

# Coupling into the Base Pair Stack Is Necessary for DNA-Mediated Electrochemistry

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## **Abstract:**

The electrochemistry of DNA films modified with different redox probes linked to DNA through saturated and conjugated tethers was investigated. Experiments feature two redox probes bound to DNA on two surfaces: anthraquinone (AQ)-modified uridines incorporated into thiolated DNA on gold (Au) and 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO)-modified uridines in pyrene-labeled DNA on highly oriented pyrolytic graphite (HOPG). The electrochemistry of these labels when incorporated into DNA has been examined in DNA films containing both well matched and mismatched DNA. DNA-mediated electrochemistry is found to be effective for the TEMPO probe linked with an acetylene linker but not for a saturated TEMPO connected through an ethylenediamine linker. For the AQ probe, DNA-mediated electrochemistry is found with an acetylene linker to uridine but not with an alkyl chain to the 5' terminus of the oligonucleotide. Large electrochemical signals and effective discrimination of intervening base mismatches are achieved for the probes connected through the acetylene linkages, while probes connected through saturated linkages exhibit small electrochemical signals associated only with direct surface to probe charge transfer and poor mismatch discrimination. Thus DNA electrochemistry with these probes is dramatically influenced by the chemical nature of their linkage to DNA. These results highlight the importance of effective coupling into the  $\pi$ -stack for long-range DNA-mediated electrochemistry.

Full Text: <http://pubs.acs.org/cgi-bin/article.cgi/bcches/2007/18/i05/pdf/bc0700483.pdf>