Supporting Information: Measuring and controlling the local environment of surface bound DNA in self assembled monolayers on gold when prepared using potential-assisted deposition

Kaylyn K. Leung,[†,‡,¶] Isaac Martens,[†,‡,§] Hua-Zhong Yu,[‖] and Dan Bizzotto[*,†,‡]

†*AMPEL, University of British Columbia, Vancouver, Canada*

‡*Department of Chemistry*

¶*Present address: University of California, Santa Barbara, USA*

§*Present address: ESRF, Grenoble, France*

‖*Department of Chemistry, Simon Fraser University, Burnaby, Canada*

E-mail: bizzotto@chem.ubc.ca

Comparing potential-assisted and OCP deposition conditions

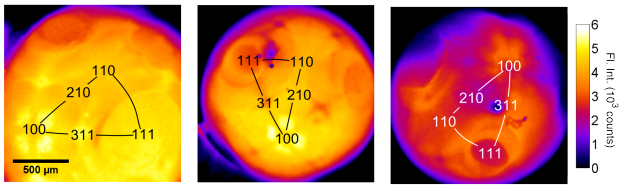

Figure S1: Fluorescence image of a DNA modified gold bead surface that was prepared using TRIS chloride IB containing 0.5 µM DNA. a) 24 hr deposition at open circuit conditions, b) E_{dc} = +0.4V/SCE for 5min, c) E_{SW} = +0.4V/-0.3V 50Hz for 5 min. Each sample was immersed for 90 min in 1mM MCH.

DNA reorientation model

The measurements of fluorescence modulation were taken in a low ionic strength electrolyte (10 mM) which allows for an estimate of the length of DNA based on its persistence length which is approximately 10 nm. The effective diameter of the DNA depends on the ionic strength of the buffer as detailed in[S1]. The maximum angle was calculated by solving the equations for a given d_{eff}, $l_{DNA}$and L_a. The DNA was assumed to be arranged in a hexagonal close packed manner as in[S1].

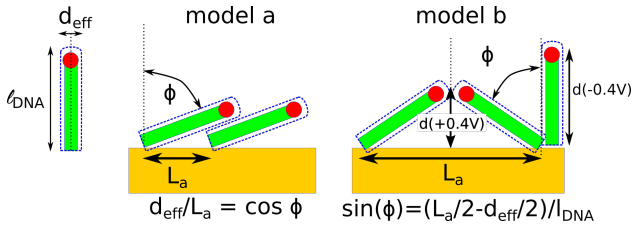

Figure S2: Models of DNA reorientation used to estimate the changes in fluorescence with DNA reorientation. Model a is correlated motion, model b is independent motion of the tethered DNA.

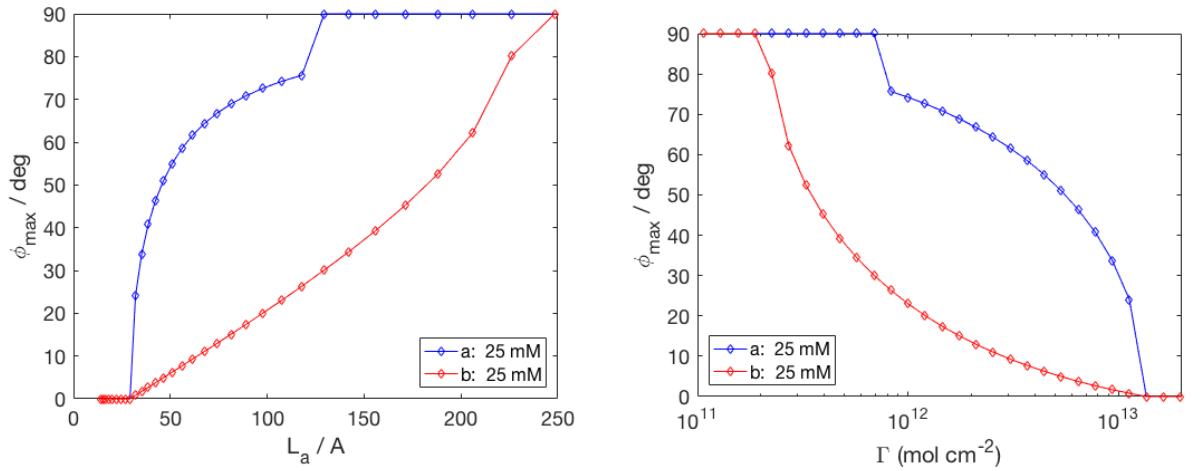

Figure S3: Model results showing the maximum angular motion possible (ϕ_{max}) for tethered DNA arranged in a hexagonal pattern at average spacing or different surface densities in a 25mM NaCl buffer.

