Mixing behavior in binary anionic gemini surfactant – perfluorinated fatty acid Langmuir monolayers.

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Supporting Information

Figure S1: Compressibility modulus plots (Cs^{-1} vs. π) for PF:Ace(12)-2-Ace(12) mixed monolayer films. (A) 4:1, B) 3:1, C) 2:1, D) 1:2, E) 1:3, F) 1:4.

Figure S2: BAM images of pure monolayer films. A) PF, B) Ace(12)-2-Ace(12). Images were collected at π = 30.0 mN·m^{-1} and T = 21±1 °C.

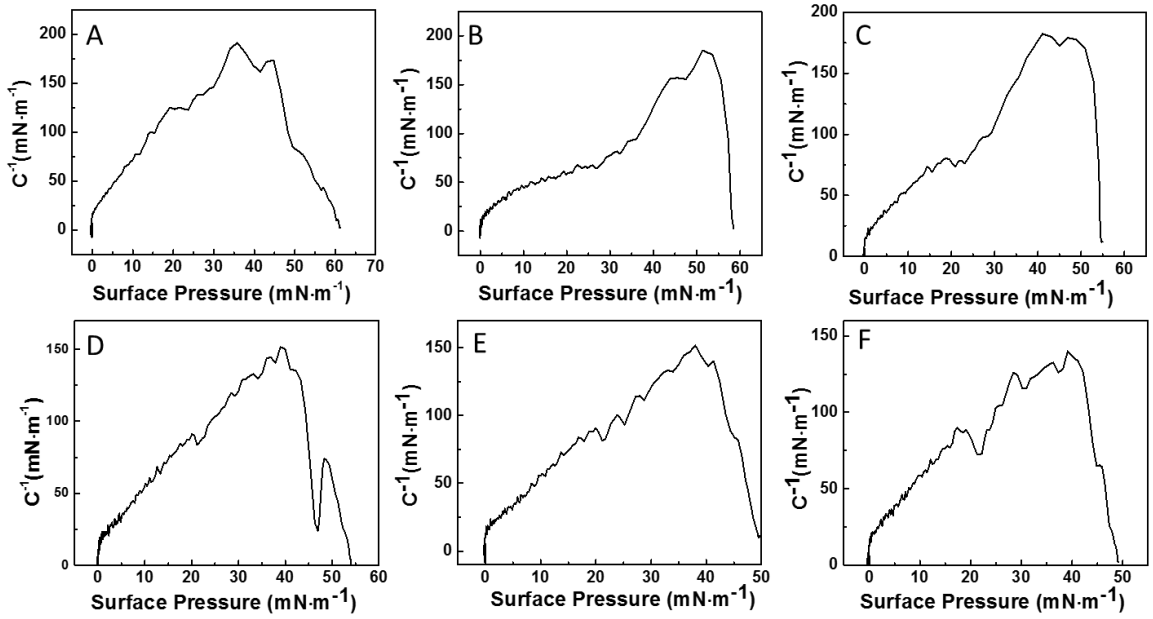
Figure S3: AFM images (15 μm × 15 μm) and corresponding cross-sectional analysis of LB films of mixed monolayers (composition of mixtures shown as insets) deposited onto glass substrates.

Table S1. XR parameters for head layer of monolayer films at π = 30.0 mN·m^{-1}.

Table S2. XR parameters for tail layer of monolayer films at π = 30.0 mN·m^{-1}.

Figure S4: GIXD patterns for pure PF and pure Ace(12)-2-Ace(12), with corresponding plot of intensity along q_z at $\pi = 30.0$ mN·m^{-1}.

Figure S5: GIXD patterns for mixed monolayer films of PF:Ace(12)-2-Ace(12) at 1:1, 1:2, 1:2.5, 1:3, 1:4, with corresponding plot of intensity along q_z at $\pi = 30.0$ mN·m^{-1}.



