

DNA-Mediated Charge Transport Requires Conformational Motion of the DNA Bases: Elimination of Charge Transport in Rigid Glasses at 77 K

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Abstract:

We have proposed that DNA-mediated charge transport (CT) is gated by base motions, with only certain base conformations being CT-active; a CT-active conformation can be described as a domain, a transiently extended π -orbital defined dynamically by DNA sequence. Here, to explore these CT-active conformations, we examine the yield of base-base CT between photoexcited 2-aminopurine (Ap^*) and guanine in DNA in rigid LiCl glasses at 77 K, where conformational rearrangement is effectively eliminated. Duplex DNA assemblies (35-mers) were constructed containing adenine bridges $\text{Ap}(\text{A})_n\text{G}$ ($n = 0-4$). The yield of CT was monitored through fluorescence quenching of Ap^* by G. We find, first, that the emission intensity of Ap^* in all DNA duplexes increases dramatically upon cooling and becomes comparable to free Ap^* . This indicates that all quenching of Ap^* in duplex DNA is a dynamic process that requires conformational motion of the DNA bases. Second, DNA-mediated CT between Ap^* and G is not observed at 77 K; rather than hindering the ability of DNA to transport charge, conformational motion is *required*. Moreover, the lack of DNA-mediated CT at 77 K, even through the shortest bridge, suggests that the static structures adopted upon cooling do not represent optimum CT-active conformations. These observations are consistent with our model of conformationally gated CT. Through conformational motion of the DNA bases, CT-active domains form and break-up transiently, both facilitating and limiting CT.

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<http://pubs.acs.org/cgi-bin/abstract.cgi/jacsat/2004/126/i41/abs/ja0455897.html>