Bioconjugate Chemistry

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Supporting Material

Electrochemistry of Methylene Blue bound to a DNA-Modified Electrode

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Figure Captions

(S1) Plot of $E-E_{pc}$ *vs.* $\log(\nu/k^o)$; comparison of theoretical curve (line, ref. *29*) to data for 0.1 μM methylene blue at a gold electrode derivatized with 5'SH-$(CH_2)_6$-p-AGTACAGTCATCGCG 3' hybridized to its complement (filled triangles) in 25 mM phosphate, 75 mM NaCl, pH=7. The fit yields a value of k^o equal to 60(5) s^{-1}. We note that the formalism described in reference 29 is based on Marcus theory and was derived for redox-active species immobilized on electrode surfaces. In our case, the strong adsorption of MB to DNA in both its oxidized and reduced states, and the adherence to a Langmuir isotherm ensure that electron-transfer is not diffusion controlled (see ref. *30*). Additionally, this treatment assumes symmetric cathodic and anodic shifts about the reduction potential (a transfer coefficient, α, of 0.5, within the Butler-Volmer formalism); this condition appears to hold for MB reduction at our DNA-modified electrodes. Additionally, in aqueous solution at pH

7, MB undergoes a 2e-, 1H+ transfer *via* an ECE mechanism (*25*). Previous work has shown that the follow-up reactions are fast, and we have assumed this to hold for our system. Spectroelectrochemical experiments show isobestic conversion between the oxidized and doubly reduced states. Therefore, we have treated this system assuming a $2e^-$ transfer.

(S2) Cyclic voltammograms of 0.1 mM MB at a octadecanethiol-modified electrode. (B) Plots of i_{pc} and i_{pa} versus scan rate$^{1/2}$.

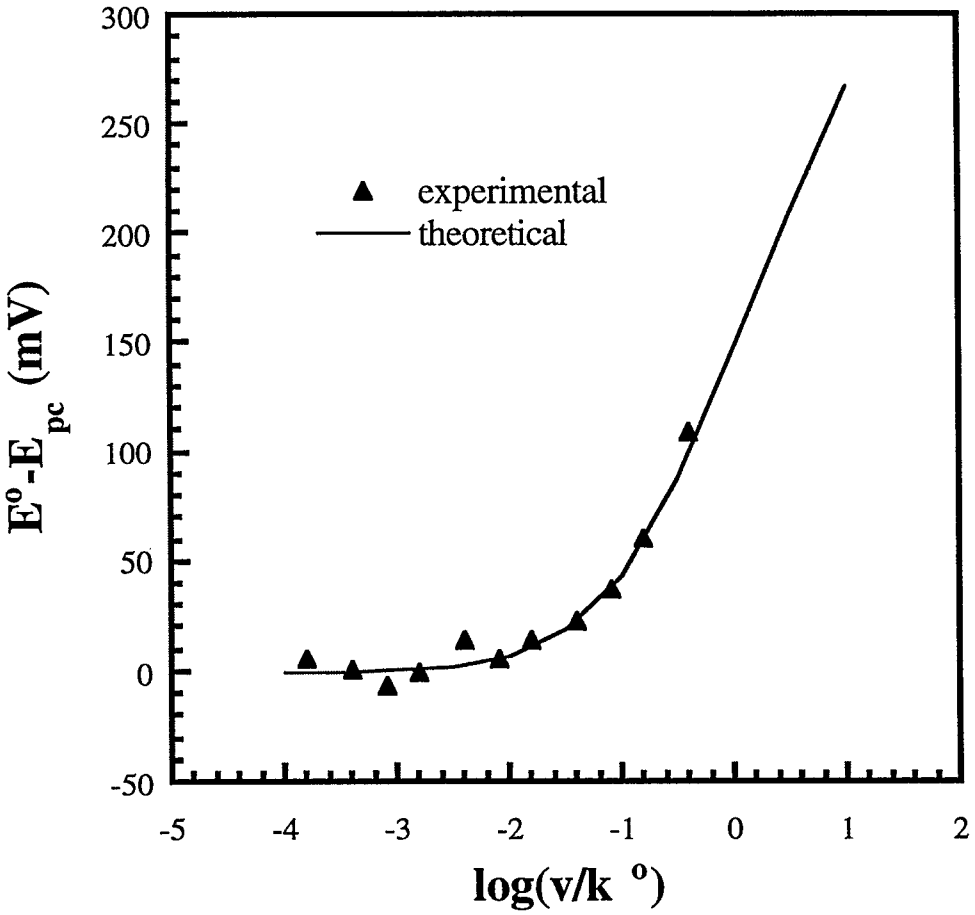
300
250
200
150
100
50
0
-50
-5
-4
-3
-2
-1
0
1
2
experimental
theoretical
E^o-E_{pc} (mV)
log(v/k ^{o})

