The monolayer ionization degree ($\alpha$) is determined by the proton concentration at the surface ([H$^+$]$_s$) and the surface equilibrium constant for the acid group dissociation ($K_s$):

$$\frac{\alpha}{1 - \alpha} = \frac{K_s}{[H^+]_s}$$  \hspace{1cm} (2)

If the proton concentration in the bulk ([H$^+$]$_b$) is known, the surface proton concentration can be calculated using the Boltzmann equation,

$$[H^+]_s = [H^+]_b \exp\left(-\frac{ze\varphi}{kT}\right)$$  \hspace{1cm} (3)

where $z$ denotes the charge number of monolayers, $e$ is the elementary electric charge, and $\varphi$ is the potential difference of the ionic layer. Furthermore, the Gouy-Chapman approach$^1$ is used to relate $\varphi_0$ to the charge density ($\rho \approx aze/A$) under the condition of NaCl solution at 298.2 K,

$$\varphi_0 = \frac{2kT}{ze} \sinh^{-1}\left(1.37\frac{\alpha}{\sqrt{c}}\right)$$  \hspace{1cm} (4)

where $c$ (in mol/L) is the 1-1 electrolyte concentration. As for the negatively charged monolayer ($z = -1$), the following equation is derived from combining eqs. (2)–(4).

$$\text{pH}_b = pK_s + \log \frac{\alpha}{1 - \alpha} + 0.87 \sinh^{-1}\left(1.37\frac{\alpha}{\sqrt{c}}\right)$$  \hspace{1cm} (5)

Reference

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**Fig. S1** The $\pi-A$ and $\Delta V-A$ isotherms of (A) PA and (B) Hel 13-5 monolayers on a 0.02 M Tris buffer solution with 0.13 M NaCl at 298.2 K. The subphase pH is prepared to pH 6.4, 7.4, and 8.4.
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**Fig. S2**  Typical AFM topographic images of the DPPC/PA (= 90/10, by weight)/Hel 13-5 preparation ($X_{\text{Hel 13-5}} = 0.025$) at 35, 45, and 55 mN m$^{-1}$ on a 0.02 M Tris buffer solution (pH 6.4–8.4) with 0.13 M NaCl at 298.2 K. All images exhibit LC domains of the ternary monolayer, which are expressed by bright contrast in the FM images. The cross-sectional profiles along the scanning line (white lines) are given just below the respective AFM images. The height difference between the arrowheads is indicated in the cross-sectional profile.
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Fig. S3  Typical AFM topographic images of the DPPC/TD (= 90/10, by weight)/Hel 13-5 and DPPC/HD (= 90/10, by weight)/Hel 13-5 preparations ($X_{\text{Hel 13-5}} = 0.025$) at 35, 45, and 55 mN m$^{-1}$ on a 0.02 M Tris buffer solution (pH 7.4) with 0.13 M NaCl at 298.2 K. All images exhibit LC domains of the ternary monolayer, which are expressed by bright contrast in the FM images. The cross-sectional profiles along the scanning line (white lines) are given just below the respective AFM images. The height difference between the arrowheads is indicated in the cross-sectional profile.
Fig. S4  Typical AFM topographic images of the DPPC/PA(= 90/10, by weight) preparation at 35, 45, and 55 mN m$^{-1}$ on a 0.02 M Tris buffer solution (pH 7.4) with 0.13 M NaCl at 298.2 K. The cross-sectional profiles along the scanning line (white lines) are given just below the respective AFM images. The height difference between the arrowheads is indicated in the cross-sectional profile.