

## Supplementary Information

### Monolayer Formation

Using the conditions delineated in the Experimental section of the manuscript, film formation was attempted on the Ti-6Al-4V and its component oxides. In the subsequent tables, the resulting CH<sub>2</sub> symmetric and asymmetric values for each sample, as determined by DRIFT spectroscopy, can be found after deposition and sonication. Only substrates with *all-trans* alkyl chains through sonication are considered to be ordered, stable films. An *all-trans* alkyl chain film will have methylene peaks with  $\nu_{\text{CH}_2\text{asymm}} < 2918 \text{ cm}^{-1}$  and  $\nu_{\text{CH}_2\text{symm}} < 2850 \text{ cm}^{-1}$ . Methylene peaks at wavenumbers greater than these indicate a film with a liquid-like structure with *gauche* alkyl chain interactions. Table S1 summarizes the protocols used in attempted film formation on the oxide surfaces. Tables S2 and S3 contain the results obtained using Protocol 1 for triacontanoic and octacosanoic acid, respectively. Tables S4–S8 show the results obtained for hexacosanoic, tetracosanoic, docosanoic, eicosanoic and octadecanoic acids, respectively, using the six protocols described here.

#### Protocol 1

Protocol 1 utilized a TLC aerosol spray deposition method. Cleaned coupons were cooled in a glass dish on ice for one hour, and then a 1 mM acid solution was sprayed onto the coupons. Following the spraying, coupons were immediately transferred to the 100 °C oven. Coupons remained in the oven for 30 minutes. Following the 30 minutes, coupons were removed and placed back on ice for 20 minutes. This entire procedure was repeated two additional times, for three total cycles.

#### Protocol 2

Protocol 2 utilized a TLC aerosol spray deposition method. Cleaned coupons were cooled in a glass dish on ice for one hour, and then a 1 mM acid solution was sprayed onto the coupons. Following the spraying, coupons were immediately transferred to the 120 °C oven. Coupons remained in the oven for 30 minutes. Following the 30 minutes, coupons were removed and placed back on ice for 20 minutes. This entire procedure was repeated two additional times, for three total cycles.

#### Protocol 3

Protocol 3 utilized a TLC aerosol spray deposition method. The coupons were first cooled on ice in a glass dish for one hour then sprayed with a 1 mM acid solution. Coupons were immediately transferred to a 100 °C oven for 45 minutes. Coupons were placed back on ice for 20 minutes and cooled before the next spray. This procedure was repeated an additional four times.

#### Protocol 4

Protocol 4 utilized a TLC aerosol spray deposition method. Ti-6Al-4V coupons were placed in a glass dish on ice for one hour. A 1 mM acid solution was sprayed onto the coupons, and solvent is removed at ambient conditions. After solvent removal coupons were placed into a 100 °C oven for 30 minutes.

Once removed from the oven, coupons were cooled for 20 minutes. The procedure was repeated two additional times.

### Protocol 5

Protocol 5 utilized a TLC aerosol spray deposition method. Ti-6Al-4V coupons were placed in a glass dish on ice for one hour. A 1 mM acid solution was sprayed onto the coupons, and solvent is removed using a 0.1 torr vacuum line. After solvent removal coupons were placed into a 100 °C oven for 30 minutes. Once removed from the oven, coupons were cooled for 20 minutes. The procedure was repeated four additional times.

### Protocol 6

Protocol 6 utilized a solution deposition method. Ti-6Al-4V coupons were placed in a glass dish on ice for one hour. A 2 mM acid solution was heated to 50 °C and cold coupons were immersed for 3 hours. After 3 hours the coupons were removed and placed into a 100 °C oven.

