Supporting Information for

Specific and Nonspecific Metal Ion–Nucleotide Interactions at Aqueous/Solid Interfaces Functionalized with Adenine, Thymine, Guanine, and Cytosine Oligomers

*Joseph G. Holland, Jessica N. Malin, David S. Jordan, Esmeralda Morales, and Franz M. Geiger**

*Department of Chemistry and the International Institute for Nanotechnology,
Northwestern University,
2145 Sheridan Road, Evanston, IL 60208 (USA)*

E-mail: geigerf@chem.northwestern.edu

Methods

Fused silica hemispheres were used as the substrates for functionalization with ssDNA (ISP Optics). Prior to DNA functionalization, each hemisphere was cleaned in the following manner. First, the lens was treated with NoChromix (Godax Laboratories) for 1 hr. The hemispheres were then rinsed with Millipore water (18.2 M Ω), and sonicated in methanol (VWR) for 10 min. Next, the hemispheres were placed in an oven at 100°C for 30 min. Lastly, the hemispheres underwent plasma cleaning (Harrick Plasma, Ithaca, NY) on the highest setting for 1 min each. The lenses were then functionalized with the ssDNA using our previously established method.¹⁻³ The 21-mer DNA sequences (Integrated DNA Technologies) used in these experiments had the following sequences: (A₁₅+T₆): 5'-AAA AAA AAA AAA AAA TTT TTT /3AmMO/-3', (C₁₅+T₆): 5'-CCC CCC CCC CCC CCC TTT TTT /3AmMO/-3', and (T₁₅+T₆): 5'-TTT TTT TTT TTT TTT TTT TTT /3AmMO/-3'. The strands were covalently attached to the

fused silica hemisphere via their -3' end through a peptide bond between the /3AmMO/ modification and an N-hydroxysuccinimide linker, as described in our previous work.¹⁻³ Care was taken to ensure that the substrates were not reacted with the DNA any sooner than 15 hrs before their experimental use.

All of the solutions used in these experiments were prepared with Millipore water and maintained at pH 7.0 ± 0.2 by addition of dilute HCl (E.M.D., ACS grade) and NaOH (Sigma-Aldrich, 99.99%). The aqueous Mg^{2+} solutions used in all adsorption experiments were made from $\text{MgCl}_2(\text{H}_2\text{O})_6$ (Sigma-Aldrich), and the background electrolyte solutions were prepared using NaCl (VWR 99%). All pH measurements were performed with a Thermo Fisher Scientific pH meter that was calibrated on a daily basis, and all Mg^{2+} bulk concentrations were quantified using inductively coupled plasma atomic emission spectroscopy (ICP-AES, Varian).

An advanced schematic of our setup and the laser can be found in previously published work.⁴⁻⁷ Briefly, the SHG experiments described here were performed with a regeneratively amplified Ti:sapphire laser (Hurricane, Spectra Physics, 120 fs pulse) that pumps an optical parametric amplifier (OPA-CF, Spectra Physics, 1 kHz repetition rate) tuned to a fundamental wavelength of 650 ± 5 nm, far away from any bulk or surface electronic transition of DNA or the aqueous magnesium.^{1,8} The power of the input beam was then attenuated to 0.5 ± 0.05 μJ using a variable density filter. The fundamental beam was directed through a half-wave plate that selected *p*-polarized light and that light was focused onto the ssDNA functionalized hemisphere/water interface at an angle just less than that of total internal reflection. The reflected beam, ω (650 nm), was then removed by means of a UV-grade Schott filter, while the generated beam, 2ω (325 nm),

was directed into a monochromator set at 2ω , and then into a Hamamatsu PMT. The intensity of the SH was then quantified through the use of a gated, single photon counting system. Prior to each experiment, both the SHG quadratic power dependence and the SHG bandwidth were verified. Adsorption experiments were performed at a flow rate of $\sim 1\text{ mL/sec}$, which was controlled using peristaltic pumps and verified with a flow meter. Two separate reservoirs contained the aqueous solutions used in these experiments. The first solution contained a given NaCl background solution, while the second solution contained both the same concentration of NaCl plus the Mg^{2+} concentration of interest.