The maximum fluorescence intensity F was estimated using the length of the 30 bp DNA (10nm) assuming the DNA is oriented at 90 degrees normal to the electrode surface ($F \propto l_{DNA}^3$). The maximum change in the fluorescence was estimated from the largest angle (ϕ_{max}) that the DNA could make given the steric restrictions imposed by neighboring DNA strands. The change in fluorescence was calculated using $\Delta F \propto l_{DNA}^3 - (l_{DNA}\ \sin(90 - \phi_{max}))^3$ and then normalized by F to give a simple result: $\Delta F/F = 1 - sin^3(90 - \phi_{max})$.

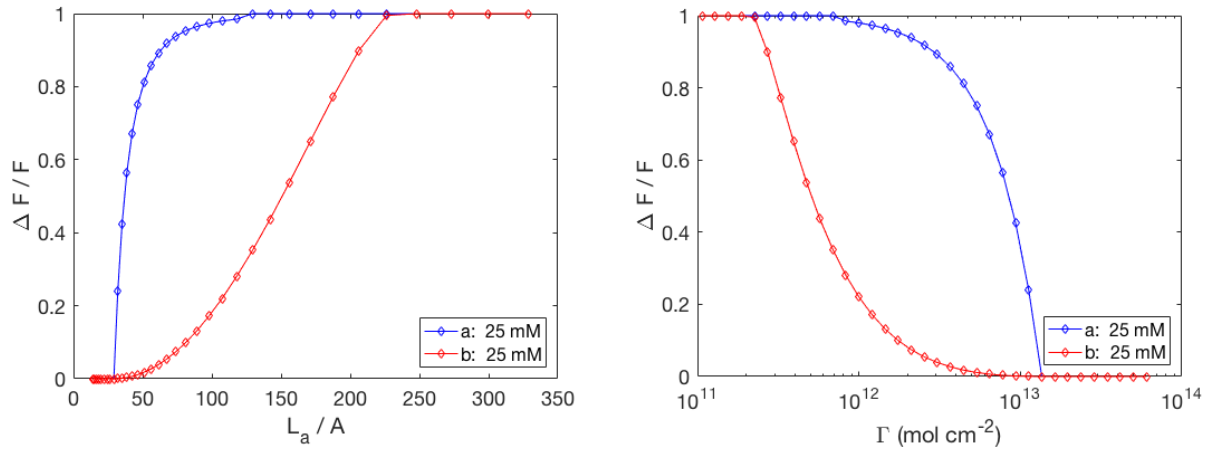

Figure S4: Model results showing the relative change in fluorescence ($\Delta F/F$) for DNA arranged in a hexagonal pattern at average spacing or different surface densities in a 25mM NaCl buffer. The fluorescence intensity was calculated from ϕ_{max} as described in the main text,

