

# Supporting Information

## Multiphasic DNA Adsorption to Silica Surfaces under varying Buffer, pH, and Ionic Strength Conditions

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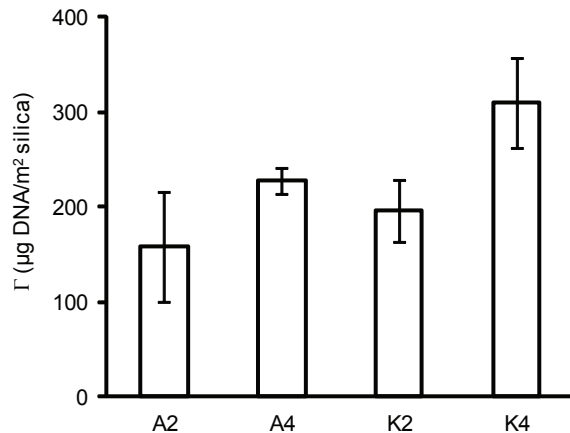
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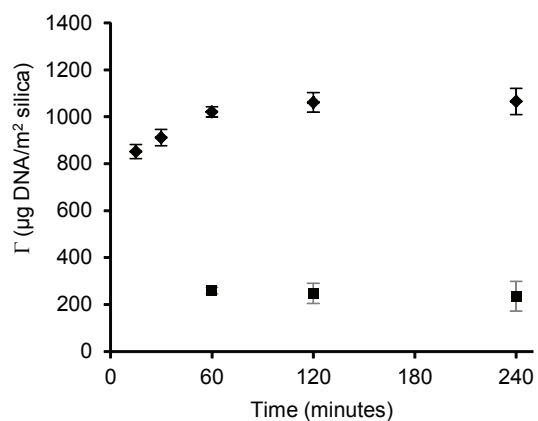
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Claremont, CA 91711*



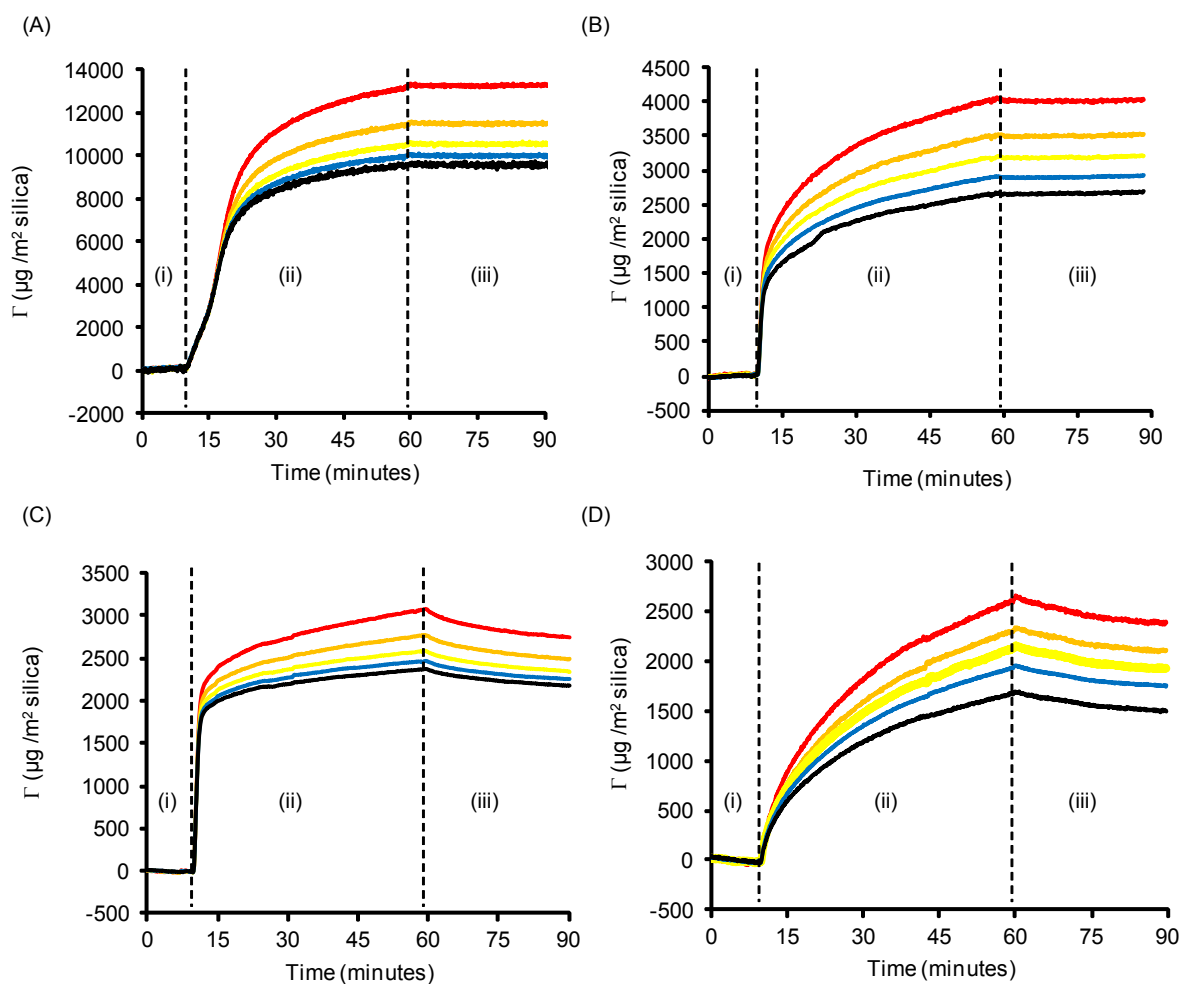
**Figure S1.** FineMix30 oscillator (Claremont BioSolutions), which allows simultaneous testing of up to 30 tubes for DNA bulk depletion experiments. The device oscillates linearly with tunable frequencies (up to 20 Hz). A photo tachometer was used to monitor the frequency of oscillation.