**Table S1.** Protocols Attempted on the oxide surfaces of Ti-6Al-4V, Ti, Al and V.

| Protocol | Organic acid | Method used          | Solution conc. (mM) | Cooling method | Sprays | Solvent removal   | Oven time (min) | Oven temp. (°C) |
|----------|--------------|----------------------|---------------------|----------------|--------|-------------------|-----------------|-----------------|
| 1        | ODA-TAA      | TLC Spray            | 1                   | Ice, 1 hr.     | 3      | Oven              | 30              | 100             |
| 2        | ODA-HCA      | TLC Spray            | 1                   | Ice, 1 hr.     | 3      | Oven              | 30              | 120             |
| 3        | ODA-HCA      | TLC Spray            | 1                   | Ice, 1 hr.     | 5      | Oven              | 45              | 100             |
| 4        | ODA-HCA      | TLC Spray            | 1                   | Ice, 1 hr.     | 3      | Ambient           | 30              | 100             |
| 5        | ODA-HCA      | TLC Spray            | 1                   | Ice, 1 hr.     | 5      | 0.1 torr vac line | 30              | 100             |
| 6        | ODA-HCA      | Solution (50°C, 3hr) | 2                   | Ice, 1 hr.     | -      | Oven              | -               | 100             |

**Table S2.** Methylene stretches of triacontanoic acid on the oxide surfaces of Ti-6Al-4V, Ti, Al and V following deposition and solvent sonication.

| Protocol | Triacontanoic acid (30 Carbons) |            | Methylene stretches ( $\nu_{\text{CH2 asymm}}$ , $\nu_{\text{CH2 symm}}$ ) |  |
|----------|---------------------------------|------------|----------------------------------------------------------------------------|--|
|          | Oxide surface                   | Deposition | Sonication                                                                 |  |
| 1        | Ti-6Al-4V                       | 2912, 2847 | 2913, 2847                                                                 |  |
|          | Ti                              | 2913, 2846 | 2912, 2847                                                                 |  |
|          | Al                              | 2914, 2847 | 2917, 2849                                                                 |  |
|          | V                               | 2914, 2847 | 2923, 2852                                                                 |  |

**Table S3.** Methylene stretches of octacosanoic acid on the oxide surfaces of Ti-6Al-4V, Ti, Al and V following deposition and solvent sonication.

| Protocol | Octacosanoic acid (28 Carbons) | Methylene stretches ( $\nu_{\text{CH2 asymm}}$ , $\nu_{\text{CH2 symm}}$ ) |            |
|----------|--------------------------------|----------------------------------------------------------------------------|------------|
|          | Oxide surface                  | Deposition                                                                 | Sonication |
| 1        | Ti-6Al-4V                      | 2914, 2847                                                                 | 2913, 2846 |
|          | Ti                             | 2914, 2847                                                                 | 2914, 2847 |
|          | Al                             | 2914, 2849                                                                 | 2914, 2848 |
|          | V                              | 2916, 2848                                                                 | -          |

**Table S4.** Methylene stretches of hexacosanoic acid on the oxide surfaces of Ti-6Al-4V, Ti, Al and V following deposition and solvent sonication.

| Protocol | Hexacosanoic acid (26 Carbons) | Methylene stretches ( $\nu_{\text{CH2 asymm}}$ , $\nu_{\text{CH2 symm}}$ ) |            |
|----------|--------------------------------|----------------------------------------------------------------------------|------------|
|          | Oxide surface                  | Deposition                                                                 | Sonication |
| 1        | Ti-6Al-4V                      | 2914, 2846                                                                 | 2922, 2952 |
|          | Ti                             | 2914, 2846                                                                 | 2913, 2846 |
|          | Al                             | 2913, 2846                                                                 | 2915, 2849 |
|          | V                              | -                                                                          | -          |
| 2        | Ti-6Al-4V                      | -                                                                          | -          |
|          | Ti                             | 2918, 2849                                                                 | -          |
|          | Al                             | 2921, 2850                                                                 | 2922, 2851 |
|          | V                              | -                                                                          | -          |
| 3        | Ti-6Al-4V                      | 2914, 2846                                                                 | -          |
|          | Ti                             | 2913, 2846                                                                 | -          |
|          | Al                             | 2912, 2846                                                                 | 2916, 2848 |
|          | V                              | -                                                                          | -          |
| 4        | Ti-6Al-4V                      | 2916, 2848                                                                 | -          |
|          | Ti                             | 2913, 2846                                                                 | -          |
|          | Al                             | 2914, 2847                                                                 | 2914, 2848 |
|          | V                              | -                                                                          | -          |
| 5        | Ti-6Al-4V                      | 2915, 2846                                                                 | -          |
|          | Ti                             | 2915, 2847                                                                 | -          |
|          | Al                             | 2914, 2848                                                                 | 2914, 2848 |
|          | V                              | -                                                                          | -          |
| 6        | Ti-6Al-4V                      | -                                                                          | -          |
|          | Ti                             | -                                                                          | -          |
|          | Al                             | -                                                                          | -          |
|          | V                              | -                                                                          | -          |