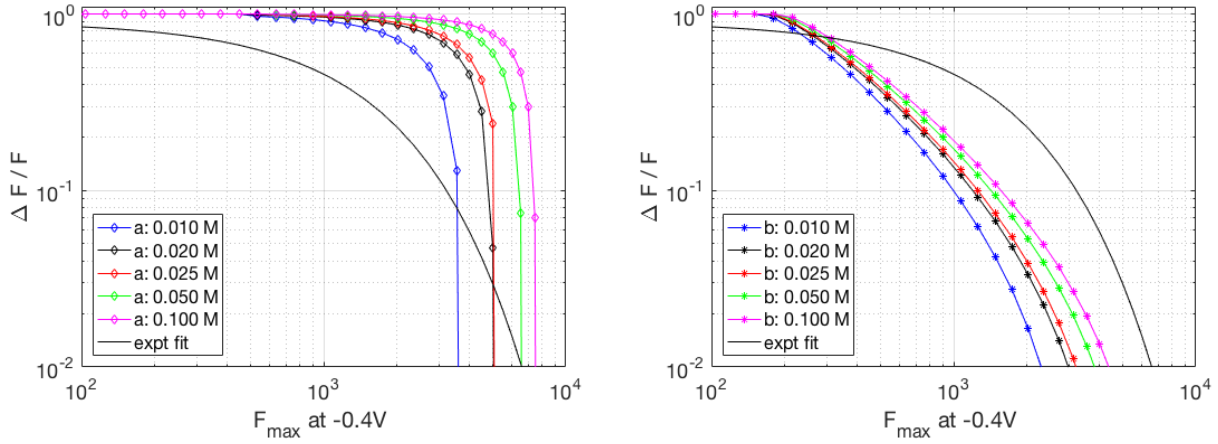

Figure S5: Model results showing $\Delta F/F$ for different coverages (represented by F_{max}) as a function of the ionic strength of the buffer for the two models of the DNA motion (left: model a and right: model b). Included is the empirical curve measured from real samples (solid line). Increasing ionic strength reduces the electrostatic repulsion between adsorbed DNA enabling a larger degree of mobility for the same packing density.

Potential profile used for fluorescence imaging to measure ΔF_{max}

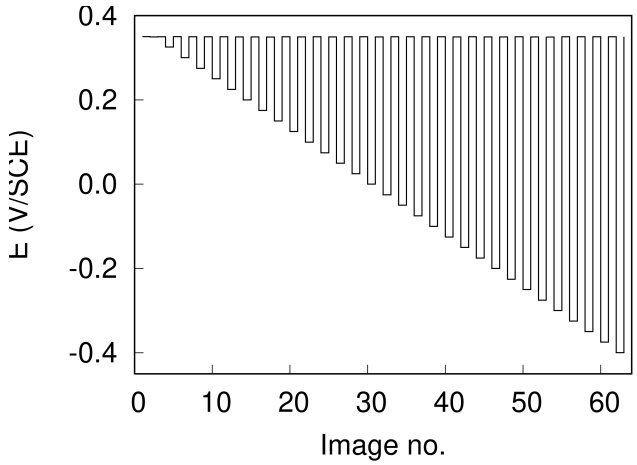

Figure S6: The potential - time profile used for measuring the DNA reorientation. Each step was 4 sec long. The images were recorded over the final 3 sec of the potential step.

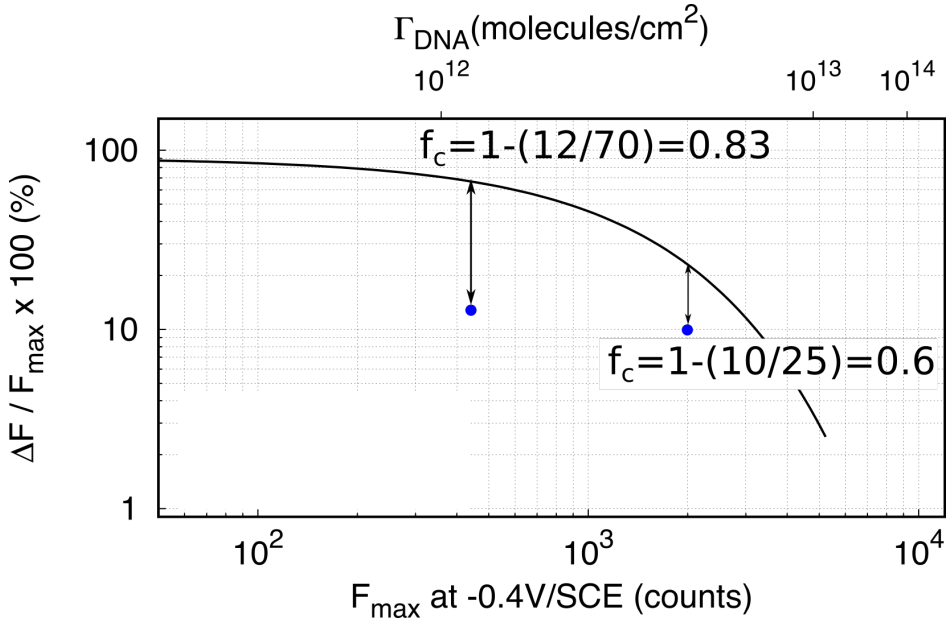

Figure S7: Schematic illustrating the calculation of the fraction of DNA in clustered regions from the fluorescence measurements.

