Supporting Information

Coupling Into the Base Pair Stack is Necessary for DNA-mediated Electrochemistry

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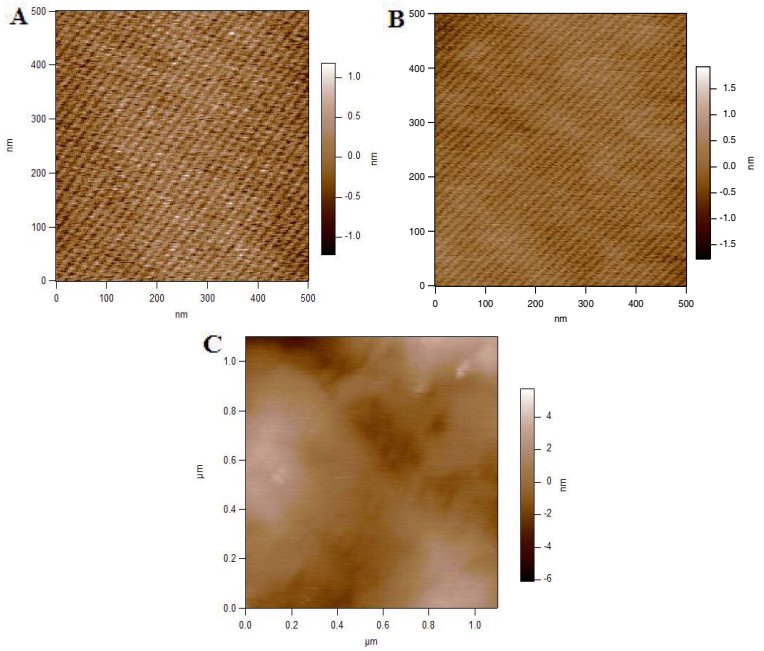

Figure S1. AFM characterization of DNA-modified and bare HOPG. Data were collected in 5 mM sodium phosphate, 50 mM NaCl, pH 7.1 (tapping mode). Typical AFM image of A: well matched DNA on HOPG, B: DNA featuring an acetylene-TEMPO modified uridine, and C: unmodified HOPG. Sequences for A are pyrene-$(CH_2)_3CONH(CH_2)_6$NHCO-5'-CTACAGTCTG- 3' pluswell matched complement and for B are pyrene-$(CH_2)_3CONH(CH_2)_6$NHCO-5'-CTACAGTCTG- 3' plus TEMPO modified complement.

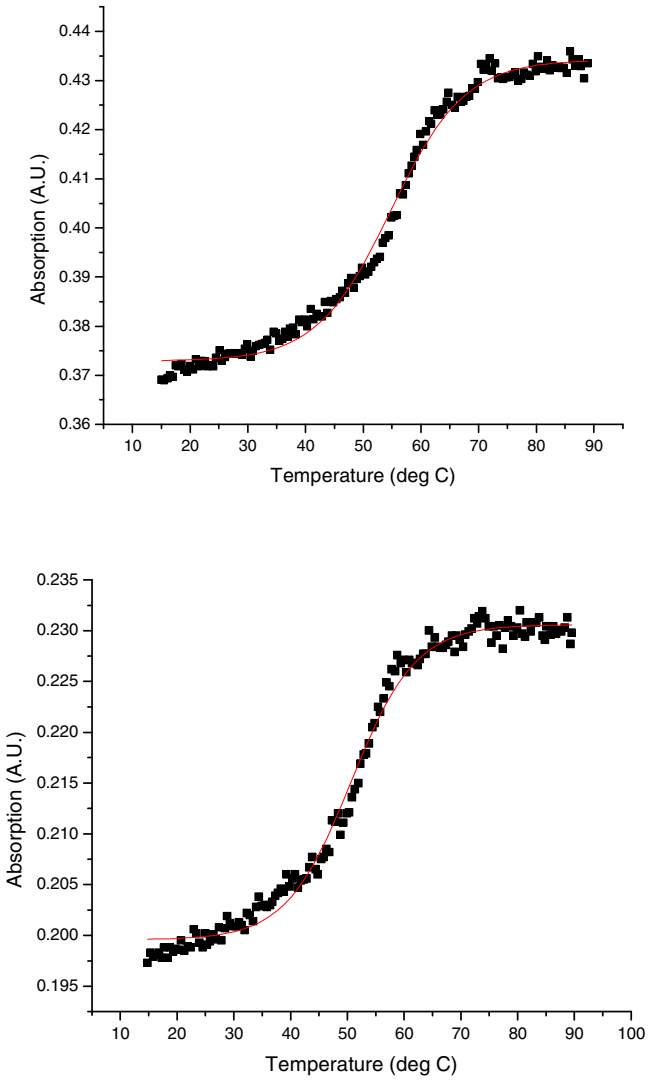

Figure S2. Melting temperature determinations of DNA modified by AQ through an acetylene linkage (top) and unmodified DNA with the same sequence (bottom). The melting temperature was determined through application of a sigmoidal fit (red), revealing a melting point of 55°C for AQ modified DNA, and 51°C for unmodified DNA. Data were collected in 5 mM sodium phosphate, 50 mM NaCl, pH 7.1.