**Table S5.** Methylene stretches of tetracosanoic acid on the oxide surfaces of Ti-6Al-4V, Ti, Al and V following deposition and solvent sonication.

| Protocol | Tetracosanoic acid (24 Carbons) | Methylene stretches ( $\nu_{\text{CH2 asymm}}$ , $\nu_{\text{CH2 symm}}$ ) |            |
|----------|---------------------------------|----------------------------------------------------------------------------|------------|
|          | Oxide surface                   | Deposition                                                                 | Sonication |
| 1        | Ti-6Al-4V                       | 2915, 2847                                                                 | -          |
|          | Ti                              | 2916, 2848                                                                 | -          |
|          | Al                              | 2915, 2847                                                                 | 2915, 2847 |
|          | V                               | -                                                                          | -          |
| 2        | Ti-6Al-4V                       | -                                                                          | -          |
|          | Ti                              | -                                                                          | -          |
|          | Al                              | -                                                                          | -          |
|          | V                               | -                                                                          | -          |
| 3        | Ti-6Al-4V                       | 2915, 2846                                                                 | -          |
|          | Ti                              | 2915, 2847                                                                 | -          |
|          | Al                              | 2923, 2853                                                                 | 2922, 2852 |
|          | V                               | -                                                                          | -          |
| 4        | Ti-6Al-4V                       | 2915, 2847                                                                 | -          |
|          | Ti                              | -                                                                          | -          |
| 4        | Al                              | 2915, 2848                                                                 | -          |
|          | V                               | -                                                                          | -          |
| 5        | Ti-6Al-4V                       | 2916, 2848                                                                 | -          |
|          | Ti                              | -                                                                          | -          |
|          | Al                              | 2915, 2848                                                                 | 2914, 2845 |
|          | V                               | -                                                                          | -          |
| 6        | Ti-6Al-4V                       | -                                                                          | -          |
|          | Ti                              | -                                                                          | -          |
|          | Al                              | -                                                                          | -          |
|          | V                               | -                                                                          | -          |

**Table S6.** Methylene stretches of docosanoic acid on the oxide surfaces of Ti-6Al-4V, Ti, Al and V following deposition and solvent sonication.

| Protocol | Docosanoic acid (22 Carbons) | Methylene stretches ( $\nu_{\text{CH2 asymm}}$ , $\nu_{\text{CH2 symm}}$ ) |            |
|----------|------------------------------|----------------------------------------------------------------------------|------------|
|          | Oxide surface                | Deposition                                                                 | Sonication |
| 1        | Ti-6Al-4V                    | 2918, 2850                                                                 | -          |
|          | Ti                           | 2914, 2847                                                                 | -          |
|          | Al                           | 2915, 2848                                                                 | 2915, 2848 |
|          | V                            | -                                                                          | -          |
| 2        | Ti-6Al-4V                    | -                                                                          | -          |
|          | Ti                           | 2917, 2848                                                                 | -          |
|          | Al                           | -                                                                          | -          |
|          | V                            | -                                                                          | -          |
| 3        | Ti-6Al-4V                    | 2918, 2848                                                                 | 2922, 2850 |
|          | Ti                           | 2915, 2847                                                                 | -          |
|          | Al                           | 2914, 2847                                                                 | 2915, 2849 |
|          | V                            | -                                                                          | -          |
| 4        | Ti-6Al-4V                    | 2917, 2848                                                                 | 2922, 2850 |
|          | Ti                           | 2916, 2848                                                                 | -          |
|          | Al                           | 2914, 2848                                                                 | 2915, 2848 |
|          | V                            | -                                                                          | -          |
| 5        | Ti-6Al-4V                    | 2914, 2847                                                                 | -          |
|          | Ti                           | 2917, 2848                                                                 | -          |
|          | Al                           | 2916, 2849                                                                 | 2916, 2849 |
|          | V                            | -                                                                          | -          |
| 6        | Ti-6Al-4V                    | -                                                                          | -          |
|          | Ti                           | -                                                                          | -          |
|          | Al                           | -                                                                          | -          |
|          | V                            | -                                                                          | -          |

