

Visible Light-Driven O₂ Reduction by a Porphyrin–Laccase System

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Abstract

Several recent studies have shown that the combination of photosensitizers with metalloenzymes can support a light-driven multielectron reduction of molecules such as CO₂ or HCN. Here we show that the association of the zinc tetramethylpyridinium porphyrin (ZnTMPyP⁴⁺) photosensitizer with the multicopper oxidase (MCO) laccase allows to link the oxidation of an organic molecule to the four electrons reduction of dioxygen into water. The enzyme is photoreduced within minutes with porphyrin/enzyme ratio as low as 1:40. With a 1:1 ratio, the dioxygen consumption rate is 1.7 μmol L⁻¹ s⁻¹. Flash photolysis experiments support the formation of the triplet excited state of ZnTMPyP⁴⁺ which reduces the enzyme to form a radical cation of the porphyrin with a $k_{ET} \approx 10^7 \text{ s}^{-1} \text{ M}^{-1}$. The long-lived triplet excited state of the ZnTMPyP⁴⁺ ($\tau_0 = 0.72 \text{ ms}$) accounts for a substantial electron-transfer quantum yield, $\phi_{ET} = 0.35$. Consequently, the enzyme-dependent photo-oxidation of the electron donor occurs with a turnover of 8 min⁻¹ for the one-electron oxidation process, thereby supporting the suitability of such enzyme/sensitizer hybrid systems for aerobic photodriven transformations on substrates. This study is the first example of a porphyrin-sensitized four-electron reduction of an enzyme of the MCO family, leading to photoreduction of dioxygen into water.

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