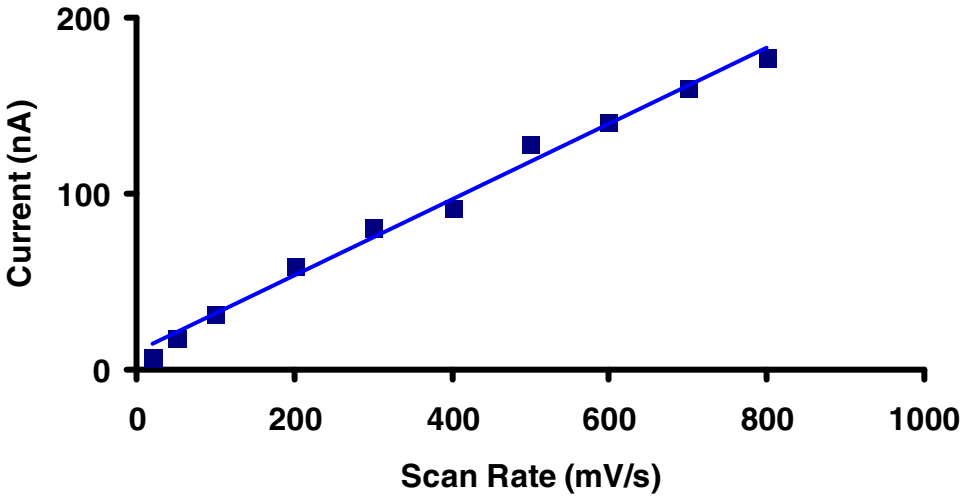

Figure S3. Scan rate dependence of DNA modified by AQ through an acetylene linkage. Data were collected in 5 mM sodium phosphate, 50 mM NaCl, pH 7.1.

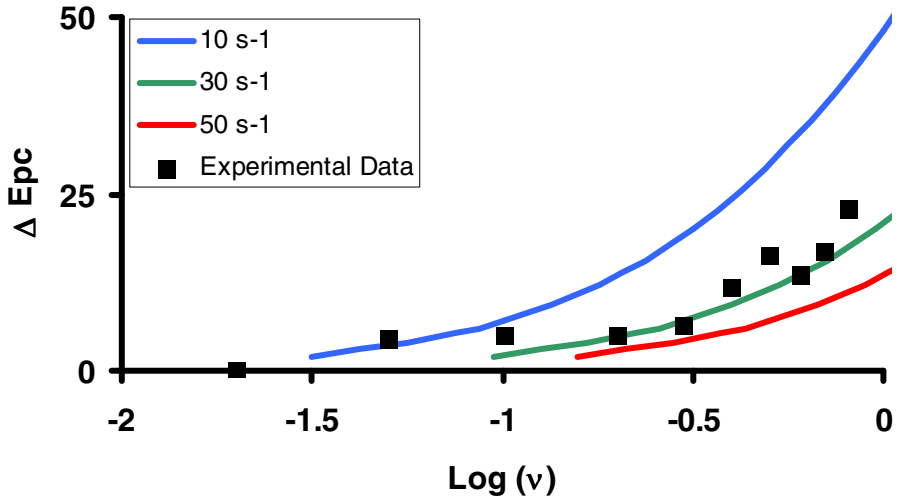

Figure S4. Plot of peak splitting ΔE_{pc} ($\Delta E_{pc} = E_{pc}-E°$) versus log (ν) (where ν = scan rate) for DNA modified by AQ through an acetylene linkage. Simulated curves corresponding to k_s values of 10 s^{-1} (blue), 30 s^{-1} (green) and 50 s^{-1} (red) are shown for comparison.[1]

[1]Tender, L., Carter, M.T., Murray, R.W., *Anal. Chem.*, **1994**, *66*, 3173-3181

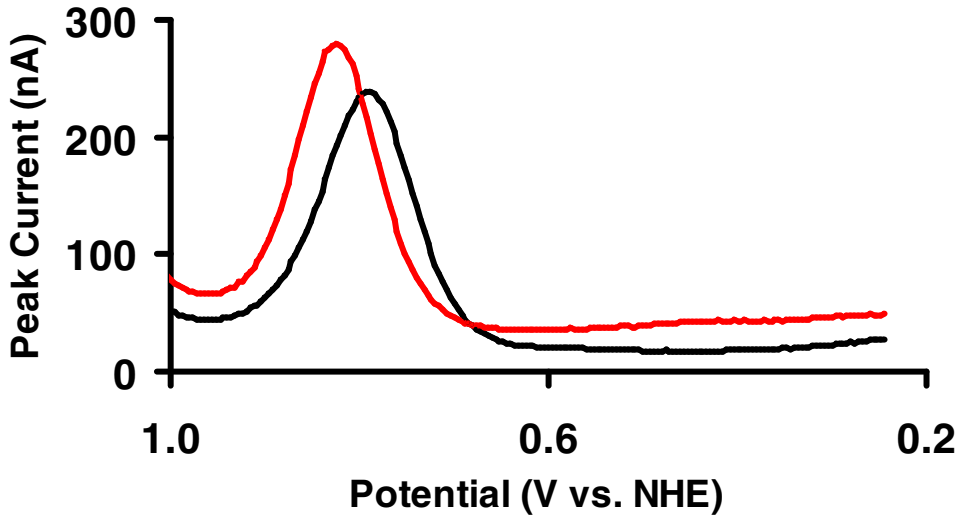

Figure S5. Square wave voltammetry of a DNA-modified surface featuring well matched DNA (black) and DNA with a CA mismatch above the TEMPO label (red). The sequence was pyrene-$(CH_2)_3CONH(CH_2)_6$ NHCO-5'-CTA C*A*G **T**CG T-3' plus TEMPO modified complement The italicized base indicates the location of the TEMPO, and the bold base indicates the location of the mismatch.