Supplemental Information

Effects of Cu(II) on the Formation and Orientation of an Arachidic Acid Langmuir-Blodgett Film

Briana A. Capistran, and G. J. Blanchard*
Michigan State University
Department of Chemistry
578 S. Shaw Lane
East Lansing, MI 48824

*Author to whom correspondence should be addressed. Email: blanchard@chemistry.msu.edu

1. BAM images from pH dependence experiments

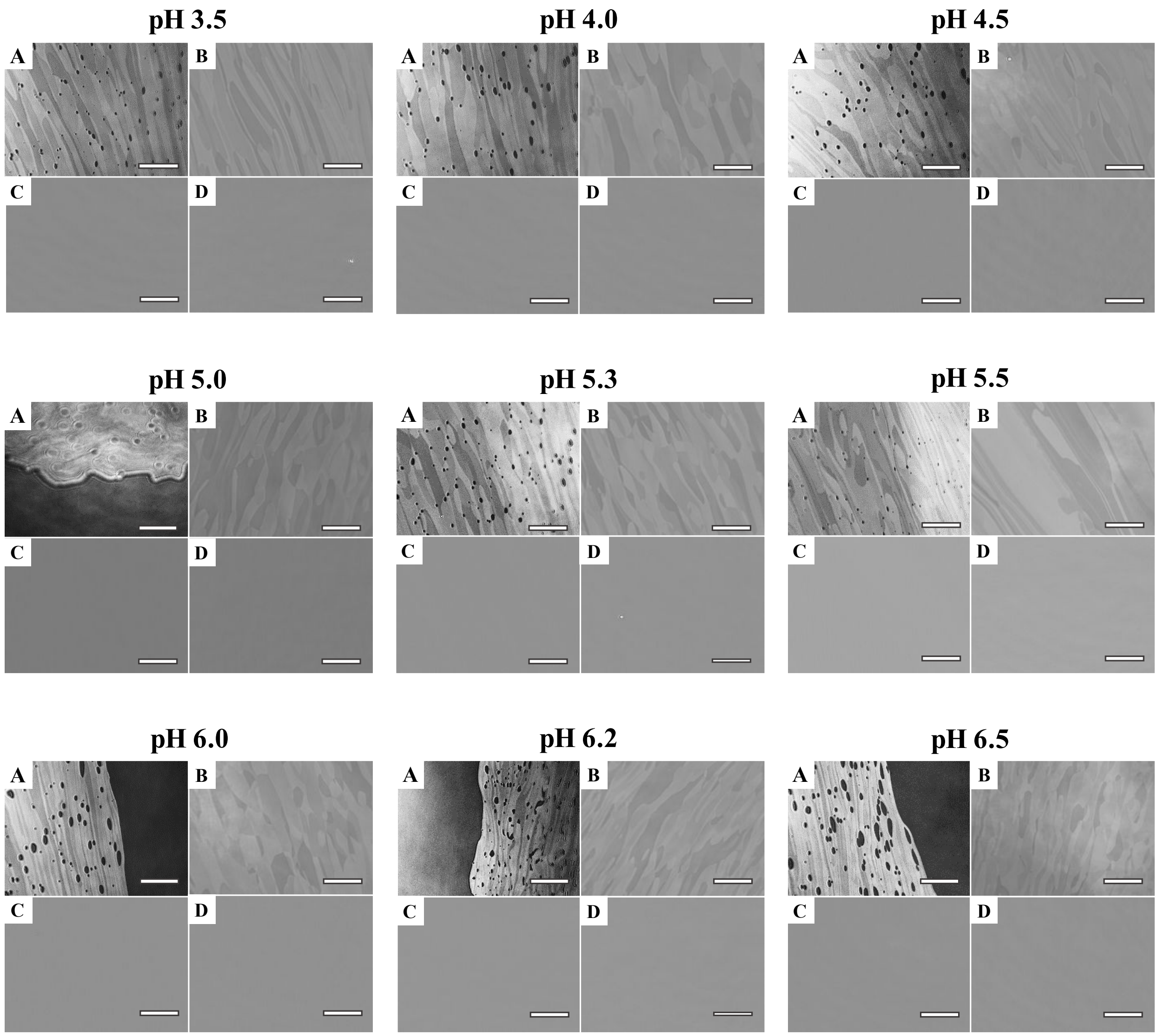

Figure S1. BAM images of AA monolayer formed on plain water subphase at incremental pH conditions across pH range. Each set of images is of the same monolayer at increasing surface pressures. For each set, individual images correspond to (A) 0.25 mN/m, (B) 10 mN/m, (C) 30 mN/m, and (D) 50 mN/m. Scale bars represent 100 μm.

