SUPPLEMENTAL INFORMATION

DNA-modified Electrodes Fabricated using Copper-Free Click Chemistry for Enhanced Protein Detection

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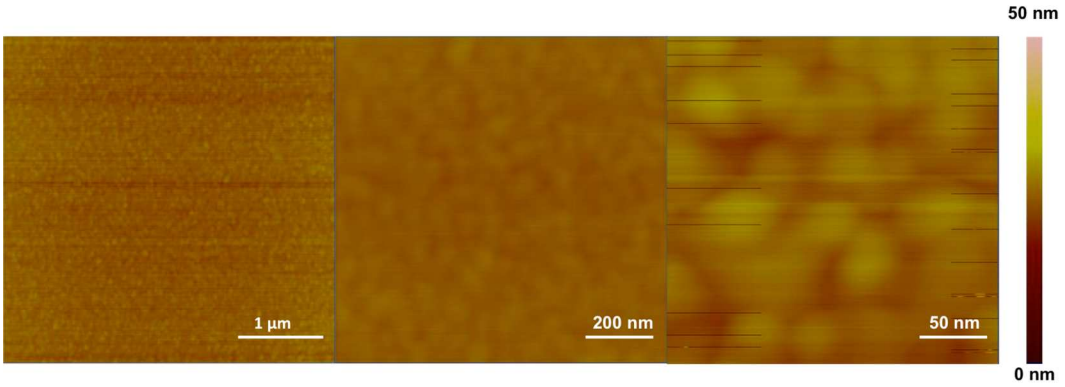

Figure S1: AFM images of OCT-DNA monolayer. The images shown are obtained in phosphate buffer (50 mM phosphate, pH 7) with a chemically-modified AFM tip. The underlying mixed alkyl thiol monolayer contains 80% mercaptoethanol and 20% thiol azide. Three magnifications are shown for clarification, and in all cases, when the area of DNA clusters is quantified relative to the total image area, approximately 20% of the surface is covered.

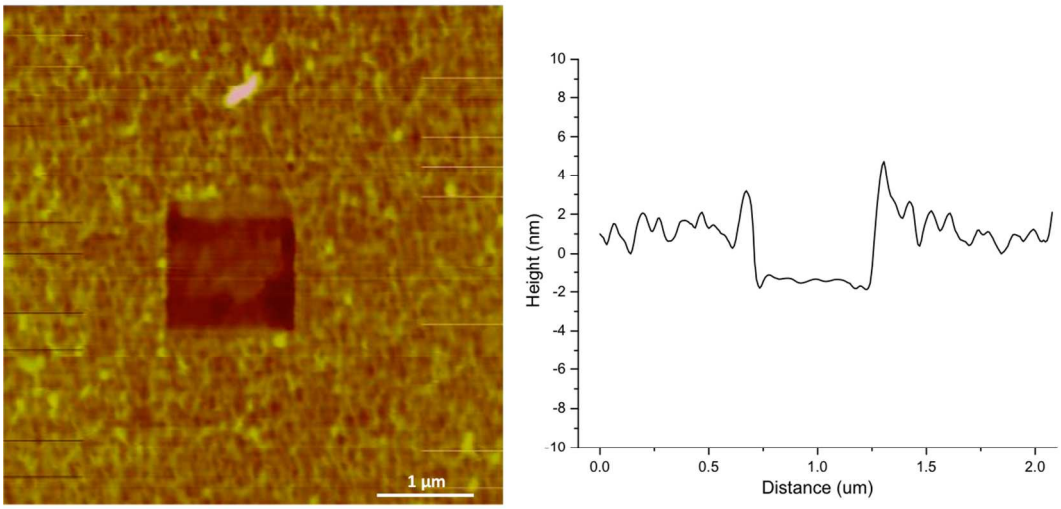

Figure S2: Depth measurement of OCT-DNA monolayer with AFM. The image shown is obtained in phosphate buffer (50 mM phosphate, pH 7) with a chemically-modified AFM tip. A hole is formed through the application of a force to the AFM tip in contact mode. When a force is no longer applied to the tip, the depth of the resulting hole is measured. When averaged over many measurements, the height of the monolayer is determined to be 3.5 nm.

