Charge equilibration between two distinct sites in double helical DNA

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DNA assemblies containing a pendant dipyridophenazine complex of Ru(II) along with two oxidative traps, a site containing the nucleoside analog methylindole (5'-GMG-3') and a 5'-GGG-3' site, have been constructed to explore long-range charge transport through the base pair stack. With these chemically well defined assemblies, in combination with the flash/quench technique, formation of the methylindole cation radical and the neutral guanine radical is monitored directly by using transient absorption spectroscopy, and yields of oxidative damage are quantitated biochemically by gel electrophoresis. In these assemblies the base radicals form with a rate of $\geq 10^7\ s^{-1}$. The rate of base radical formation does not change upon the addition of a second radical trap, the 5'-GGG-3' site; however, the yield of methylindole oxidation is significantly lower. This observation indicates that the 5'-GGG-3' site is effective in competing for the migrating charge and provides a second trapping site. Switching the orientation of the two trapping sites does not affect the yield of oxidized products at either site. Therefore, in DNA both forward and reverse charge transport occur so as to provide equilibration across the duplex on a timescale that is fast compared with trapping at a particular site. Further evidence of charge equilibration results from incorporating an intervening base-stacking perturbation and monitoring the fate of the injected charge. These experiments underscore the dynamic nature of DNA charge transport and reveal the importance of considering radical propagation in both directions along the DNA duplex.

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