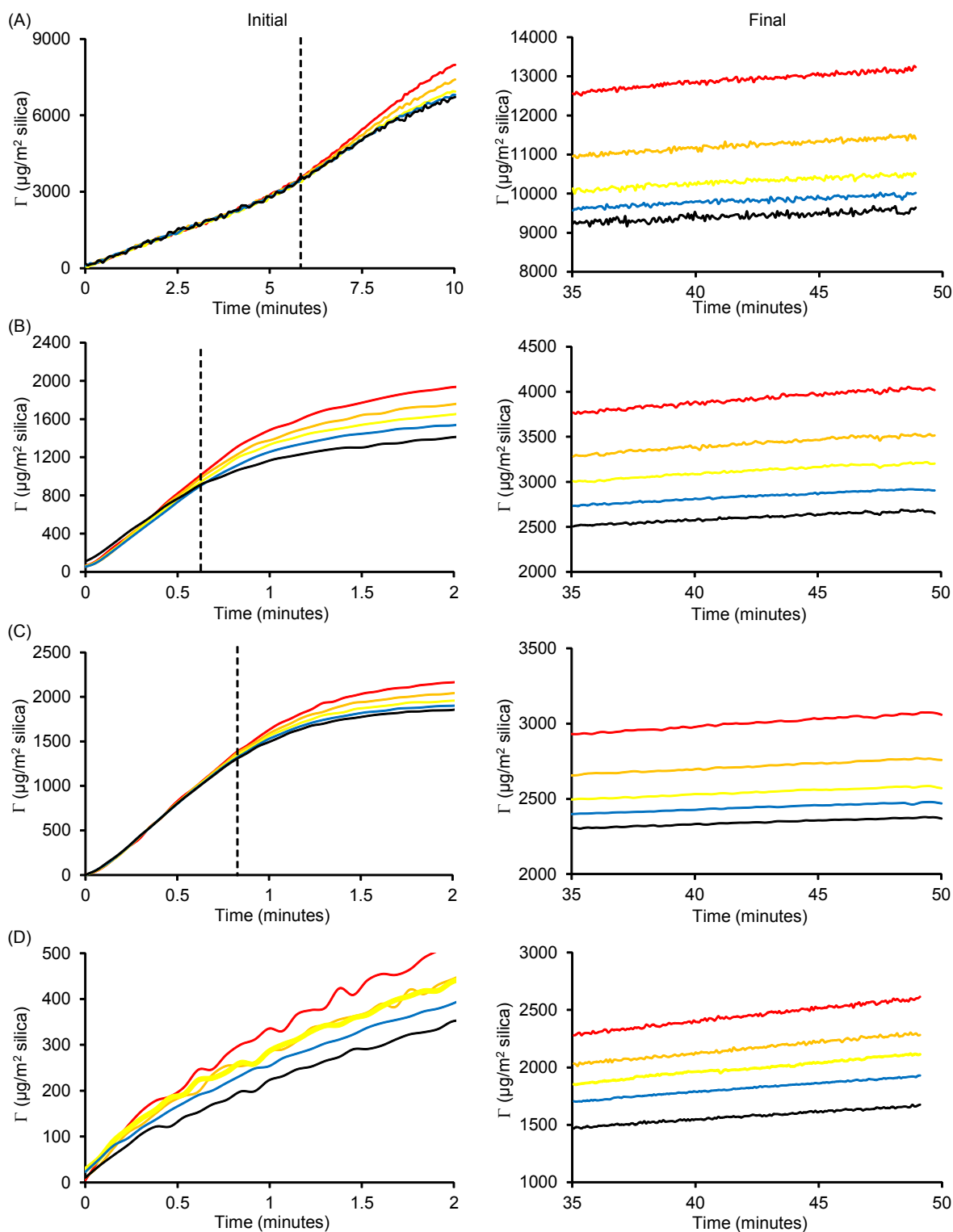
**Figure S2.** Bulk depletion experiment for DNA adsorption to Sigma-Aldrich silica particles in Tris-Acetate buffer pH 4 containing: (A2) 200 mM and (A4) 400 mM ammonium sulfate or (K2) 200 mM and (K4) 400 mM KCl. Samples were incubated for 2 hours under vigorous mixing conditions.



