

DNA-Mediated Electrochemistry of Disulfides on Graphite

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Abstract:

The electrochemistry of disulfides incorporated into the sugar-phosphate backbone of pyrene-modified DNA has been examined on highly oriented pyrolytic graphite (HOPG). Two signals, one irreversible, one reversible, are observed at -160 and -290 mV versus normal hydrogen electrode, respectively. The inclusion of a single base mismatch in the DNA duplex below the location of the disulfide leads to a significant attenuation in the electrochemical signal, while the inclusion of a mismatch above the disulfide has little effect on the electrochemistry observed. Thus disulfide reduction in the DNA backbone appears to be DNA-mediated. The redox couples found show a strong pH dependence consistent with formation of a disulfide radical anion or 2e⁻ reduction of the disulfide to the two thiols. These data demonstrate that DNA electrochemistry can be utilized to promote disulfide reduction at a distance mediated by the DNA duplex.