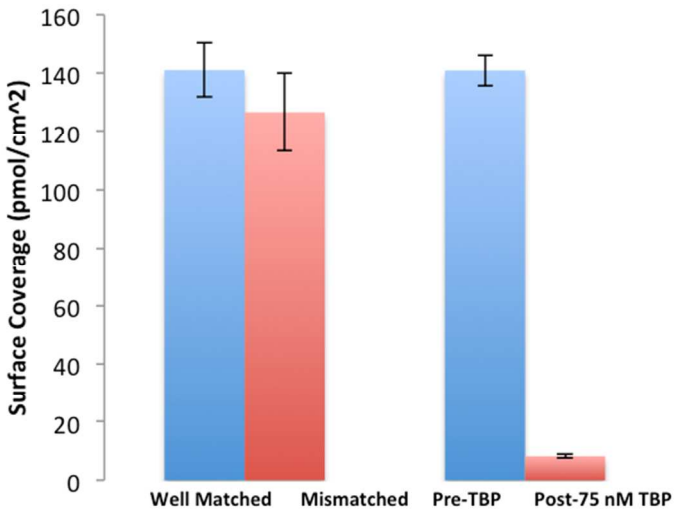

Figure S3: TBP DNA CT signal attenuation compared to quantified DNA surface coverage on an OCT-DNA monolayer. In blue is the surface coverage determined from the DNA-mediated electrochemical signal obtained from daunomycin for the TBP binding DNA sequence before and after the addition of 75 nM TBP. In red is the surface coverage determined from the electrochemical signal of ruthenium hexammine, which electrostatically interacts the phosphates in the DNA and does not report on helix integrity. Surface coverages are calculated from the quantification of the area of the anodic peak of a CV obtained for both reporters at a scan rate of 100 mV/s in Tris buffer (10 mM Tris, pH 7.6). As can be seen from the graph, the amount of DNA on the surface does not change upon addition of TBP, as quantified with ruthenium hexammine; the only observable difference in coverage is in the DNA-mediated daunomycin signal. Error bars are given for the standard deviation from three replicates for each experimental condition.

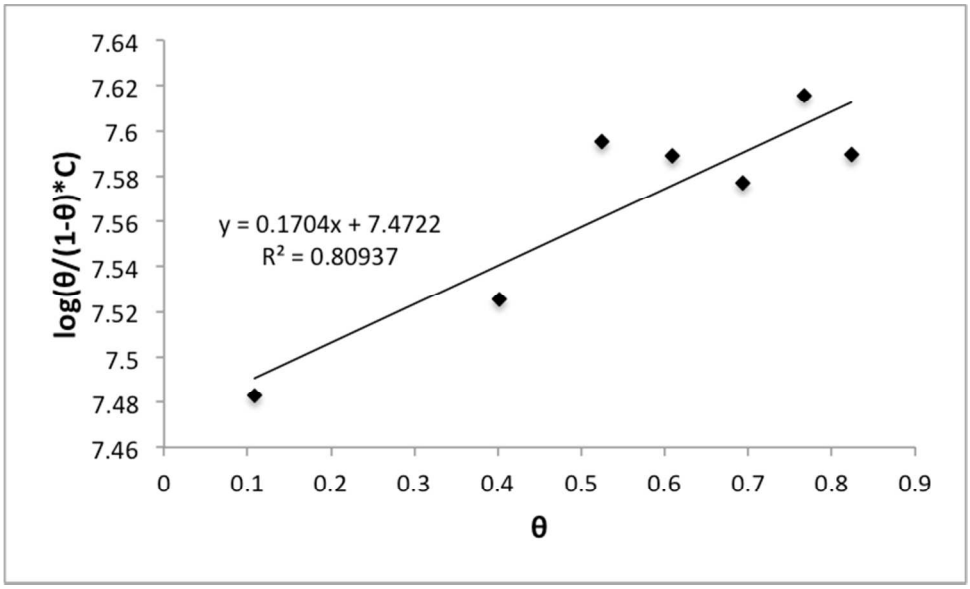

Figure S4: Linear fit of TBP titration data to the Frumkin-Fowler-Guggenheim adsorption isotherm. To determine the Frumkin coefficient (*a*) and the adsorption equilibrium constant (β) from the titration data in Figure 5, a plot of log[θ/(1-θ)C] versus the fractional surface coverage (θ), where C is the solution concentration of TBP is constructed. The linear fit of the data is shown, from which the two desired parameters are extrapolated.

