The Effect of Varied Ion Distributions on Long-Range DNA Charge Transport

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Abstract:

Long-range oxidative damage to DNA was utilized as a probe to delineate the effects of different ion distributions on DNA charge transport. DNA assemblies were constructed, containing a tethered rhodium intercalating photooxidant, spatially separated from two 5'-GG-3' sites of oxidative damage, with either an A_6-tract or a mixed DNA sequence intervening between the guanine doublets; the extent of charge transport was assessed through measurements of the ratio of yields of damage at the guanine doublet distal versus that proximal to the metal binding site. The distal/proximal damage ratios were compared after photooxidation of otherwise identical Rh-tethered assemblies, except for ^{32}P-labeling either at the 5'- or 3'-end; this labeling difference corresponds, in the absence of charge neutralization by condensed counterions, to a shift in negative charge from one end of the duplex to the other. Both with assemblies containing the mixed sequence and the A_6-tract, we observed that moving the negative charges to the proximal end of the duplex significantly decreased hole transport to the distal end. We propose that these results reflect variations in the thermodynamic potential at the proximal and distal guanine sites because of the change in charges at the termini of the oligomer. High values for the internal dielectric constant of the stacked base pairs are suggested by these data. Hence, the longitudinal polarizability of DNA may be important to consider in mechanisms for long-range DNA charge transport.