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Charge Separation in a Ruthenium-Quencher Conjugate Bound to DNA

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Abstract:

A novel tris heteroleptic dipyridophenazine complex of ruthenium(II), $[\{\text{Ru}(\text{phen})(\text{dppz})(\text{bpy}'\text{-his})\}\{\text{Ru}(\text{NH}_3)_5\}]^{5+}$, containing a covalently tethered ruthenium pentammine quencher coordinated through a bridging histidine has been synthesized and characterized spectroscopically and biochemically in a DNA environment and in organic solvent. Steady-state and time-resolved luminescence measurements indicate that the tethered Ru complex is quenched relative to the parent complexes $[\text{Ru}(\text{phen})(\text{dppz})(\text{bpy}')]^{2+}$ and $[\text{Ru}(\text{phen})(\text{dppz})(\text{bpy}'\text{-his})]^{2+}$ in DNA and acetonitrile, consistent with intramolecular photoinduced electron transfer. Intercalated into guanine-containing DNA, $[\{\text{Ru}(\text{phen})(\text{dppz})(\text{bpy}'\text{-his})\}\{\text{Ru}(\text{NH}_3)_5\}]^{5+}$, upon excitation and intramolecular quenching, is capable of injecting charge into the duplex based upon the EPR detection of guanine radicals. DNA-mediated charge transport is also indicated using a kinetically fast cyclopropylamine-substituted base as an electron hole trap. Guanine damage is not observed, however, in measurements using the guanine radical as the kinetically slower hole trap, indicating that back electron-transfer reactions are competitive with guanine oxidation. Moreover, transient absorption measurements reveal a novel photophysical reaction pathway for $[\{\text{Ru}(\text{phen})(\text{dppz})(\text{bpy}'\text{-his})\}\{\text{Ru}(\text{NH}_3)_5\}]^{5+}$ in the presence of DNA that is competitive with the intramolecular flash-quench process. These results illustrate the remarkably rich redox chemistry that can occur within a bimolecular ruthenium complex intercalated in duplex DNA.

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