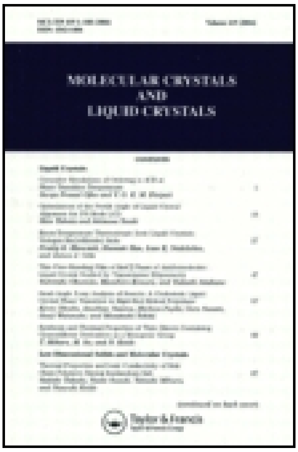

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Manganese-Cerium Porphyrin Tri-nuclear Complex as a Catalyst for Water Oxidation

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The oxidation of water to O_2 was carried out by bulk electrolysis. As a catalyst for the oxidation, the effect of cerium double decker porphyrin as an electron mediator was evaluated. The best performance was observed when the $Ce(TCPP)_2$ was added to the MnTPPS-MnTMPyP as a catalyst.

Keywords: 4-electron oxidation of water; dinuclear Mn-porphyrin; double decker cerium porphyrin; multi-nuclear complex

INTRODUCTION

Multi-electron transfer plays an important role in many chemical and life reactions. For examples, the 4-electron reduction of oxygen molecules is in the breath reaction and the water molecule is the 4-electron donor for the reduction of carbon dioxide in photosynthesis. Also, the water oxidation is a key reaction not only for realizing artificial photosynthesis, but also for the photo-energy conversion to hydrogen.

The oxidation of water consists of the electron transfer process,[1] which possesses a large activation energy. Therefore, a catalyst of H_2O oxidation such as manganese or ruthenium complexes[2-9] requires the efficient electron withdrawing from the catalytic center. The 4-step, 4-electron oxidation of water results in applying a highly anodic potential (2.74 V vs. NHE) as an overvoltage. The standard redox potential of one-step 4 electron oxidation of water is thermodynamically determined to be 1.21 V vs. NHE. Therefore, water oxidation takes place at a lower potential in the one-step 4-electron process.

The water-soluble manganese porphyrin assembly is reported as a catalyst for water oxidation.[10]

$Ce(TCPP)_2$ as an electron mediator, which has similar redox potential to the catalytic center, is expected to facilitate effective multi-electron transfer reaction. This paper reported the effect of electron mediation by the cerium double-decker porphyrin for the catalysis of water oxidation in comparison with binuclear complex system, in which the oxygen evolution is detected during the electrolysis.

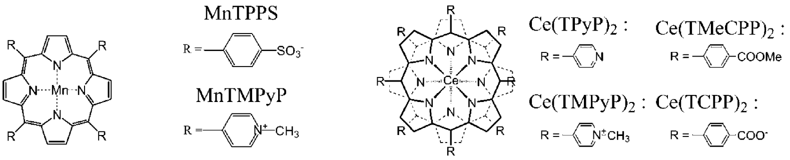

FIGURE 1 The structures of Water-soluble Mn and Ce Porphyrin

EXPERIMENTAL

The manganese porphyrins with ionic substituent (Mn(III)TPPS and Mn(III)TMPyP) were synthesized as the method of previous report.[11,12] Cerium double-decker porphyrin ($Ce(III)(TMPyP)_2$ and $Ce(IV)(TCPP)_2$) were synthesized according to the modified method of literature.[13-15]

$Ce(III)(TMPyP)_2$ Bis(meso-tetrakis(1-methyl-4-pyridinium)porphyrinato)cerium(III)

$Ce(IV)(TpyP)_2$ was synthesized as a precursor. *meso*-tetrakis(4-pyridyl)porphine (H_2TPyP) was dissolved in tetrachlorobenzene under Ar, and stirred for 20 min at room temperature after adding n-BuLi (8eq). $Ce(acac)_3$ (tetra-hydrate was dehydrated under vacuum at 80°C) was added (3eq) to the solution and refluxed for 5 hr. The reaction mixture was chromatographed on aluminum oxide and eluted with MeOH/ CH_2Cl_2 = 0.5~2 %. $Ce(IV)(TPyP)_2$ was characterized by comparing ^{1}H-NMR to literature. Ce(IV)(TPyP)$_2$ was dissolved in $CHCl_3$ and added CH_3I under Ar. The mixture was stirred for 3 days at 50°C. The precipitate was filtered and purified using an ion exchange resin (Amberlite CG400 Cl^- form). The UV-vis spectrum of Ce(III)(TMPyP)$_2$ was agreed with the literature data.[16]

Ce(IV)(TCPP)$_2$ Bis(*meso*-tetrakis(4-carboxyphenyl)porphynato)cerium(IV)

meso-tetrakis(4-(methoxycarbonyl)phenyl)porphine (H_2TMeCPP) was synthesized from pyrrole and methyl-4-formylbenzene in refluxing propionic acid. The precipitate was filtered and washed with methanol. Ce(IV)(TMeCPP)$_2$ was synthesized as the same procedure of Ce(IV)(TPyP)$_2$. The crude product was chromatographed on aluminum oxide and eluted with AcOEt/CH_2Cl_2 = 4~20%. Ce(IV)(TCPP)$_2$ was prepared from hydrolysis of Ce(IV)(TMeCPP)$_2$ in THF was performed by adding 1N NaOH aq and stirred for 3days. UV-vis : (NaOH / H_2O, pH 12) 395nm ($\varepsilon = 2.9 \times 10^5$ M^{-1} cm^{-1})

