

# Synthesis and Characterization of Iridium(III) Cyclometalated Complexes with Oligonucleotides: Insights into Redox Reactions with DNA

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## **Abstract:**

Heteroleptic cyclometalated complexes of Ir(III) containing the dipyrrophenazine ligand are synthesized through the direct introduction of a functionalized dipyrrophenazine ligand onto a bis(dichloro)-bridged Ir(III) precursor and characterized by <sup>1</sup>H NMR, mass spectrometry, as well as spectroscopic and electrochemical properties. The excited state of the Ir(III) complexes have sufficient driving force to oxidize purines and to reduce pyrimidine nucleobases. Luminescence and EPR measurements of the Ir(III) complex with an unmodified dppz bound to DNA show the formation of a guanine radical upon irradiation, resulting from an oxidative photoinduced electron-transfer process. Evidence is also obtained indirectly for reductive photoinduced electron transfer from the excited complex to the thymine base in DNA. We have also utilized cyclopropylamine-substituted nucleosides as ultrafast kinetic traps to report transient charge occupancy in oligonucleotides when DNA is irradiated in the presence of noncovalently bound complexes. These experiments establish that the derivatized Ir(III) complexes, with photoactivation, can trigger the oxidation of guanine and the reduction of cytosine.