

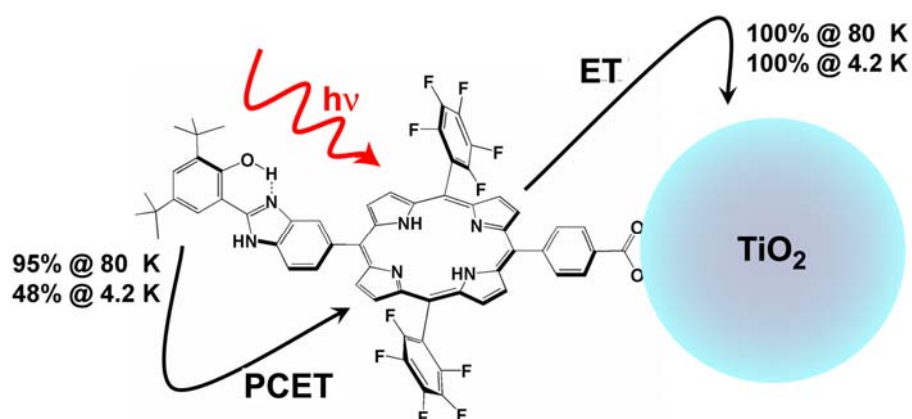
A Bioinspired High Potential Mediator that Mimics the Proton Coupled Electron Transfer between P680⁺ and the TyrZ-His190 Pair of Photosystem II

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Both biological and technological systems for the production of solar fuels inevitably have to interface single-electron photochemistry with multielectron catalytic reactions, such as the oxidation of water and the reduction of CO₂. In biological systems, such reactions involve the coupling of electron transfer to proton motion, aiding the accumulation of multiple redox equivalents. Proton coupled electron transfer (PCET) is involved in the basic mechanisms of myriad bioenergetic schemes and a mechanistic understanding of how electrons and protons are transferred in these reactions is fundamental to the design of successful energy conversion systems. One of the most discussed examples of PCET in natural energy systems is the conversion of tyrosine to the corresponding tyrosyl radical in Photosystem II. Recently, we have designed a photochemical system in which a modified bis-pentafluorophenyl porphyrin is attached to colloidal TiO₂. The TiO₂ conduction band serves as the primary electron acceptor from the photoexcited porphyrin moiety. Hole transport, facilitated by PCET, from the photo-oxidized porphyrin to a covalently attached tyrosine-histidine mimic (a phenol-benzimidazole pair) produces a phenoxyl radical that is chemically reversible and thermodynamically poised to oxidize water.



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