

Effect of Protonation State upon the Electrochemical and Photochemical Behavior of Porphyrin–Phenol Constructs

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A key aspect of photosynthesis is the coupling of single-electron photoexcitation events to multielectron, multiproton chemistry at catalytic centers. In photosystem II (PSII), the accumulation of oxidizing equivalents on the oxygen evolving complex (OEC) is aided by proton coupled electron transfer (PCET). PCET is also involved in the mediation of charge between the oxidized chromophore ($P_{680}^{+\bullet}$) and the OEC, a role filled by a tyrosine residue. In x-ray crystal structures, this species (tyrosine-Z) is observed within hydrogen bonding distance of a histidine residue. A hydrogen bond between the phenolic proton and imidazole base is believed to tune the reduction potential of tyrosine-Z to an appropriate value, and possibly contributes to rectifying behavior within PSII.

Herein we present the electrochemical behavior of a series of phenolic compounds, with or without a covalently attached base. These compounds mimic essential aspects of the tyrosine-histidine interaction found in PSII. We explore the influence of an intramolecular hydrogen bond upon phenol redox chemistry, as well as the effect of protonation/deprotonation by the introduction of exogenous acid/base. We further explore the importance of the phenol protonation state in controlling photoinduced electron transfer in a porphyrin-phenol molecular dyad. An improved understanding of PCET is basic to the development of biomimetic constructs for solar-to-chemical energy conversion.

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