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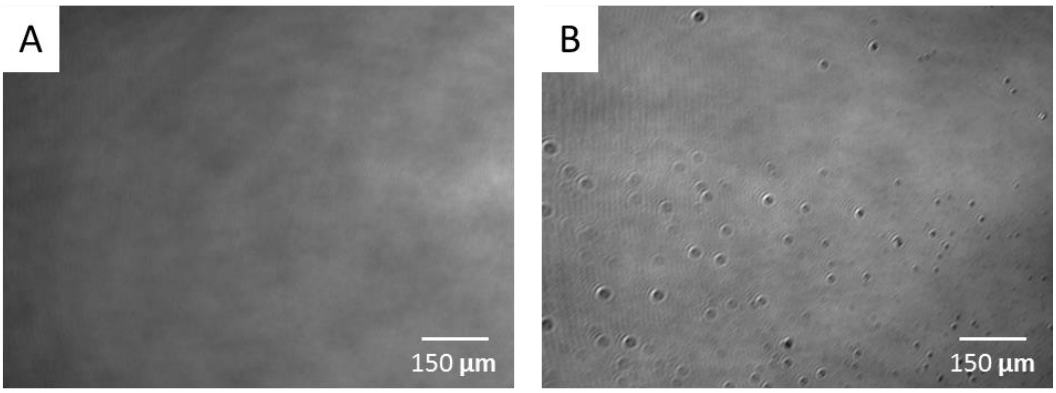

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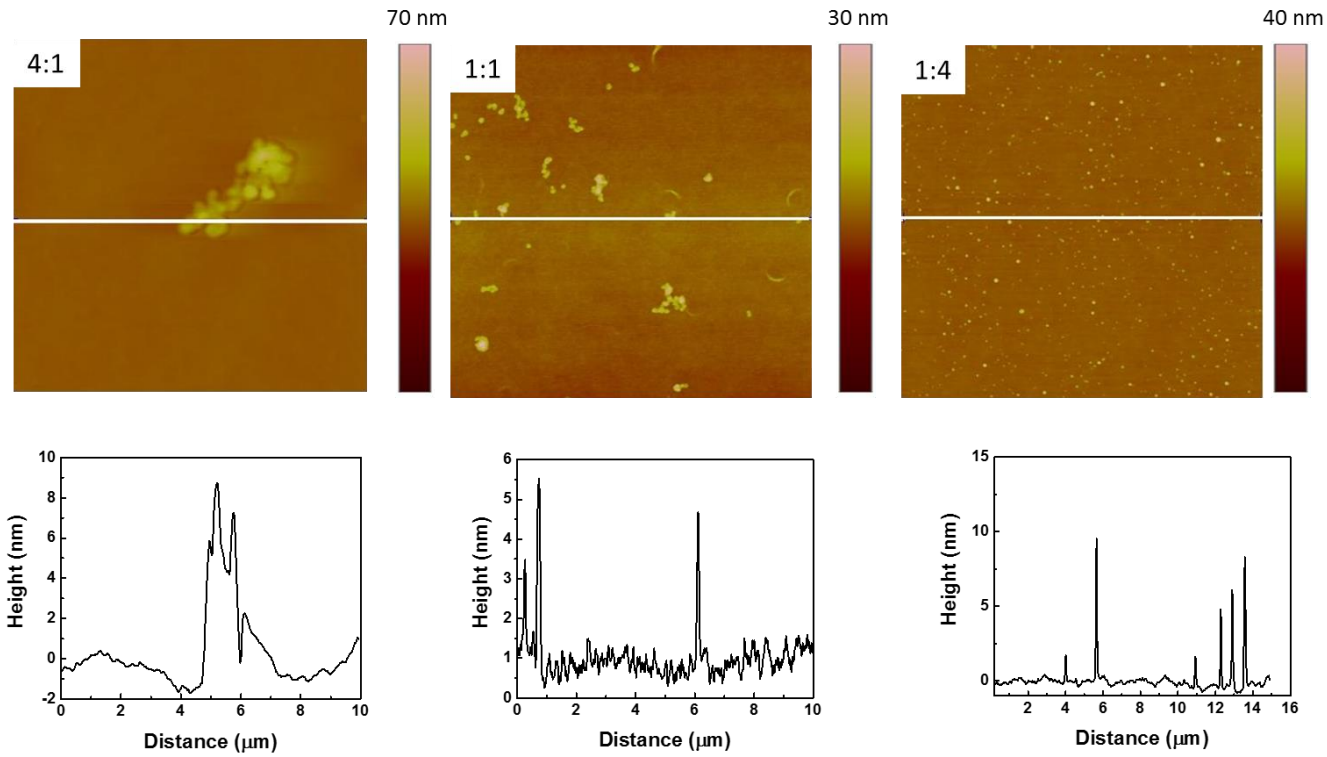


Figure S3: AFM images (15 μm × 15 μm) and corresponding cross-sectional analysis of LB films of mixed monolayers (composition of mixtures shown as insets) deposited onto glass substrates.