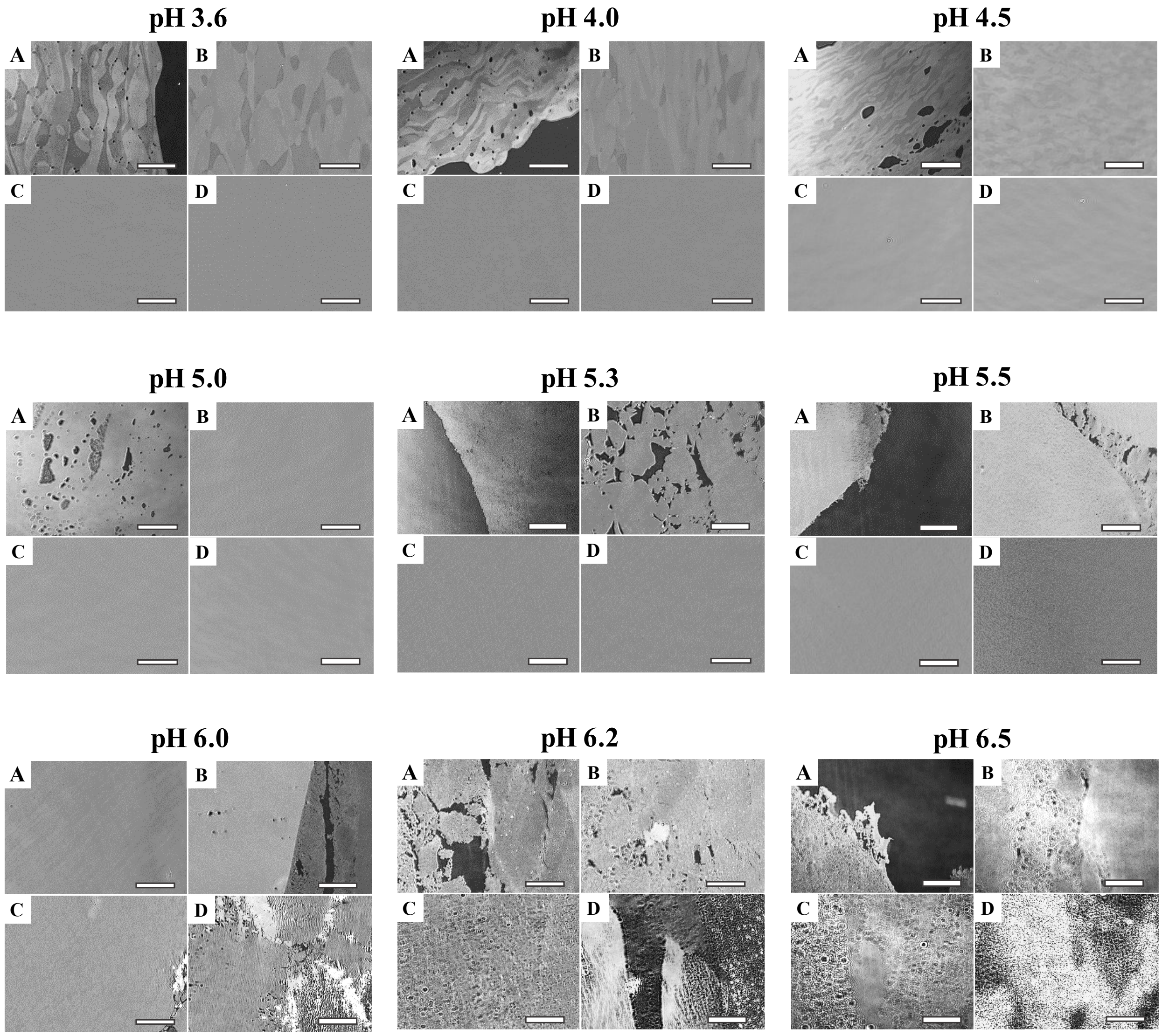

Figure S2. BAM images of AA monolayer formed on 1 mM Cu^{2+} water subphase at incremental pH conditions across pH range. Each set of images is of the same monolayer at increasing surface pressures. For each set, individual images correspond to (A) 0.25 mN/m, (B) 10 mN/m, (C) 30 mN/m, and (D) 50 mN/m. Scale bars represent 100 μm.