Comparing clustered regions for the systems studied

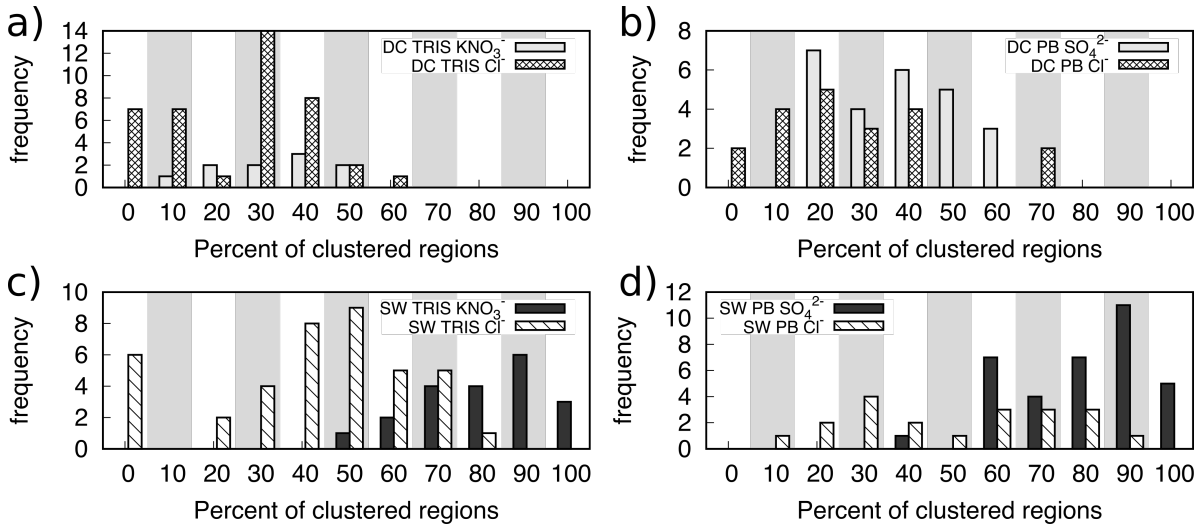

Figure S8: Fractional distribution of clustered regions for DNA SAMs prepared in the four deposition buffers studied (TRIS and phosphate buffers with or without Cl-). The results are organized with the E_{dc} deposition in TRIS IB (a) and phosphate IB (b) and E_{SW} deposition in TRIS IB (c) and phosphate IB (d). The data includes all surface crystallographic regions analyzed.

SEM of DNA SAMs and the measured change in the fluorescence as a result of DNA reorientation

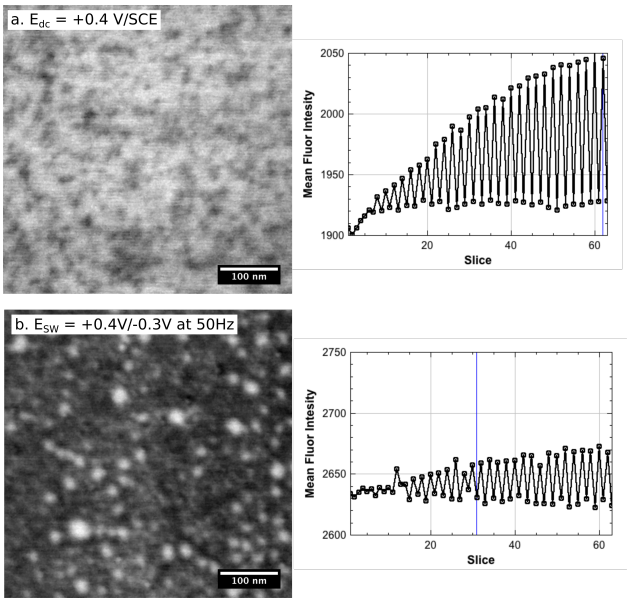

Figure S9: SEM images of DNA SAMs on Au(111) facets on the bead electrodes prepared at (a) constant potential and (b) using square-wave potential.

