Back-Electron Transfer Suppresses the Periodic Length Dependence of DNA-Mediated Charge Transport across Adenine Tracts

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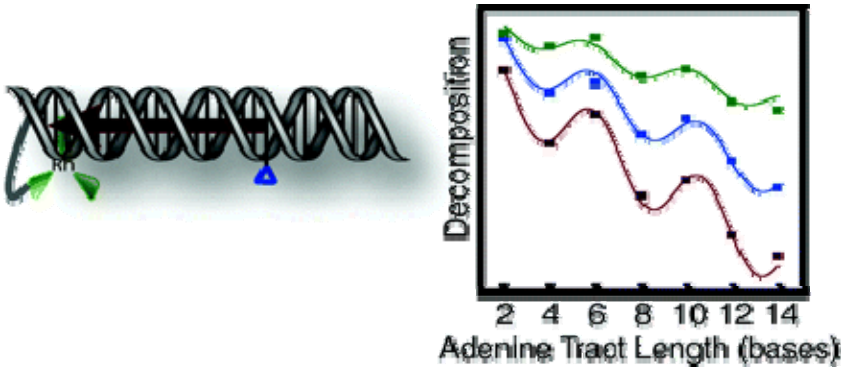

Abstract:

DNA-mediated charge transport (CT) is exquisitely sensitive to the integrity of the bridging π-stack and is characterized by a shallow distance dependence. These properties are obscured by poor coupling between the donor/acceptor pair and the DNA bridge, or by convolution with other processes. Previously, we found a surprising periodic length dependence for the rate of DNA-mediated CT across adenine tracts monitored by 2-aminopurine fluorescence. Here we report a similar periodicity by monitoring N_2-cyclopropylguanosine decomposition by rhodium and anthraquinone photooxidants. Furthermore, we find that this periodicity is attenuated by consequent back-electron transfer (BET), as observed by direct comparison between sequences that allow and suppress BET. Thus, the periodicity can be controlled by engineering the extent of BET across the bridge. The periodic length dependence is not consistent with a periodicity predicted by molecular wire theory but is consistent with a model where multiples of four to five base pairs form an ideal CT-active length of a bridging adenine domain.