

The Effects of Oligonucleotide Overhangs on the Surface Hybridization in DNA films: An Impedance Study.

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SUPPORTING INFORMATION

Table S1. Values of Randle's equivalent circuit elements for ss-DNA and ds-DNA films. Parentheses show the standard deviation of the measured results.

ID	Strand Type	R_s $k\Omega \cdot cm^2$	CPE 10^{-5} ($S \cdot sec^n \cdot cm^{-2}$)	n	R_{CT} $k\Omega \cdot cm^2$	ΔR_{CT} $k\Omega \cdot cm^2$
a	ss-DNA	0.1	4.0 (1.0)	0.82	0.99 (0.4)	
1	ds-DNA	0.1	3.9 (1.0)	0.84	1.35 (0.1)	0.26 (0.1)
2	ds-DNA	0.1	4.0 (1.0)	0.83	1.73 (0.5)	0.74 (0.2)
3	ds-DNA	0.1	3.1 (0.6)	0.86	1.51 (0.5)	0.52 (0.1)
4	ds-DNA	0.1	3.0 (0.4)	0.86	2.35 (0.7)	1.36 (0.1)
5	ds-DNA	0.1	3.4 (0.9)	0.82	1.71 (0.6)	0.72 (0.2)
6	ds-DNA	0.1	2.8 (0.5)	0.84	2.77 (0.7)	1.78 (0.3)
7	ds-DNA	0.1	4.7 (0.7)	0.80	1.98 (0.4)	0.99 (0.2)

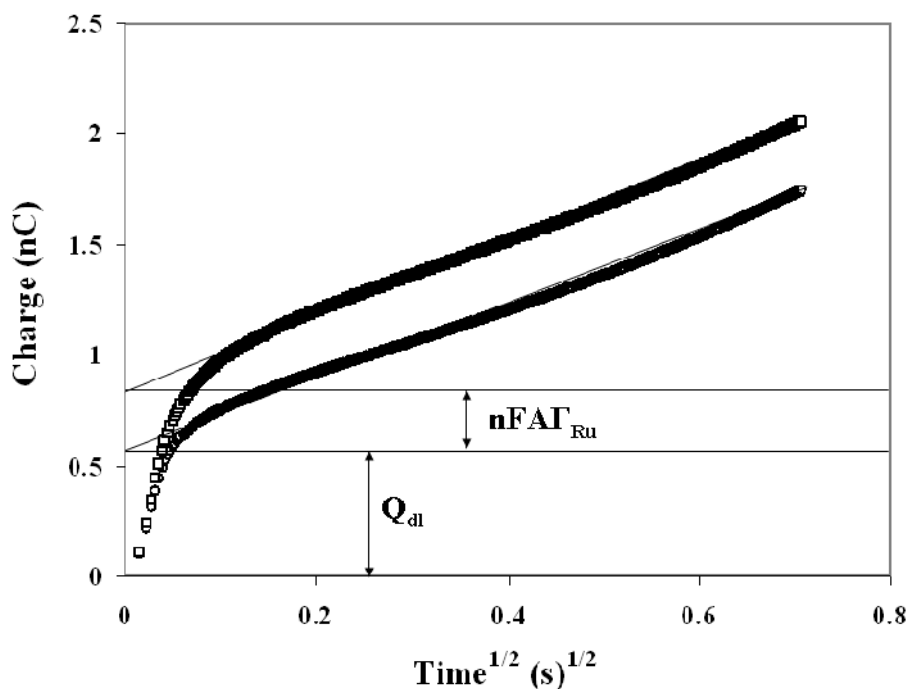


Figure S1. Chronocoulometry plots (charge vs. time^{1/2}) of ss-DNA capture strand in 10 mM Tris (○) and ss-DNA in 10 mM Tris + 5 μM Ru(NH₃)₆³⁺ (□). Regression lines show the value of charge on Y-axis in absence and presence of Ru(NH₃)₆³⁺.

The total charge passing through the electrode is given by the integrated Cottrell equation

[A.J. Bard, L.R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, second ed., Wiley, New York, 2001;]:

$$Q = 2nFAC \left(\frac{D}{\pi} \right)^{1/2} t^{1/2} + Q_{dl} + nFA\Gamma_{Ru} \quad (1)$$

where n is the number of electrons per molecule for reduction, F the Faraday constant (96500 C/mol), A the electrode area (cm²), D the diffusion coefficient (cm²/s), C the bulk concentration (mol/ cm³), Q_{dl} the capacitive charge (C), and $nFA\Gamma_{Ru}$ the charge from the reduction of Γ_{Ru} (mol/cm²). The Chronocoulometry intercept of the Q vs. $t^{1/2}$ plot at $t = 0$ represents the sum of the charges of double-layer capacitance and the surface-confined species, [Ru(NH₃)₆]³⁺ in this case. By subtracting the capacitive charge (intercept at $t = 0$

in the absence of redox cation), the total charge of surface-confined $[\text{Ru}(\text{NH}_3)_6]^{3+}$ were evaluated using following formula.

$$\Gamma_{\text{DNA}} = \Gamma_{\text{Ru}} (z/m) N_{\text{A}} \quad (2)$$

where Γ_{DNA} is the capture surface density in molecules/ cm^2 , m is the number of nucleotides in the probe DNA, z is the charge of the redox molecule, and N_{A} is Avogadro's number.

Table S3. Calculation for density of DNA on gold surface.	
Number of phosphates in each strand m	51
Charge on Ru z	3
Number of electron transfer n	1
Calculated Charge $Q_{\text{dl}} - \Gamma_{\text{Ru}} nFA$ (nC)	0.25
Faraday's Constant F (C/mol)	96500
Avagadro's Number N_{A}	6.02×10^{23}
Area of electrode A (cm^2)	2.7×10^{-5}
Density of Ru $\Gamma_{\text{Ru}} = Q/nFA$ (mol/ cm^2)	6.9×10^{-11}
Density of DNA $\Gamma_{\text{DNA}} = \Gamma_{\text{Ru}} N_{\text{A}} (z/m)$ (number/ cm^2)	2.4×10^{12}