Samples for AFM imaging were prepared by Langmuir Blodgett deposition, using the same trough system as described in the main article. The mixed surfactant solutions were spread on a clean water subphase surface and the spreading solvent was allowed to evaporate thoroughly before film compression. Films were compressed to a surface pressure of 30.0 $mN \cdot m^{-1}$ at a rate of 2 - 4 $Å^2$ $molecule^{-1}$ $minute^{-1}$ and were allowed to stabilize for ~ 30 minutes before the solid substrate was pulled upwards through the film at a rate of 5 mm $minute^{-1}$. Deposited films were allowed to dry thoroughly at room temperature before imaging in the AFM.

Specular X-ray Reflectivity (XR)

XR provides the electron density distribution of the monolayer film across the interface. The electron density profile was extracted from a homogeneous two-slab model describing the head group and the tail chains of the lipid molecule.[1] The StochFit 1.7.0.[2] software was used in performing the fit, with parameters such as layer length, electron density (ρ/ρ_{H2O}), interfacial roughness, and subphase roughness obtained by χ^2 minimization.[2]

Table S1. XR parameters for head layer of monolayer films at π = 30.0 mN·m^{-1}.

Monolayer composition	Electron density (ρ/ρ_{H2O})	Interfacial roughness (Å)
Pure Ace(12)-2-Ace(12)	1.18 ± 0.01	1.6 ± 0.4
1:1	1.382 ± 0.001	3.112 ± 0.001
2:1	1.423 ± 0.007	3.162 ± 0.008
2.5:1	1.42 ± 0.02	3.12 ± 0.02
3:1	1.43 ± 0.03	2.93 ± 0.01
4:1	1.29 ± 0.03	3.02 ± 0.01
Pure PF	1.379 ± 0.001	2.041 ± 0.001

Table S2. XR parameters for tail layer of monolayer films at π = 30.0 mN·m^{-1}.

Monolayer composition	Electron density (ρ/ρ_{H2O})	Interfacial roughness (Å)
Pure Ace(12)-2-Ace(12)	0.89 ± 0.06	3.9 ± 0.2
1:1	1.250 ± 0.001	3.112 ± 0.001
2:1	1.363 ± 0.008	3.162 ± 0.008
2.5:1	1.38 ± 0.03	3.12 ± 0.02
3:1	1.52 ± 0.02	2.93 ± 0.01
4:1	1.64 ± 0.01	3.02 ± 0.01
Pure PF	1.927 ± 0.001	2.997 ± 0.001

The average subphase roughness in all monolayer compositions was 2.88 ± 0.04 Å.

Glancing Incidence X-ray Diffraction (GIXD)

GIXD provides information about crystallographic structure of the monolayer directly at the air-water interface. Bragg peak positions were used to obtain d-spacing of the diffracting planes according to the relation $d = (2\pi)/q_{xy}$.[1] A Lorentzian function was used in the fitting of the Bragg peaks, in order to obtain fitting parameters. The coherence length (L_{xy}) was obtained according to the Scherrer relation, $L_{xy} = (0.9 \times 2\pi)/W$[1] where 'W' is the peak's full width at half maximum (FWHM) corrected for instrumental resolution ($W = (FWHM_{measured}^2 - FWHM_{res}^2)^{1/2}$, with $FMWHM_{res}$ being the slit-limited instrumental resolution, with a value of 6×10^{-3} Å^{-1} for the system

used here). Bragg rods were analysed from the diffracted X-ray beam intensity along the vertical momentum transfer component (q_z) according to the relation $q_z = (2\pi/\lambda)\,[\sin(\alpha_i) + \sin(\alpha_f)] \approx (2\pi/\lambda)\,\sin(\alpha_f)$.[1]