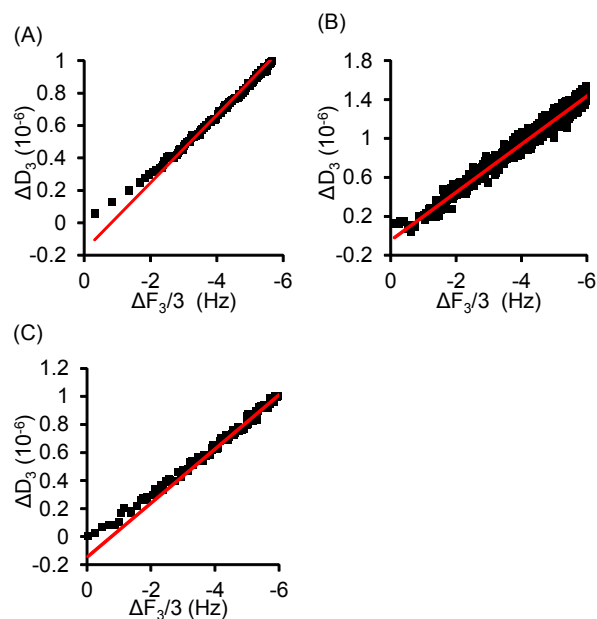
**Figure S3.** Bulk depletion experiment monitoring the adsorption of DNA to (♦) MagPrep and (■) Sigma Aldrich silica particles as a function of time using glycine buffer at pH 5 with 400 mM KCl. The amount of adsorbed DNA plateaus after 2 hours.



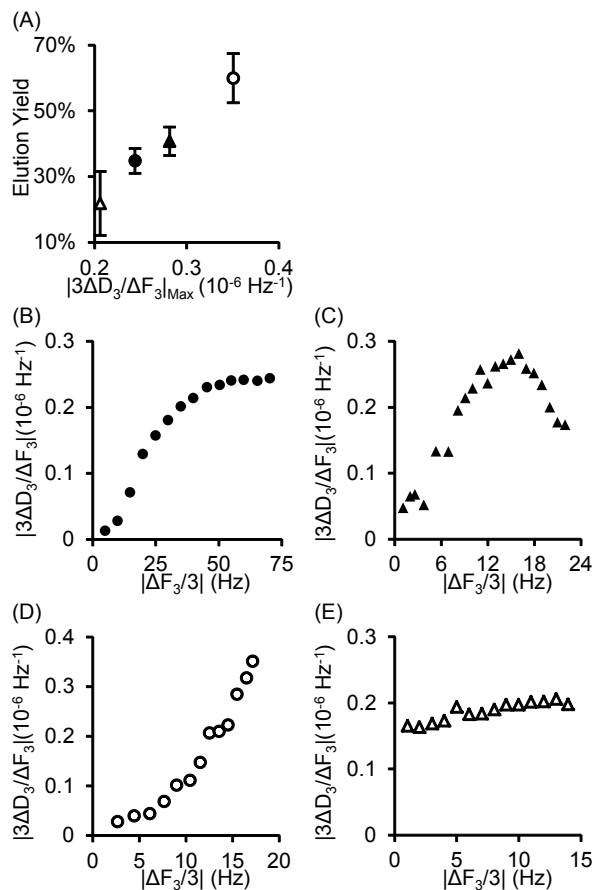
**Figure S4.** Averaged Sauerbrey mass of replicate runs for the 3<sup>rd</sup> (red), 5<sup>th</sup> (orange), 7<sup>th</sup> (yellow), 9<sup>th</sup> (blue), and 11<sup>th</sup> (black) overtones of DNA adsorbed in pH 5 solution with (A) 6 M sodium perchlorate 50 mM Tris, (B) acetic acid with 400 mM K<sup>+</sup>, (C) glycine with 400 mM KCl, (D) and sodium citrate with 400 mM KCl. A baseline was established using the test solution (without DNA) for 10 minutes (i), followed by 50 minutes of the test solution with 10 ng/μL DNA (ii), then 30 minutes of the test solution (without DNA) (iii). The Sauerbrey mass diverges during phases (ii) and (iii).