**Table S7.** Methylene stretches of eicosanoic acid on the oxide surfaces of Ti-6Al-4V, Ti, Al and V following deposition and solvent sonication.

| Protocol | Eicosanoic acid (20 Carbons) | Methylene stretches ( $\nu_{\text{CH2 asymm}}$ , $\nu_{\text{CH2 symm}}$ ) |            |
|----------|------------------------------|----------------------------------------------------------------------------|------------|
|          | Oxide surface                | Deposition                                                                 | Sonication |
| 1        | Ti-6Al-4V                    | 2914, 2847                                                                 | -          |
|          | Ti                           | 2916, 2847                                                                 | -          |
|          | Al                           | 2915, 2848                                                                 | 2923, 2851 |
|          | V                            | -                                                                          | -          |
| 2        | Ti-6Al-4V                    | 2915, 2847                                                                 | -          |
|          | Ti                           | -                                                                          | -          |
|          | Al                           | 2922, 2851                                                                 | -          |
|          | V                            | -                                                                          | -          |
| 3        | Ti-6Al-4V                    | 2914, 2847                                                                 | 2921, 2850 |
|          | Ti                           | 2916, 2848                                                                 | -          |
|          | Al                           | 2922, 2851                                                                 | 2921, 2851 |
|          | V                            | -                                                                          | -          |
| 4        | Ti-6Al-4V                    | 2921, 2851                                                                 | -          |
|          | Ti                           | -                                                                          | -          |
|          | Al                           | 2914, 2848                                                                 | -          |
|          | V                            | -                                                                          | -          |
| 5        | Ti-6Al-4V                    | 2914, 2846                                                                 | -          |
|          | Ti                           | 2917, 2850                                                                 | -          |
|          | Al                           | 2916, 2849                                                                 | 2915, 2848 |
|          | V                            | -                                                                          | -          |
| 6        | Ti-6Al-4V                    | -                                                                          | -          |
|          | Ti                           | -                                                                          | -          |
|          | Al                           | -                                                                          | -          |
|          | V                            | -                                                                          | -          |

**Table S8.** Methylene stretches of octadecanoic acid on the oxide surfaces of Ti-6Al-4V, Ti, Al and V following deposition and solvent sonication.

| Protocol | Octadecanoic acid (18 Carbons) | Methylene stretches ( $\nu_{\text{CH2 asymm}}$ , $\nu_{\text{CH2 symm}}$ ) |            |
|----------|--------------------------------|----------------------------------------------------------------------------|------------|
|          | Oxide surface                  | Deposition                                                                 | Sonication |
| 1        | Ti-6Al-4V                      | 2917, 2849                                                                 | -          |
|          | Ti                             | 2915, 2847                                                                 | -          |
|          | Al                             | 2915, 2847                                                                 | 2917, 2849 |
|          | V                              | -                                                                          | -          |
| 2        | Ti-6Al-4V                      | 2919, 2850                                                                 | -          |
|          | Ti                             | 2915, 2846                                                                 | -          |
|          | Al                             | 2918, 2850                                                                 | -          |
|          | V                              | -                                                                          | -          |
| 3        | Ti-6Al-4V                      | 2916, 2848                                                                 | -          |
|          | Ti                             | 2914, 2846                                                                 | -          |
|          | Al                             | 2916, 2848                                                                 | 2917, 2849 |
|          | V                              | -                                                                          | -          |
| 4        | Ti-6Al-4V                      | 2915, 2845                                                                 | -          |
|          | Ti                             | 2914, 2845                                                                 | -          |
|          | Al                             | 2916, 2847                                                                 | 2915, 2847 |
|          | V                              | -                                                                          | -          |
| 5        | Ti-6Al-4V                      | -                                                                          | -          |
|          | Ti                             | 2916, 2846                                                                 | -          |
|          | Al                             | 2918, 2849                                                                 | 2916, 2847 |
|          | V                              | -                                                                          | -          |
| 6        | Ti-6Al-4V                      | -                                                                          | -          |
|          | Ti                             | -                                                                          | -          |
|          | Al                             | -                                                                          | -          |
|          | V                              | -                                                                          | -          |