Photoinduced Oxidation with Metal Phenoxyls

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Photoinduced charge separation in the reaction center of photosystem II provides the driving force for the unfavorable reactions involved in carbon fixation. Motivations for preparing synthetic systems which model the efficient conversion of light into chemical potential include understanding fundamental steps in photosynthesis, as well as engineering new complexes capable of harnessing solar energy to permit unfavorable chemistry. Such systems require two components, one a photosensitizer, and the other a quencher capable of catalytic chemistry. Ru(II) polypyridyl systems are ideal photosensitizers due to their long-lived excited states, photoluminescence, and accessible potentials that can be coupled to other redox processes. Metal-phenolates catalyze the oxidation of primary alcohols to aldehydes. By covalently linking the two components, light can drive oxidation catalysis.

The mechanism of $Ru(bpy)_3^{2+}$ quenching by metal-phenolates is explored using Stern-Volmer analysis of steady state fluorimetry and lifetime data. The excited state $Ru(bpy)_3^{2+*}$ oxidizes the metal-phenolate, generating the active phenoxyl radical catalyst. Results of studies of catalytic turnover will be presented. The intermolecular studies elucidate the charge transfer properties of these complexes, leading to the design of photochemical dyads capable of the same behavior.