Figure S1

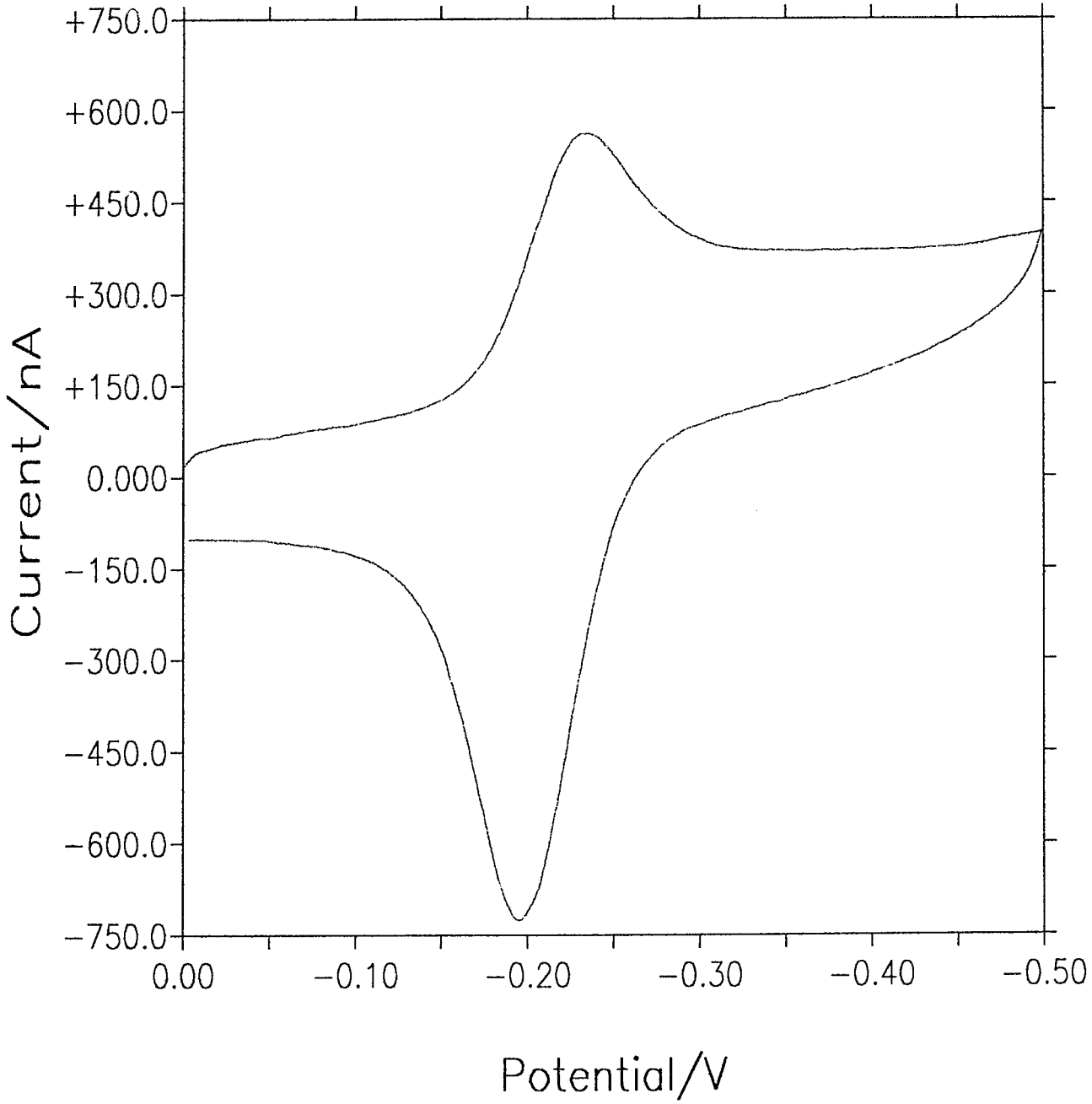
+750.0
+600.0
+450.0
+300.0
+150.0
0.000
−150.0
−300.0
−450.0
−600.0
−750.0
Current/nA
0.00
−0.10
−0.20
−0.30
−0.40
−0.50
Potential/V