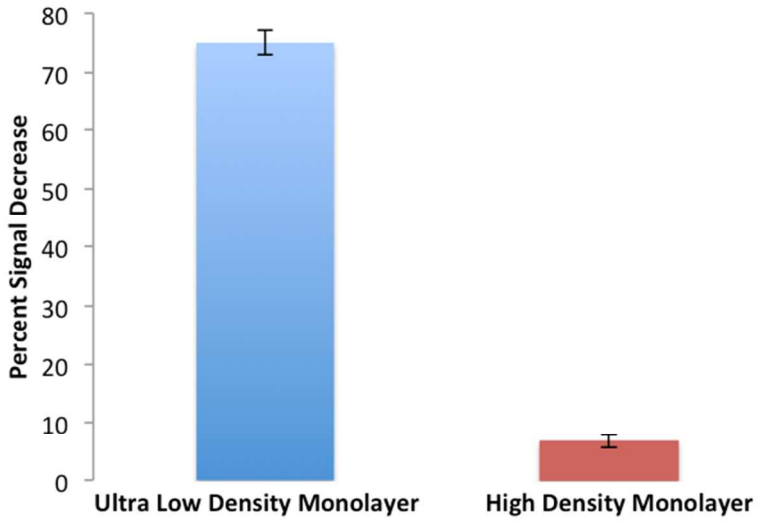

Figure S5: DNA CT TBP binding compared to quantified DNA surface coverage. In blue is the surface coverage determined from the DNA-mediated electrochemical signal obtained from daunomycin for TBP binding DNA in an OCT-DNA monolayer before the addition of TBP and after the addition of 75 nM TBP. In red is the surface coverage determined from the electrochemical signal of ruthenium hexammine, which electrostatically interacts the phosphates in the DNA and does not report on helix integrity. Surface coverages are calculated from the quantification of the area of the anodic peak of a CV obtained for both reporters at a scan rate of 100 mV/s in Tris buffer (10 mM Tris, pH 7.6). Error bars are given for the standard deviation from three replicates for each experimental condition.

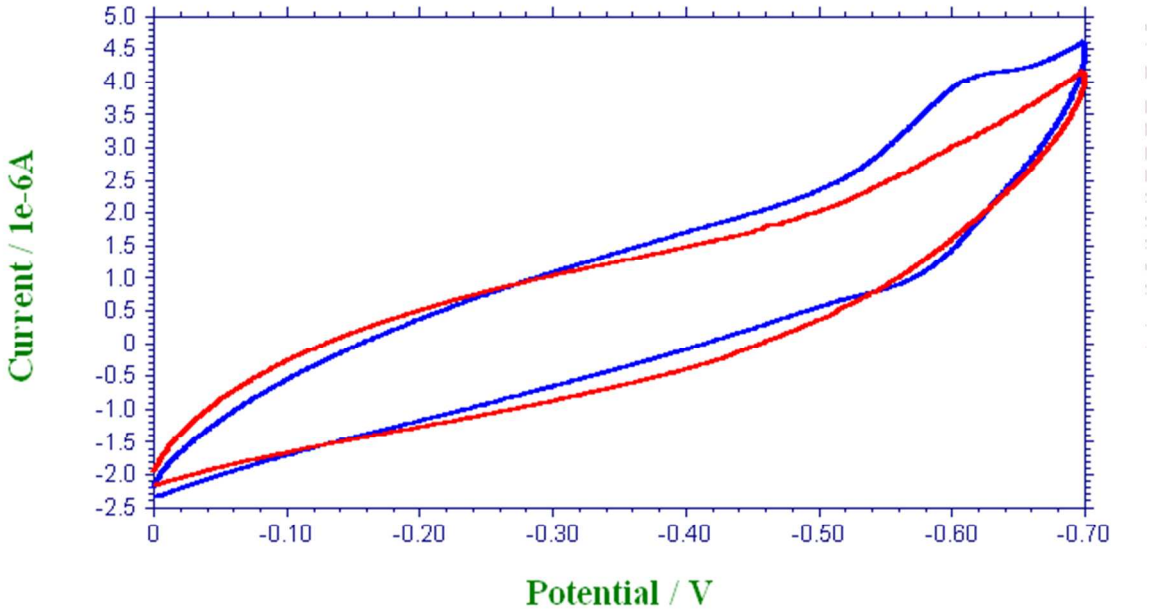

Figure S6: Raw cyclic voltammogram (CV) of the electrochemical signal discrimination observed between well-paired helices in an OCT-DNA monolayer (blue) and an OCT-DNA monolayer with DNA containing a CA mismatch (red) is shown. The background-subtracted CV is shown in Figure 2B. The CV was obtained with a scan rate of 100 mV/s. Both DNA duplexes were 17 base pairs in length. Traces were obtained with 2 μM daunomycin in Tris buffer (10 mM Tris, pH 7.6). Almost a complete signal loss is observed upon incorporation of a single CA mismatch.