Sequence Dependence of Charge Transport through DNA Domains

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Abstract:

Here we examine the photooxidation of two kinetically fast electron hole traps, N4-cyclopropylcytosine (CP) and N2-cyclopropylamine-guanosine (CPG), incorporated in DNA duplexes of various sequence using different photooxidants. DNA oxidation studies are carried out either with noncovalently bound [Ru(phen)(dppz)(bpy')]+ (dppz = dipyridophenazine) and [Rh(phi)2(bpy)]3+ (phi = phenanthrenequinone diimine) or with anthraquinone tethered to DNA. Because the cyclopropylamine-substituted bases decompose rapidly upon oxidation, their efficiency of decomposition provides a measure of relative hole localization. Consistent with a higher oxidation potential for CP versus CPG in DNA, CP decomposes with photooxidation by [Rh(phi)2(bpy)]3+, while CPG undergoes ring-opening both with photoexcited [Rh(phi)2(bpy)]3+ and with [Ru(phen)(dppz)(bpy')]+. Anthraquinone-modified DNA assemblies of identical base composition but different base sequence are also probed. Single and double base substitutions within adenine tracts modulate CP decomposition. In fact, the entire sequence within the DNA assembly is seen to govern CP oxidation, not simply the bases intervening between CP and the tethered photooxidant. These data are reconciled in the context of a mechanistic model of conformationally gated charge transport through delocalized DNA domains. Photooxidations of anthraquinone-modified DNA assemblies containing both CP and CPG, but with varied distances separating the modified bases, point to a domain size of at least three bases. Our model for DNA charge transport is distinguished from polaron models. In our model, delocalized domains within the base pair stack form transiently based upon sequence-dependent DNA structure and dynamics. Given these results, DNA charge transport is indeed remarkably sensitive to DNA sequence and structure.

Full Text: (May Require Subscription):
http://pubs.acs.org/cgi-bin/abstract.cgi/jacsat/2005/127/i49/abs/ja0563399.html