RESULTS AND DISCUSSION

The aggregation of cerium porphyrin with manganese porphyrin was characterized by the Job's method[17] using the UV-vis titration. The Job plots of Ce(III)(TMPyP)$_2$-Mn(III)TPPS and Ce(IV)(TCPP)$_2$-Mn(III)TMPyP show maximum spectra changes ($F(x)$) at the 1:2 equivalence points ($x = 0.33$) in each system (FIGURE 2). These results support the idea that tri-nuclear complexes (Mn : Ce = 2 : 1) are formed by the interaction between each porphyrin ring (FIGURE 3). The association constants of the dimer (K_D) and trimer (K_T) were estimated by the curve fitting of the theoretical line to the experimental one (Ce(III)(TMPyP)$_2$-Mn(IV)TPPS : $K_D = K_T = 1 \pm 1 \times 10^8$ mol^{-1} l, Ce(IV)(TCPP)$_2$-Mn(III)TMPyP : $K_D = K_T = 2 \pm 1 \times 10^6$ mol^{-1} l). Mn(III)TPPS and Mn(III)TMPyP also ionically form a binuclear complex; the association constant was determined to be $K_D = 1 \pm 1 \times 10^5$ mol^{-1} l by the curve fitting method using the Job plots.

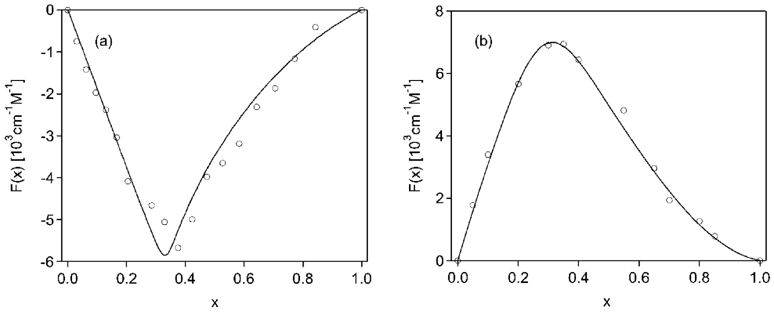

FIGURE 2 Job Plots of Mn *vs*. Ce porphyrin in aqueous solution (pH 12). Plot : experimental value, line : Curve fitting. x = ratio of Ce porphyrin.
(a) [Ce(TMPyP)$_2$] + [MnTPPS] = 4 μM (λ = 466 nm)
(b) [Ce(TCPP)$_2$] + [MnTMPyP] = 5 μM (λ = 395 nm)

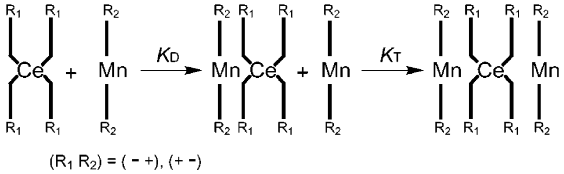

FIGURE 3 Cofacial stucking of water soluble porphyrin complex.

The catalytic activity toward H_2O oxidation was investigated by bulk electrolysis in pH 12 aqueous solution. First, the result of the electrolysis with Mn(III)TPPS-Mn(III)TMPyP is shown in FIGURE 3. Mn(III)TPPS-Mn(III)TMPyP shows catalytic activity compared with the blank experiment. During the electrolysis using the mononuclear Mn complex as a catalyst, no O_2 generation was detected. These results agree with those in the literature.[10]

A larger amount of O_2 gas evolution was observed when Ce(IV)(TCPP)$_2$ was added to the aqueous solution of Mn(III)TPPS-Mn(III)TMPyP (FIGURE 4). These results indicate that the multi-electron transfer is facilitated by the cerium porphyrin associated with manganese porphyrin.

The redox of manganese porphyrin was observed at 0.73 V vs. SCE (MnTPPS), 0.95 V vs. SCE (MnTMPyP) and they are

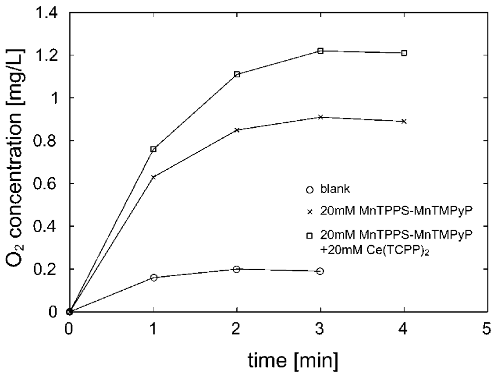

FIGURE 4 Plot of the dioxygen formed during the bulk electrolysis of H_2O in argon saturating 0.1 M $(Et)_4NClO_4$ + 0.2 M $(Et)_4NOH$ / H_2O (pH 12). The potential of working electrode (Pt) was fixed at at 1.1V vs. SCE . The detection of O_2 was performed with a dissolved-oxygen electrode.

considered as the generation of Mn(V)=O.[18-21] Then, two reversible redoxes of Ce(IV)$(TCPP)_2$ (0.56 V, 0.80 V vs. SCE) was assigned as the reduction of the porphyrin ring[22] by the spectral evidences with electrolysis. The multi-electron transfer through porphyrin complex of Ce with Mn-Mn is promoted based on the similar redox potentials of each one[23], witch is well known to be form associating porphyrin complexes with anionic substituents for the compensation of the positive charge at higher valence state of metal ion.[24]

The same experiment employing MnTPPS-MnTMPyP and $Ce(TMPyP)_2$ did not show any enhancement in the catalytic behavior because of the large potential separation between $Ce(TMPyP)_2$ (0.4 V vs. SCE) and manganese porphyrin dimer.

CONCLUSION

To attempt the efficient multi-electron transfer for water oxidation, manganese porphyrins with cerium double-decker porphyrin were used as a catalyst for the electrolysis of water. An obvious enhancement in the catalytic activity was observed when the $Ce(TCPP)_2$ was used as electron mediator to MnTPPS-MnTMPyP complex.

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