Sensitivity Analysis

In order to test the robustness of our fitting equation, a sensitivity analysis was performed on the SHG Gouy-Chapman fitting equation (General Text Eq. 1). This analysis was carried out by taking the partial derivative of the fitting equation with respect to A , B , K_{obs} , ϵ_0 , and ϵ_m . These derivatives were then plotted respectively as a function of A , B , K_{obs} , ϵ_0 , and ϵ_m in Figure S1, S2, S3, S4, and S5 of the Supporting Information. In all sensitivity analyses the input parameters of: $B = -0.32$, $\epsilon_0 = -0.016 \text{ C/m}^2$, $\epsilon_m = 0.005 \text{ C/m}^2$, $K_{\text{obs}} = 10,000 \text{ M}^{-1}$, $[M] = 1 \times 10^{-3} \text{ M}$, $C_{\text{elec}} = 0.01 \text{ M}$; were used as needed.

Figure S1. Sensitivity analysis for the fitting parameter A.

Figure S2. Sensitivity analysis for the fitting parameter B.

Figure S3. Sensitivity analysis for the observed binding constant, K_{obs} .

Figure S4. Sensitivity analysis for the initial surface charge density, σ_0 .

Figure S5. Sensitivity analysis for the maximum surface charge density, σ_m .

Adsorption Isotherms

All of the SHG adsorption isotherms for the data presented in this work are shown here (Figures S6-S10).

Figure S6. Adsorption isotherm for Mg^{2+} binding to the A_{21} functionalized silica interface at pH 7, in the presence of 10 mM NaCl.

Figure S7. Adsorption isotherm for Mg^{2+} binding to the C_{21} functionalized silica interface at pH 7, in the presence of 10 mM NaCl.

Figure S8. Adsorption isotherm for Mg^{2+} binding to the T_{21} functionalized silica interface at pH 7, in the presence of 10 mM NaCl.

Figure S9. Adsorption isotherm for Mg^{2+} binding to the G_{21} functionalized silica interface at pH 7, in the presence of 10 mM NaCl.

Figure S10. Adsorption isotherm for Mg^{2+} binding to the C_{15}T_6 functionalized silica interface at pH 7, in the presence of 10 mM NaCl.

Additional Method Fit Results

(Please reference paragraph 2 of Results)

	A₂₁	C₂₁	T₂₁	G₂₀	A₁₅T₆	C₁₅T₆
K_{bind} [M⁻¹]	5(2) x10 ³ 6(1) x10 ³	8(2) x10 ³ 10(3) x10 ³	22(9) x10 ³ 10(20) x10 ³	36(5) x10 ³ 80(20) x10 ³	6(1) x10 ³ 7(2) x 10 ³	12(3) x10 ³ 9(3) x10 ³
-ΔG_{bind} [kJ/mol]	31(1) 31.5(5)	32.2(7) 32.8(8)	35(1) 32.8(6)	35.9(4) 38(1)	31.9(4) 31.9(8)	33.2(7) 33(1)
Ion Density [Mg²⁺ ions/strand]	3(2) 11(1)	11(2) 11(1)	3(1) 9(4)	11(2) 11(1)	7(1) 10(1)	4(1) 10(1)
-ΔG_{total} [kJ/mol]	90(60) 350(30)	350(70) 360(70)	110(40) 300(100)	400(70) 420(80)	220(30) 320(30)	130(30) 330(30)

Table S1. Binding constants, free energies, ion number densities, and total free binding energies for Mg²⁺ interacting with fused silica/water interfaces functionalized with single stranded 21-mers at 298K, pH 7, and 10 mM NaCl concentration. The top value in each cell was calculated using by assuming that the screening electrolyte is monovalent (1:1). For this scenario, C_{elec} is expressed as the sum of both the background Na⁺ concentration (0.01 M) and the Mg²⁺ concentration. The bottom value in each cell was calculated by assuming the screening electrolyte to be divalent (2:2) and thus C_{elec} was expressed solely as the Mg²⁺ concentration. Free energies were obtained after referencing to the 55.5 molarity of water.

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