Figure S2A

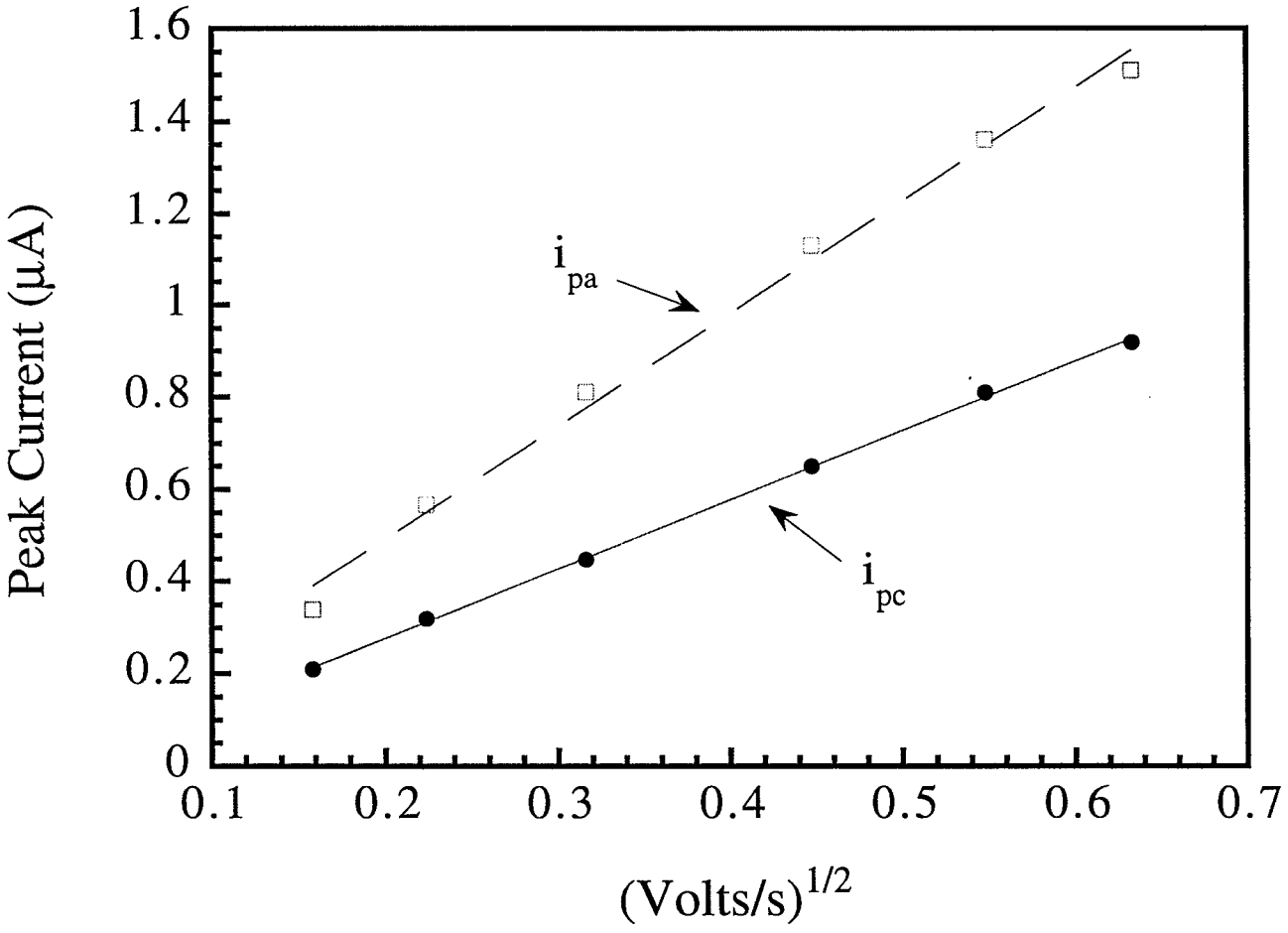
Peak Current (μA)
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
(Volts/s)^1/2
i pa
i pc

Figure S2B