EXPLORING DNA-MEDIATED CHARGE TRANSPORT WITH FAST RADICAL TRAPS

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ABSTRACT

The π-stack of double stranded DNA is a competent bridge for mediating charge transport (CT), both by single-step (coherent) and multi-step (hopping) mechanisms. The yield of long-range single-step CT from photoexcited 2-aminopurine, a fluorescent analogue of adenine, to guanine across adenine tracts has a shallow, periodic distance - measure total CT yield to the DNA bases, herein we employ the fast radical traps N_2-cyclopropylguanine (^{CP}G), N_6-cyclopropyladenine (^{CP}A), and N_4-cyclopropylcytosine (^{CP}C), which are energetically similar to the unmodified bases, but undergo rapid decomposition upon oxidation or reduction. We find that decomposition of ^{CP}G by a photoexcited rhodium intercalator across an adenine tract has a similar periodic distance dependence to the quenching of 2-aminopurine by guanine, and the same temperature dependence as well. In contrast, decomposition of ^{CP}G by photoexcited 2-aminopurine is monotonic with respect to adenine tract length, and also competes with back electron transfer. Eliminating back electron transfer by separating 2-aminopurine from the adenine tract with three high-potential inosine bases restores the non-monotonic distance dependence. We also determined decomposition of ^{CP}A along adenine tracts by photoexcited rhodium, and found the CT yield to be distance-independent, demonstrating that the periodicity associated with guanine oxidation is with respect to adenine tract length, not donor-acceptor separation. This length-dependent periodicity, and the associated temperature dependence, support a model of conformational gating in the formation of CT-active domains along the DNA.

DNA-mediated electrochemistry is facile in self-assembled monolayers on electrodes, and redox-active dyes are reduced through the DNA π-stack at potentials far lower than those of the individual bases. Since cytosine is the most readily reduced base, we incorporated ^{CP}C into DNA monolayers to assay for bridge occupation, and ^{CP}C decomposition was not observed.

To explore the relative contributions of single-step and multi-step mechanisms to CT yield across adenine tracts, we compared quantum yields previously collected from 2-aminopurine fluorescence quenching experiments to those from ^{CP}G decomposition. We find that for seven or eight intervening adenines, single-step CT accounts for the entire CT yield, while for four to six adenines, multi-step CT is the dominant mechanism. We interrupted multi-step CT by substituting ^{CP}A for an adenine on the bridge, and found the total CT yield across five or six intervening adenines is lowered to the single-step CT yield. Blocking coherent CT by replacing the terminal guanine with redox-inactive inosine does not affect ^{CP}A decomposition on the bridge. These results imply that single-step and multi-step CT processes are not in direct competition for these assemblies, consistent with the model of conformationally gated CT-active states.

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