m^{-1}	45 mN m^{-1}	free D_2O surface
thickness tail (Å)	21.64	22.59	22.52	22.88	22.80	22.94	22.85	23.23	23.21	
thickness headgroup (Å)	3.11	3.23	3.25	3.18	3.33	3.37	3.46	3.44	3.44	
SLD tail (x10^{-6} $Å^2$)	-0.245	-0.300	-0.340	-0.350	-0.360	-0.360	-0.360	-0.360	-0.360	
SLD headgroup (x10^{-6} $Å^2$)	3.033	3.003	3.052	3.074	3.071	3.081	3.092	3.101	3.100	
SLD backing (x10^{-6} $Å^2$)	6.357	6.357	6.357	6.357	6.357	6.357	6.357	6.357	6.357	6.357
roughness tail (Å)	2.83	3.1	3.8	4.3	5.1	5.7	6.9	7.3	7.8	
roughness headgroup (Å)	2.83	3.1	3.8	4.3	5.1	5.7	6.9	7.3	7.8	
roughness backing (Å)	2.83	3.1	3.8	4.3	5.1	5.7	6.9	7.3	7.8	2.83
BACKGROUND										
3.8E-7										
SCALE										
1										

NR 18-MEA:EA 75:25

Table S5. Neutron reflectivity fitting parameters for 18-MEA:EA 75:25.

Model parameter	0 mN m^{-1}	10 mN m^{-1}	20 mN m^{-1}	30 mN m^{-1}	40 mN m^{-1}	42.5 mN m^{-1}	45 mN m^{-1}	free D_2O surface
thickness tail (Å)	22.44	22.65	22.87	23.08	23.29	23.41	23.40	
thickness headgroup (Å)	3.24	3.28	3.32	3.35	3.39	3.41	3.41	
SLD tail (x10^{-6} $Å^2$)	-0.270	-0.310	-0.330	-0.360	-0.360	-0.360	-0.360	
SLD headgroup (x10^{-6} $Å^2$)	3.045	3.050	3.056	3.062	3.068	3.071	3.071	
SLD backing (x10^{-6} $Å^2$)	6.357	6.357	6.357	6.357	6.357	6.357	6.357	6.357
roughness tail (Å)	2.83	3.4	4.5	6.3	8.2	8.9	9.7	
roughness headgroup (Å)	2.83	3.4	4.5	6.3	8.2	8.9	9.7	
roughness backing (Å)	2.83	3.4	4.5	6.3	8.2	8.9	9.7	2.83
BACKGROUND								
3.80E-07								
SCALE								
1								

NR 18-MEA:EA 50:50

Table S6. Neutron reflectivity fitting parameters for 18-MEA:EA 50:50.

Model parameter	0 mN m^{-1}	10 mN m^{-1}	20 mN m^{-1}	30 mN m^{-1}	40 mN m^{-1}	42.5 mN m^{-1}	45 mN m^{-1}	free D_2O surface
thickness tail (Å)	22.89	23.04	23.20	23.35	23.50	23.59	23.58	
thickness headgroup (Å)	3.37	3.37	3.37	3.37	3.37	3.37	3.37	
SLD tail (x10^{-6} Å^2)	-0.360	-0.360	-0.360	-0.360	-0.360	-0.360	-0.360	
SLD headgroup (x10^{-6} Å^2)	3.075	3.068	3.060	3.053	3.045	3.041	3.041	
SLD backing (x10^{-6} Å^2)	6.357	6.357	6.357	6.357	6.357	6.357	6.357	6.357
roughness tail (Å)	2.83	3.8	5.1	6.8	9.3	9.7	10.6	
roughness headgroup (Å)	2.83	3.8	5.1	6.8	9.3	9.7	10.6	
roughness backing (Å)	2.83	3.8	5.1	6.8	9.3	9.7	10.6	2.83
BACKGROUND								
3.80E-07								
SCALE								
1								

NR 18-MEA:EA 38:62

Table S7. Neutron reflectivity fitting parameters for 18-MEA:EA 38:62.

Model parameter	0 mN m^{-1}	10 mN m^{-1}	20 mN m^{-1}	30 mN m^{-1}	40 mN m^{-1}	42.5 mN m^{-1}	45 mN m^{-1}	free D_2O surface
thickness tail (Å)	23.13	23.25	23.37	23.49	23.61	23.64	23.67	
thickness headgroup (Å)	3.45	3.43	3.41	3.40	3.39	3.37	3.36	
SLD tail (x10^{-6} Å^2)	-0.221	-0.360	-0.360	-0.360	-0.360	-0.360	-0.360	
SLD headgroup (x10^{-6} Å^2)	3.090	3.090	3.062	3.055	3.048	3.041	3.034	
SLD backing (x10^{-6} Å^2)	6.357	6.357	6.357	6.357	6.357	6.357	6.357	6.357
roughness tail (Å)	2.82	4.1	4.1	4.3	4.6	4.6	4.9	
roughness headgroup (Å)	2.82	4.1	4.1	4.3	4.6	4.6	4.9	
roughness backing (Å)	2.82	4.1	4.1	4.3	4.6	4.6	4.9	2.83
BACKGROUND								
1.70E-07								
SCALE								
1								

NR 18-MEA:EA 25:75

Table S8. Neutron reflectivity fitting parameters for 18-MEA:EA 25:75.

Model parameter	0 mN m^{-1}	10 mN m^{-1}	20 mN m^{-1}	25 mN m^{-1}	30 mN m^{-1}	35 mN m^{-1}	40 mN m^{-1}	42.5 mN m^{-1}	45 mN m^{-1}	free D_2O surface
thickness tail (Å)	23.37	23.46	23.55	23.59	23.64	23.68	23.73	23.77	23.77	
thickness headgroup (Å)	3.52	3.48	3.44	3.42	3.40	3.38	3.36	3.33	3.33	
SLD tail (x10^{-6} $Å^2$)	-0.330	-0.360	-0.360	-0.360	-0.360	-0.360	-0.360	-0.360	-0.360	
SLD headgroup (x10^{-6} $Å^2$)	3.105	3.085	3.064	3.053	3.043	3.033	3.022	3.011	3.012	
SLD backing (x10^{-6} $Å^2$)	6.357	6.357	6.357	6.357	6.357	6.357	6.357	6.357	6.357	6.357
roughness tail (Å)	2.83	2.6	2.8	2.85	2.9	3.1	3.4	3.6	3.7	
roughness headgroup (Å)	2.83	2.6	2.8	2.85	2.9	3.1	3.4	3.6	3.7	
roughness backing (Å)	2.83	2.6	2.8	2.85	2.9	3.1	3.4	3.6	3.7	2.83
BACKGROUND										
3.80E-07										
SCALE										
1										

References

1 C. A. Schneider, W. S. Rasband and K. W. Eliceiri, *Nat. Methods*, 2012, **9**, 671–675.