

Efficient Water Oxidation Catalyzed by Homogeneous Cationic Cobalt Porphyrins

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A series of water-soluble cationic Co- and Mn-porphyrins was found to catalyze water oxidation to O₂ efficiently at room temperature and neutral pH. Co-TDMImP, with the most electron deficient porphyrin ring, was the most efficient catalyst, showing unusually high currents for Co-based homogeneous molecular catalysts. Faradaic efficiency was near 90%. Mechanistic investigations indicate the generation of a high-valent Co-porphyrin species as the reactive oxidant that has accumulated two oxidizing equivalents above Co^{III}-TDMImP. The buffer base in solution was shown to play several critical roles during the catalysis by facilitating both redox-coupled proton transfer processes leading to the reactive oxidant and subsequent O–O bond formation. The mechanisms of these homogeneous WOC processes will be compared and contrasted to other manganese and cobalt catalyzed heterogeneous systems.

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