

Photochemical Water Oxidation Reaction Catalyzed by a Doubly N-Confused Hexaphyrin Dinuclear Cobalt Complex

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The water oxidation reaction is a four-electron process; therefore, it is important that water oxidation catalysts (WOCs) can undergo multielectron transfer reactions. WOCs having redox-active ligands with a large

π -conjugated system such as Co porphyrins are known as highly active water oxidation catalysts.^{1,2} Thus, we were interested in evaluating the benefits of the unique structural and electronic features of a related binuclear cobalt complex to develop WOCs with enhanced performance. Doubly N-confused hexaphyrin (DNCH), which is a kind of expanded porphyrin, is a large macrocyclic ligand with a Hückel aromatic 26π system that can accommodate two metal ions. In this study, we report water oxidation activity of a doubly N-confused hexaphyrin dinuclear cobalt complex (Co_2DNCH).

The water oxidation activity of Co_2DNCH was investigated using $[\text{Ru}(\text{bpy})_3]^{2+}/\text{S}_2\text{O}_8^{2-}$ -based photosystem. By photoirradiation with visible light ($430 \text{ nm} < \lambda < 510 \text{ nm}$), oxygen was obtained maximum with turnover number (TON) = 1200, turnover frequency (TOF) = 3.9 s^{-1} (Fig. 2).³ Under the same conditions, CoPF_5 , which has the same aryl groups as those in Co_2DNCH , also evolved oxygen with TOF = 0.051 s^{-1} and TON = 83. Thus, we revealed that Co_2DNCH is highly efficient WOC. The study of electrochemical water oxidation behavior will also be discussed.

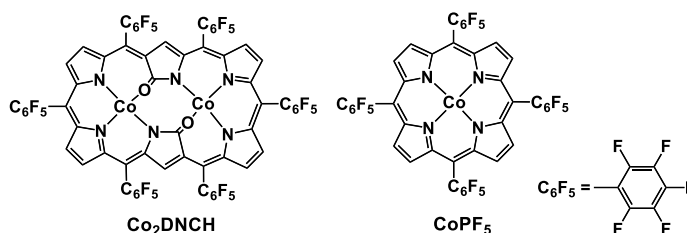


Fig. 1 Structures of Co_2DNCH and CoPF_5 .

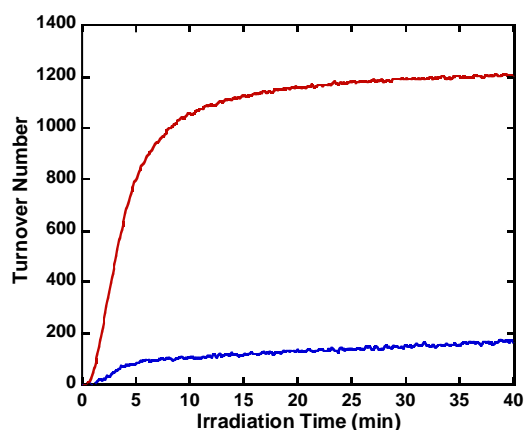


Fig. 2 Photochemical oxygen evolution from a 9:1 water/acetone- d_6 mixture. (Red) Co_2DNCH , (Blue) CoPF_5

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