

Intercalative Stacking: A Critical Feature of DNA Charge-Transport Electrochemistry

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Abstract:

In electrochemistry experiments on DNA-modified electrodes, features of the redox probe that determine efficient charge transport through DNA-modified surfaces have been explored using methylene blue (MB^+) and $\text{Ru}(\text{NH}_3)_6^{3+}$ as DNA-binding redox probes. The electrochemistry of these molecules is studied as a function of ionic strength to determine the necessity of tight binding to DNA and the number of electrons involved in the redox reaction; on the DNA surface, MB^+ displays $2e^-/1\text{H}^+$ electrochemistry (pH 7) and $\text{Ru}(\text{NH}_3)_6^{3+}$ displays $1e^-$ electrochemistry. We examine also the effect of electrode surface passivation and the effect of the mode (intercalation or electrostatic) of MB^+ and $\text{Ru}(\text{NH}_3)_6^{3+}$ binding to DNA to highlight the importance of intercalation for reduction by a DNA-mediated charge-transport pathway. Furthermore, in experiments in which MB^+ is covalently linked to the DNA through a σ -bonded tether and the ionic strength is varied, it is demonstrated that intercalative stacking rather than covalent σ -bonding is essential for efficient reduction of MB^+ . The results presented here therefore establish that efficient charge transport to the DNA-binding moiety in DNA films requires intercalative stacking and is mediated by the DNA base pair array.

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