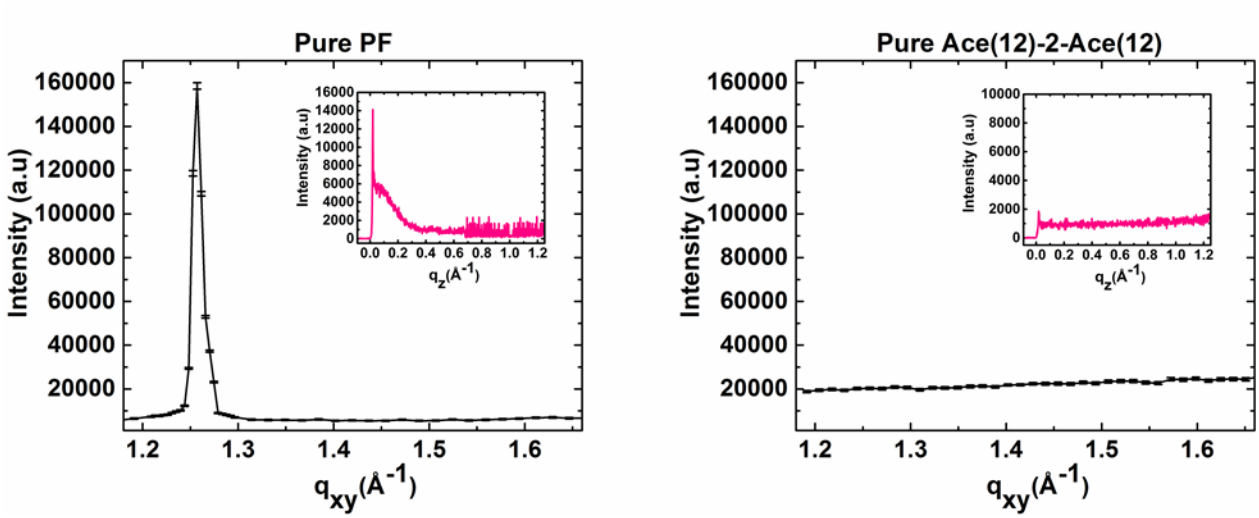
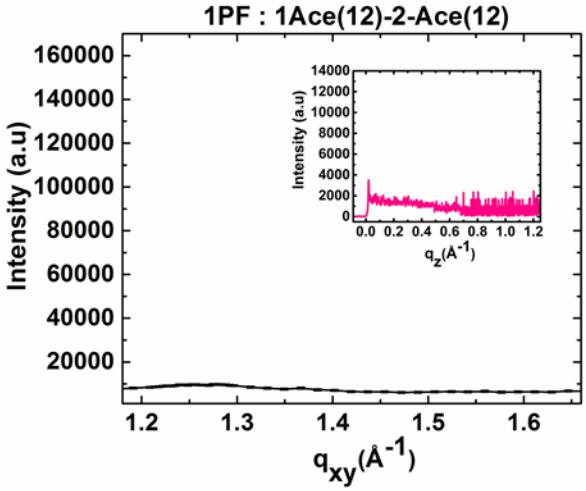
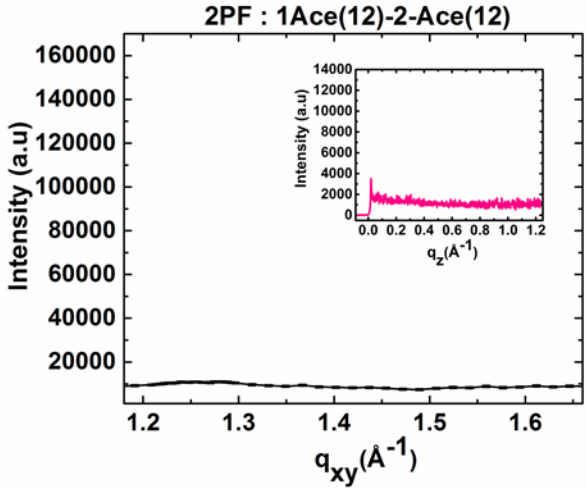
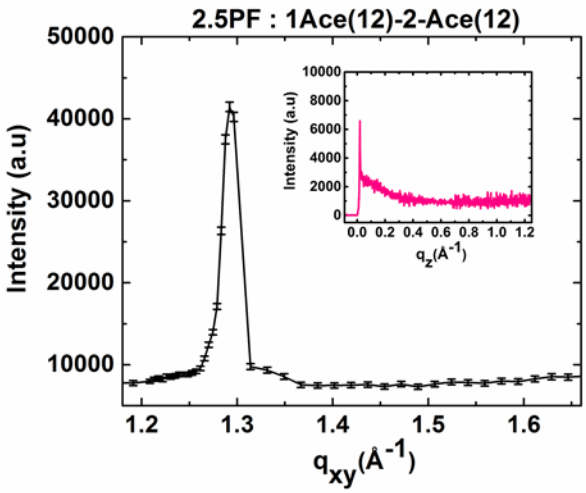
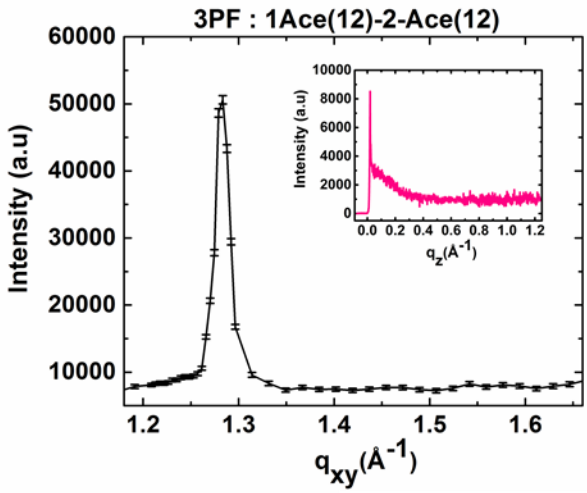