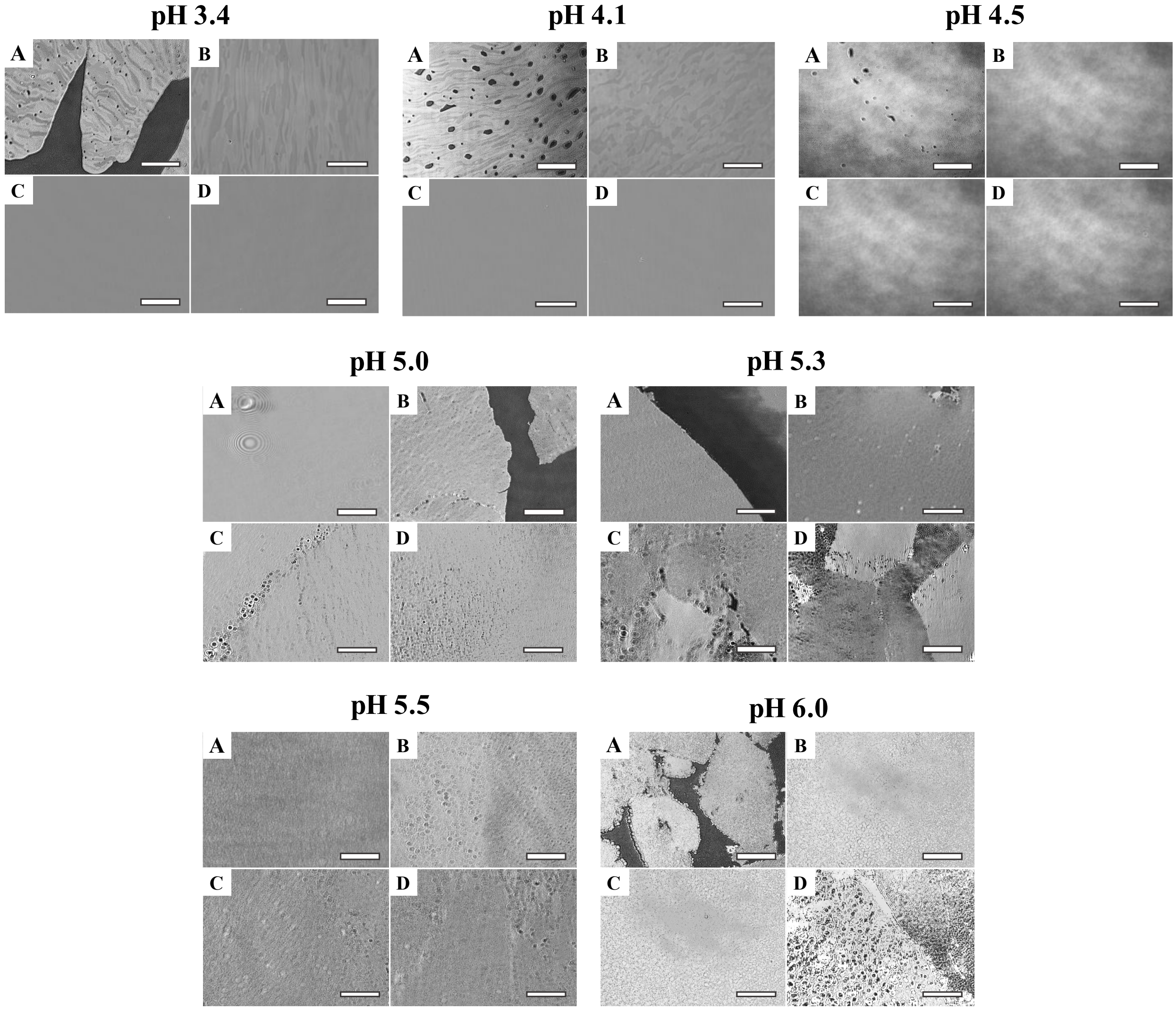

Figure S3. BAM images of AA monolayer formed on 5 mM Cu^{2+} water subphase at incremental pH conditions across pH range. Each set of images is of the same monolayer at increasing surface pressures. For each set, individual images correspond to (A) 0.25 mN/m, (B) 10 mN/m, (C) 30 mN/m, and (D) 50 mN/m. Scale bars represent 100 μm. Experiments for pH 6.2 and 6.5 subphases not possible due to the precipitation of $CuOH_2$ as a result of the increased Cu^{2+} concentration.

