

Direct Electrochemistry of Endonuclease III in the Presence and Absence of DNA

Alon A. Gorodetsky, Amie K. Boal, and Jacqueline K. Barton*

Department of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125

jkbarton@caltech.edu

Received July 5, 2006

Abstract:

The electrochemistry of the base excision repair enzyme Endonuclease III (Endo III) in the presence and absence of DNA has been examined on highly oriented pyrolytic graphite (HOPG). At the surface modified with pyrenated DNA, a reversible signal is observed at 20 mV versus NHE for the $[4\text{Fe-4S}]^{3+/2+}$ couple of Endo III, similar to Au. Without DNA modification, oxidative and reductive signals for the $[4\text{Fe-4S}]$ cluster of Endo III are found on bare HOPG, allowing a direct comparison between DNA-bound and free redox potentials. These data indicate a shift of approximately -200 mV in the $3+/2+$ couple upon binding of Endo III to DNA. This potential shift reflects a difference in affinity for DNA of more than 3 orders of magnitude between the oxidized $3+$ and reduced $2+$ protein and provides quantitative support for our model utilizing DNA-mediated charge transport to redistribute base excision repair enzymes in the vicinity of damaged DNA.