Figure S4: GIXD patterns for pure PF and pure Ace(12)-2-Ace(12), with corresponding plots of intensity along q_z at $\pi = 30.0$ mN·m^{-1}.


1PF : 1Ace(12)-2-Ace(12)
Intensity (a.u)
q_{xy}(Å^{-1})
Intensity (a.u)
q_z(Å^{-1})


2PF : 1Ace(12)-2-Ace(12)
Intensity (a.u)
q_{xy}(Å^{-1})
Intensity (a.u)
q_z(Å^{-1})


2.5PF : 1Ace(12)-2-Ace(12)
Intensity (a.u)
q_{xy}(Å^{-1})
Intensity (a.u)
q_z(Å^{-1})


3PF : 1Ace(12)-2-Ace(12)
Intensity (a.u)
q_{xy}(Å^{-1})
Intensity (a.u)
q_z(Å^{-1})

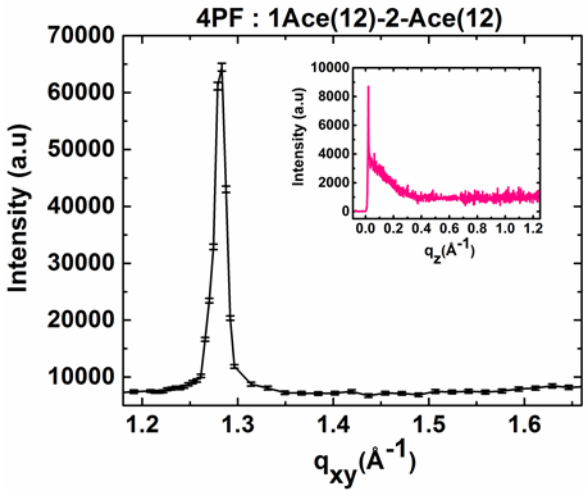

4PF : 1Ace(12)-2-Ace(12)
Intensity (a.u)
q_{xy}(Å^{-1})
Intensity (a.u)
q_z(Å^{-1})

Figure S5: GIXD patterns for mixed monolayer films of PF:Ace(12)-2-Ace(12) at 1:1, 1:2, 1:2.5, 1:3, 1:4, with corresponding plots of intensity along q_z at $\pi = 30.0$ mN·m^{-1}.

References

(1) Jensen, T. R.; Balashev, K.; Bjornholm, T.; Kjaer, K. Novel methods for studying lipids and lipases and their mutual interaction at interfaces. Part II. Surface sensitive synchrotron X-ray scattering. *Biochimie* **2001,** 83 (5), 399-408.

(2) Martynowycz, M. W.; Hu, B.; Kuzmenko, I.; Bu, W.; Hock, A.; Gidalevitz, D. Monomolecular siloxane film as a model of single site catalysts. *J. Am. Chem. Soc.* **2016,** 138, 12432-12439.