Results from studying other DNA deposition conditions

Figure S10 shows the results from: potential-assisted deposition at E_{dc} = +0.4V/SCE; at E_{dc} = -0.3V/SCE in phosphate sulfate IB; at no-applied potential (OCP). For these three cases, no significant clustering was observed. Figure S10 also shows the results from potential-assisted deposition at E_{SW} = +0.4V/-0.5V (SCE) and at E_{SW} = +0.5V/-0.3V (SCE) in phosphate sulfate IB. Changing the positive or negative potential limits used in E_{SW} did not prevent cluster formation.

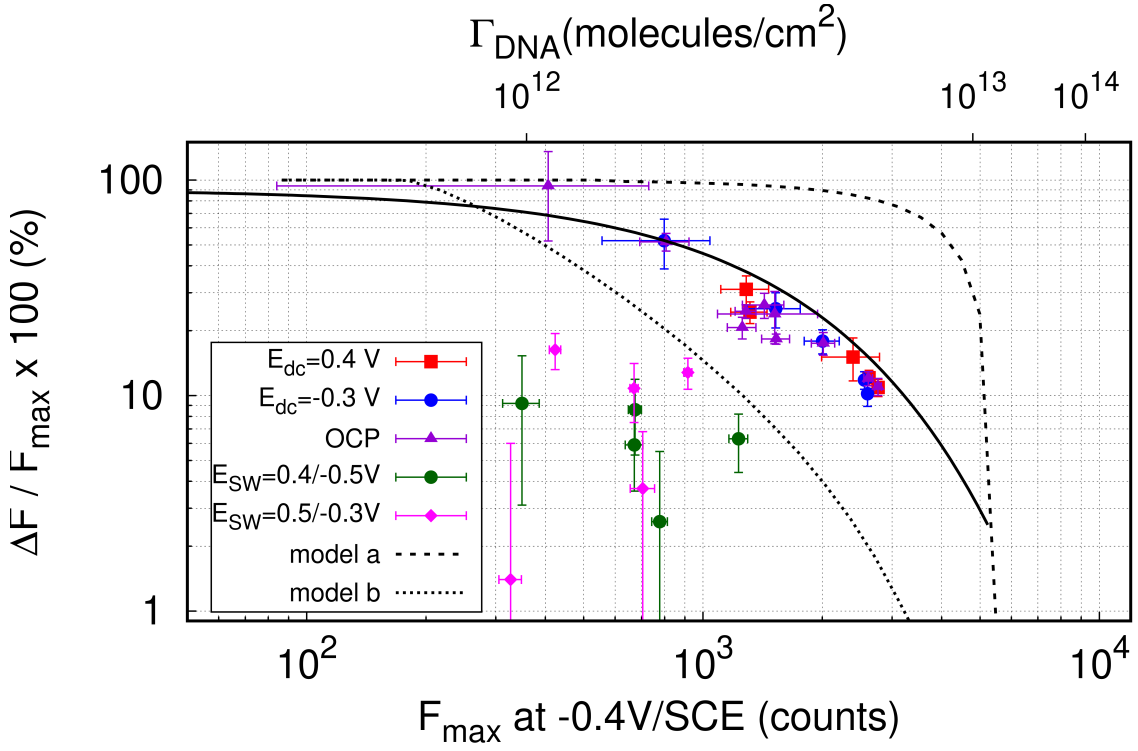

Figure S10: Comparison of the open circuit (OCP), E_{dc} potential-assisted deposition at E_{dc} = +0.4V/SCE and at E_{dc} = -0.3V/SCE in phosphate sulfate IB showing little clustered formations. Surfaces prepared with different positive or negative potential limits used in E_{SW} does not eliminate cluster formation. An empirical line (black line) is drawn through the data representing the maximum $\Delta F/F_{max}$ observed from many measurements and samples. Also included are the calculated behaviour for both models (a: correlated and b: independent as dashed lines).