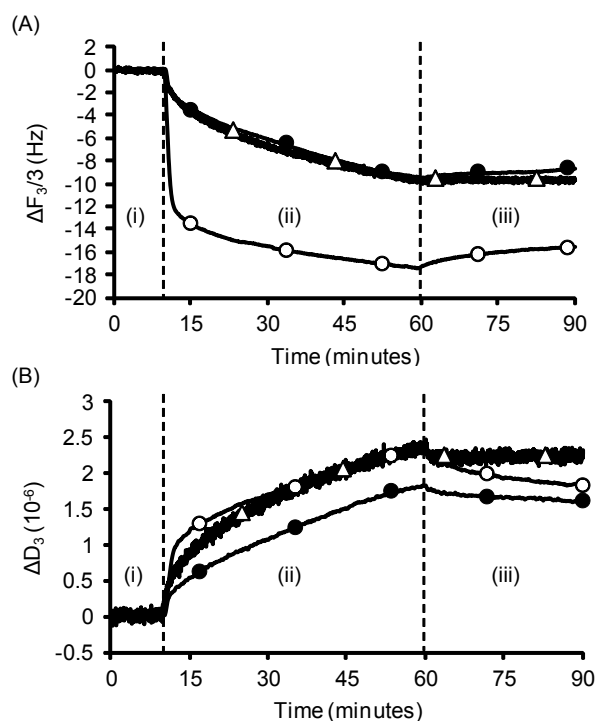
**Figure S5.** Averaged Sauerbrey masses for the initial and final parts of the adsorption process (phase ii, Figure 3) using the 3<sup>rd</sup> (red), 5<sup>th</sup> (orange), 7<sup>th</sup> (yellow), 9<sup>th</sup> (blue), and 11<sup>th</sup> (black) overtones. DNA was adsorbed from pH 5 solutions with (A) 6 M sodium perchlorate 50 mM Tris, (B) acetic acid with 400 mM K<sup>+</sup>, and (C) glycine with 400 mM KCl, and (D) sodium citrate with 400 mM KCl. The dotted line marks the end of the region where the linear fit was performed ( $R^2 \geq 0.99$ ).



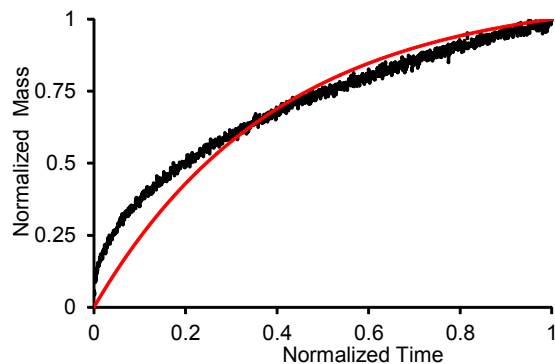
**Figure S6.** Experimental QCM-D data (■) and linear fit (red line) of  $\Delta D$  as a function of  $\Delta F$  for DNA adsorption out of (A) sodium citrate with 400 mM KCl at pH 5, (B) glycine with 400 mM KCl at pH 6, and (C) glycine with 200 mM KCl at pH 5 (all “weaker binding” conditions). While in all cases,  $R^2 > 0.99$ , there is a deviation between the linear fit and the experimental data for initial data points, with the initial slopes ( $\Delta D/\Delta F$ ) being lower than the predominant final slopes.



**Figure S7.** (A) Comparison of the elution yield for the bulk depletion experiments (DNA eluted/DNA adsorbed, Figure 1B) to the maximum slope in the graph of  $\Delta D$  vs  $\Delta F$  (Figure 4) for buffer conditions SP (●), AA (▲), GL (○), SC (Δ).  $|\Delta D/\Delta F|_{\text{max}}$  represents the maximum value of  $|\Delta D/\Delta F|$ , which was calculated as the numerical derivative of  $\Delta D$  versus  $|\Delta F|$ , using the third overtone, for the buffer conditions (B) SP, (C) AA, (D) GL, and (E) SC.