2. Mathematical model workflow

For the mathematical model plots of the fractional amount of species present at the subphase surface at a given pH and Cu^{2+} concentration, the following reactions and corresponding equilibria expressions were used:

$$\mathrm{Cu^{2+} + AA^- \overset{K_1}{\rightleftharpoons} CuAA^+ + AA^- \overset{K_2}{\rightleftharpoons} CuAA_2} \tag{1.1}$$

$$K_1 = \frac{[\mathrm{CuAA^+}]}{[\mathrm{Cu^{2+}}][\mathrm{AA^-}]} \tag{1.2}$$

$$K_2 = \frac{[\mathrm{CuAA_2}]}{[\mathrm{CuAA^+}][\mathrm{AA^-}]} \tag{1.3}$$

where K_1 and K_2 represent equilibrium constants for the formation of copper (II) monoacetate ($Cu(OAc)^+$) and copper (II) diacetate ($Cu(OAc)_2$) to represent the interactions of Cu^{2+} ions with the carboxylate headgroups of the arachidate molecules. Literature values for K_1 and K_2 were used ($K_1 = 140$; $K_2 = 11$);[1]

$$\mathrm{HAA \overset{K_a}{\rightleftharpoons} H^+ + AA^-} \tag{2.1}$$

$$K_a = \frac{[\mathrm{H^+}][\mathrm{AA^-}]}{[\mathrm{HAA}]} \tag{2.2}$$

where the literature value for the pK_a of arachidic acid was used ($pK_a = 5.4$);[2]

$$\mathrm{Cu^{2+} + OH^- \overset{K_{OH_1}}{\rightleftharpoons} Cu(OH)^+ \overset{K_{OH_2}}{\rightleftharpoons} Cu(OH)_2} \tag{3.1}$$

$$K_{OH_1} = \frac{[\mathrm{CuOH^+}]}{[\mathrm{Cu^{2+}}][\mathrm{OH^-}]} \tag{3.2}$$

$$K_{OH_2} = \frac{[\mathrm{Cu(OH)_2}]}{[\mathrm{CuOH^+}][\mathrm{OH^-}]} \tag{3.3}$$

where the K_{sp} for copper (II) hydroxide (2×10^{-20})[1] was used as the product of K_{OH_1} and K_{OH_2}. Using this plus the expression for the dissociation of water molecules

$$K_w = [\mathrm{H^+}][\mathrm{OH^-}] \tag{4}$$

an expression for the concentration of free Cu^{2+} ions in the subphase was derived:

$$[\mathrm{Cu^{2+}}] = \frac{C_{\mathrm{Cu}} \, {K_{sp}}/{K_w^{\,2}} \, [\mathrm{H^+}]^2}{1 + {K_{sp}}/{K_w^{\,2}} \, [\mathrm{H^+}]^2} \tag{5}$$

Among the variables in Eqs. 1.2 – 5, the independent variables are $[H^+]$ (pH) and $[Cu^{2+}]$ (subphase concentration), and the dependent variables are [HAA], $[AA^-]$, $[CuAA^+]$, and $[CuAA_2]$.

