

Long-Range Electron and Hole Transport through DNA with Tethered Cyclometalated Iridium(III) Complexes

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Abstract:

A cyclometalated complex of Ir(III) is covalently tethered to DNA oligonucleotides and serves as both a photooxidant and photoreductant in the study of DNA-mediated hole transport (HT) and electron transport (ET). Spectroscopic and melting temperature studies support intercalation of the tethered complex into the DNA duplex through the functionalized dppz ligand. Using these tethered assemblies, ET and HT is initiated in DNA by the same photoredox probe. Cyclopropylamine substituted bases, N₄-cyclopropylcytosine (^{CP}C) and N₂-cyclopropylguanine (^{CP}G) are used as kinetically fast electron and hole traps to probe the resulting electron migration processes after direct irradiation of the tethered Ir assembly. Oxidation of ^{CP}G and ^{CP}C is promoted efficiently by HT from photoexcited Ir(III) when the modified bases are positioned in the purine strands of the A-tract. In contrast, when ^{CP}C is embedded in a pyrimidine tract, ET to yield reductive decomposition is observed. Thus, the Ir(III)-tethered DNA assembly containing cyclopropyl-modified bases provides a unique model system to explore the two DNA-mediated electron migration processes using the same photoredox probe and the same DNA bridge.