Rapid Radical Formation by DNA Charge Transport through Sequences Lacking Intervening Guanines

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Abstract:

Using the flash-quench technique to probe DNA charge transport in assemblies containing a tethered ruthenium intercalator, the kinetics and yield of methylindole radical formation as a function of DNA sequence were studied by laser spectroscopy and biochemical methods. In these assemblies, the methylindole moiety serves as an artificial base of low oxidation potential. Hole injection and subsequent formation of the methylindole radical cation were observed at a distance of over 30 Å at rates $\geq 10^7$ s^{-1} in assemblies containing no guanine bases intervening the ruthenium intercalator and GMG oxidation site. Radical yield was, however, strikingly sensitive to an intervening base mismatch; no significant methylindole radical formation was evident with an intervening AA mismatch. Also critical is the sequence at the injection site; this sequence determines initial hole localization and hence the probability of hole propagation. With guanine rather than inosine near the site of hole injection, decreased yields of radicals and long-range oxidative damage are observed. The presence of the low-energy guanine site in this case serves to localize the hole and therefore diminish charge transport through the base pair stack.

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