**Figure S8.** QCM-D results for DNA adsorption to quartz out of glycine buffer, ( $\circ$ ) pH 5, 400 mM KCL, ( $\bullet$ ) 200 mM KCL, and ( $\Delta$ ) pH 6, 400 mM KCL as monitored by QCM-D, for (A)  $\Delta F$  versus time, (B)  $\Delta D$  versus time. A baseline was established using (i) the buffer solution (without DNA) for 10 minutes, followed by (ii) 50 minutes of the buffer solution with 10 ng/ $\mu$ L DNA, then (iii) 30 minutes of the buffer solution again.



**Figure S9:** Model for reversible DNA adsorption directly out of solution (A) into the extended conformation (C). As a “weaker binding” case, we used glycine pH 6 with 400 mM KCL. Allowing  $t'$  and  $K_6$  to vary, and normalizing the x and y axis to 1, for both the experimental data (black) and mathematical model (red), the highest  $R^2$  value obtained was 0.942, with  $t'=1$  and  $K_6=1.5$ .  $\epsilon$  was treated as a constant and set to  $10^{-2}$ .



**Mathematical Model I:** The mass-action kinetics for the potential reactions (equations 2 to 4) yields the following differential equations (5-8):

$$\frac{\partial A}{\partial t} = -k_5 A S + k_6 C - k_1 B S^n - k_2 B \quad (5)$$

$$\frac{\partial B}{\partial t} = k_1 A S^n - k_2 B + k_4 C S^{n-1} - k_3 B \quad (6)$$

$$\frac{\partial C}{\partial t} = k_5 A S - k_6 C - k_4 C S^{n-1} + k_3 B \quad (7)$$

$$\frac{\partial S}{\partial t} = -k_5 A S + k_6 C - n k_1 A S^n + n k_2 B - (n-1)k_4 C S^{n-1} + (n-1)k_3 B \quad (8)$$

To render equations 5 to 8 dimensionless, the following substitutions were made (9-13):

$$a = \frac{A}{A_{max}} \quad (9)$$

$$b = \frac{B}{S_{max}} \quad (10)$$

$$c = \frac{C}{S_{max}} \quad (11)$$

$$s = \frac{S}{S_{max}} \quad (12)$$

$$t' = k_1 A_{max} S_{max}^{n-1} t \quad (13)$$

$A_{max}$  and  $S_{max}$  are the initial concentrations of DNA in solution and available binding sites on the silica surface, respectively.  $a(t)$  and  $s(t)$  are the dimensionless concentrations of DNA in solution and available surface binding sites, respectively, and are initially set to 1.  $b(t)$  and  $c(t)$  are the dimensionless concentrations of DNA tightly and loosely bound to the surface, respectively, and are initially set to 0.  $t'$  is the dimensionless time scale. Assuming that only  $k_1$  and  $k_3$  are non-zero, and making the substitutions of equations 9 to 13 into equations 5 to 8, we obtain (14-17):

$$\frac{\partial a}{\partial t'} = -\epsilon a s^n \quad (14)$$

$$\frac{\partial b}{\partial t'} = a s^n - K_3 b \quad (15)$$

$$\frac{\partial c}{\partial t'} = K_3 b \quad (16)$$

$$\frac{\partial s}{\partial t'} = -nas^n + (n-1)K_3 b \quad (17)$$

Here  $\varepsilon = \frac{S_{max}}{A_{max}}$  and  $K_3 = \frac{k_3}{k_1 A_{max} S_{max}^{n-1}}$ . The surface concentrations  $b$ ,  $c$ , and  $s$  obey the relation  $s+nb+c = 1$ .  $t'$  was set to 20, but was not found to substantially change the  $R^2$  values of the fit for  $t'$  at 15 and 25.

## Mathematical Model II:

In this model we assume that DNA only adsorbs to silica directly from solution in the loosely bound conformation (Figure 6, transition *A* to *C*), resulting in only  $k_5$  and  $k_6$  being non-zero. To render equations 5-8 (Mathematical Model I) dimensionless, we make the substitutions 9,11,12 (Mathematical Model I) and 18 into equations 5-8 (Mathematical Model I):

$$t' = k_5 A_{max} t \quad (18)$$

We obtain (19-20):

$$\frac{\partial a}{\partial t'} = -\epsilon a s + K_6 \epsilon c \quad (19)$$

$$\frac{\partial c}{\partial t'} = a s - K_6 c = -\frac{\partial s}{\partial t'} \quad (20)$$

Here  $\epsilon = \frac{S_{max}}{A_{max}}$  and  $K_6 = \frac{k_6}{k_3 A_{max}}$ .