Figure S11 summarizes the measurements for surfaces prepared using different time spent at the potential limits (-0.3V/SCE and +0.4V/SCE). The total deposition time remained the same at 5 min. The duty cycle was 50%. The time spent at each potential was changed from 10 msec (or a 50Hz modulation) to 10 sec (or 50 mHz). The number of potential step changes would decrease in proportion. The lowest frequency had the fewest clusters, while increasing the frequency, and therefore the number of changes in potential increased the number of clusters formed.

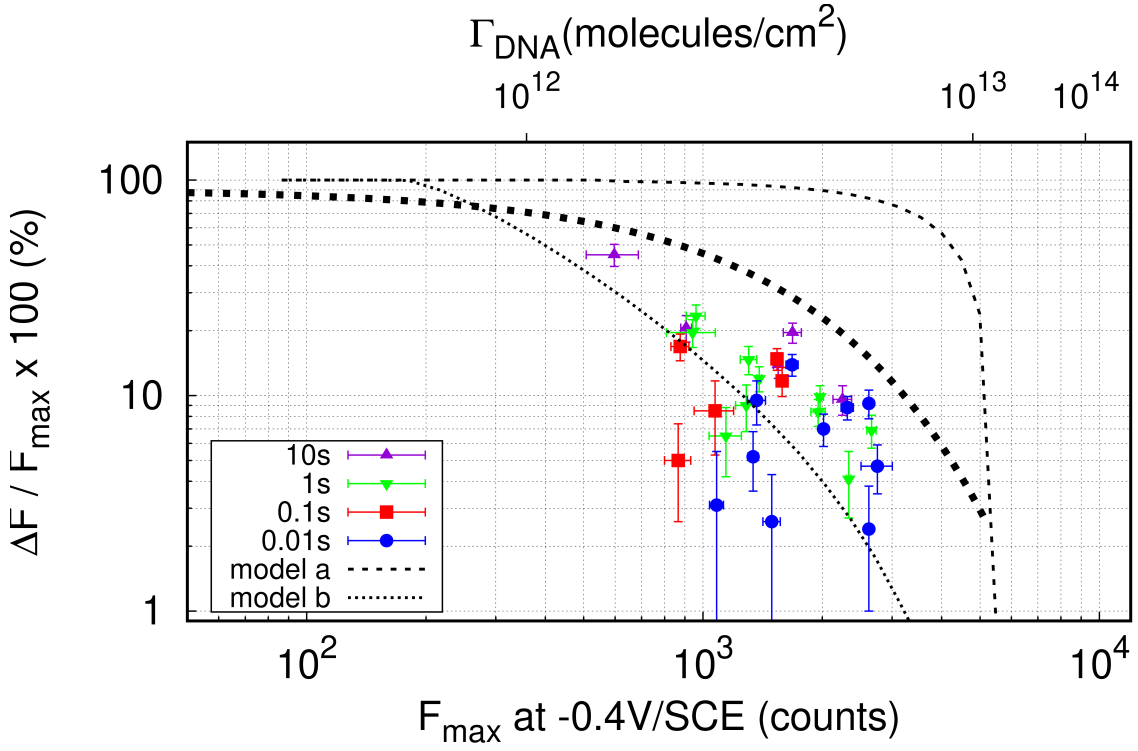

Figure S11: Analysis of the DNA SAM surfaces prepared using E_{SW} conditions in phosphate-sulfate IB with a different frequency of the square wave perturbation. The deposition conditions otherwize were the same as detailed in the main text. An empirical line (thick dashed black line) is drawn through the data representing the maximum $\Delta F/F_{max}$ observed from many measurements and samples. Also included are the calculated behaviour for both models (a: correlated and b: independent as dashed lines).

References

(S1) Li, Z.; Niu, T.; Zhang, Z.; Chen, R.; Feng, G.; Bi, S. Exploration of the specific structural characteristics of thiol-modified single-stranded DNA self-assembled monolayers on gold by a simple model. *Biosensors and Bioelectronic* **2011**, *26*, 4564–4570.