Rearranging the above equilibria expressions to solve for each of the dependent variables and assigning each one an arbitrary variable, we get:

$$[\mathrm{AA^-}] = \Phi_1 = \frac{K_a[\mathrm{HAA}]}{[\mathrm{H^+}]} \tag{6}$$

$$[\mathrm{CuAA^+}] = \Phi_2 = K_1[\mathrm{Cu^{2+}}][[\mathrm{AA^-}] \tag{7}$$

$$[\mathrm{CuAA_2}] = \Phi_3 = K_2[\mathrm{CuAA^+}][\mathrm{AA^-}] \tag{8}$$

$$[\mathrm{HAA}] = 1 - \Phi_1 - \Phi_2 - \Phi_3 \tag{9}$$

Substituting Eq. 7 into Eq. 8, we get:

$$[\mathrm{CuAA_2}] = \Phi_3 = K_1K_2[\mathrm{Cu^{2+}}][\mathrm{AA^-}]^2 \tag{10}$$

Replacing the [HAA] variables with the equivalent variables defined in Eq. 8 and all $[AA^-]$ species with Φ_1, the four dependent variables become:

$$[\mathrm{HAA}] = 1 - \Phi_1 - \Phi_2 - \Phi_3 \tag{9}$$

$$[\mathrm{AA^-}] = \Phi_1 = \frac{K_a}{[\mathrm{H^+}]}(1 - \Phi_1 - \Phi_2 - \Phi_3) \tag{11}$$

$$[\mathrm{CuAA^+}] = \Phi_2 = K_1[\mathrm{Cu^{2+}}]\Phi_1 \tag{12}$$

$$[\mathrm{CuAA_2}] = \Phi_3 = K_1K_2[\mathrm{Cu^{2+}}]\Phi_1^{\,2} \tag{13}$$

Putting all of the unknown variables in terms of Φ_1, the expression for $[AA^-]$ becomes

$$[\mathrm{AA^-}] = \Phi_1 = \frac{K_a}{[\mathrm{H^+}]}(1 - \Phi_1 - K_1[Cu^{2+}]\Phi_1 - K_1K_2[Cu^{2+}]\Phi_1^{\,2}) \tag{14.1}$$

Distributing the $\frac{K_a}{[\mathrm{H^+}]}$ term across the terms in parentheses and solving for zero, a polynomial expression is formed in which Φ_1 is the unknown variable:

$$0 = \frac{K_a}{[\mathrm{H^+}]} - \left(1 + \frac{K_a}{[\mathrm{H^+}]} + \frac{K_aK_1}{[\mathrm{H^+}]}[\mathrm{Cu^{2+}}]\right)\Phi_1 - \frac{K_aK_1K_2}{[\mathrm{H^+}]}[\mathrm{Cu^{2+}}]\Phi_1^{\,2} \tag{14.2}$$

Using the quadratic equation, the value of Φ_1 can be solved for and used to solve for the values of [$CuAA^+$] and [$CuAA_2$] in Eqs. 12 and 13, respectively. Microsoft Excel was used to calculate the values of each species from pH 2 – 7.

3. Ellipsometry thickness data

Subphase pH	Thickness (Å)
3.5	26.1 ± 0.3
4.0	26.6 ± 0.5
4.5	27.1 ± 0.4
5.0	30.4 ± 0.8
5.3	29.8 ± 1.0
5.4	29.9 ± 0.4
6.0	31.8 ± 0.6
6.2	31.9 ± 0.6
6.4	33.4 ± 0.4

Table S1. Numerical ellipsometric thickness data for AA films formed on 1 mM Cu^{2+} subphase at each pH and deposited at the solid phase. Thickness values are averages of 20 individual measurements. Errors reported are standard deviations.

Subphase pH	Thickness (Å)
3.6	24.2 ± 0.8
4.0	26.2 ± 0.3
46	27.4 ± 0.4
5.1	28.7 ± 1.0
5.4	28.4 ± 0.3
5.6	28.4 ± 0.4
6.0	29.0 ± 0.4
6.2	29.3 ± 0.7
6.5	31.3 ± 0.6

Table S2. Numerical ellipsometric thickness data for AA films formed on 1 mM Cu^{2+} subphase at each pH and deposited at surface pressures indicative of a typical collapsed film. Thickness values are averages of 20 individual measurements. Errors reported are standard deviations.

References

1. Skoog, D. A.; West, D. M. *Fundamentals of Analytical Chemistry*. 3rd ed. ed.; Holt, Rinehart and Winston: New York, 1963.

2. Kurnaz, M. L.; Schwartz, D. K. Morphology of Microphase Separation in Arachidic Acid-Cadmium Arachidate Langmuir-Blodgett Multilayers. *J. Phys. Chem.* **1996,** *100*, 11113-11119.