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KYUSHU UNIVERSITY

（様式３）

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論 文 名　：　Development of Earth-Abundant Molecular Systems for Efficient Photocatalytic CO_2 Reduction in Fully Aqueous Media
(光触媒的二酸化炭素還元を高効率に促進する
環境適合型分子システムの開発)

区　　分　：　甲

論　文　内　容　の　要　旨

Due to the vast combustion of fossil fuels in the past century, humankind currently suffers from substantial climate changes due to the global warming by excessive atmospheric greenhouse gases. Among them, carbon dioxide (CO_2) levels in the atmosphere have been steadily increasing. Recently, the International Panel on Climate Change (IPCC) predicted that CO_2 concentrations could run up to 590 parts per million (ppm) by 2100 with the temperature rising at least 1.9 °C, which may contribute to unpredictable and serious non-natural disasters. Thus, greenhouse gas emissions must be substantially suppressed by replacing fossil fuels with sustainable energy sources, such as solar, hydroelectric, oceanic, geothermal, wind, hydrogen and biomass energy. Artificial synthesis of either C1 or C2 fuels from CO_2 based on either photocatalytic or electrocatalytic process has also attracted much attention in order to develop technologies enabling renewable energy cycles.

Great efforts have been therefore devoted to developing artificial photosynthetic CO_2 reduction systems. However, many of them have been studied in organic solvents. From a practical viewpoint, photocatalytic system using water as a solvent considerably benefits, since water is highly abundant and environmentally benign solvent and provides the protons and electrons required for the CO_2 reduction. Nevertheless, it is highly challenging to use water as reaction media, since CO_2 conversion may suffer from the competition with water reduction, which is kinetically and thermodynamically more favorable, leading to diminish the efficiency and selectivity of CO_2 reduction *vs*. water reduction. In addition, environmentally friendly as well as earth-abundant systems should also be developed by limiting the use of precious metals towards the widespread implements in the future. In this regard, the aim of thesis here is to develop efficient homogeneous molecular photocatalytic systems based on the earth-abundant elements for CO_2 reduction in fully aqueous media.

Cost effective Cu(I) complexes with highly luminescent, long-lived with tunable spectroscopic and redox properties are considered as appealing alternatives to replace traditional noble-metal (*e.g.*, Ru, Ir) photosensitizers for artificial photolysis. Especially, the heteroleptic Cu(I) complexes of the type $[Cu(P\hat{}P)(N\hat{}N)]^+$ (P^P = diphosphine; N^N = diimine) were targeted. By introducing sulfonate groups, a water-soluble Cu(I) photosensitizer (**CuPS**, see **Figure 1**) was firstly obtained and characterized by photophysical and electrochemical studies. This achievement gave a substantial impact in promoting the studies in this thesis.

Metalloporphyrins are known as the robust catalysts for CO_2 reduction owing to the macrocyclic effect. To make the metalloporphyrin catalysts well soluble in aqueous media, the catalysts tethered to charged moieties, as those depicted in **Figure 1**, have been selected in this study. By employing the fully aqueous photocatalytic CO_2 reduction systems consisting of **CuPS** as a photosensitizer and different cobalt porphyrin catalysts in combination with ascorbate ($AscH^-$) as a sacrificial electron donor, the high turnover number (TON) for CO formation and selectivity of CO_2 reduction over H_2 evolution (Sel_{CO2}) were obtained. The **CuPS**-driven CO_2 reduction catalyzed by **Co(TPPS)** afforded TON_{CO} of 1085 with Sel_{CO2} of 90%. **Co(*p*TMPyP)** showed by outstanding catalytic performance in TON_{CO} of 2680 and TOF_{CO}^{max} of 2600 h^{-1} with slightly lower Sel_{CO2} of 77%. Notably, the observed photocatalytic enhancement exhibited by **Co(*p*TMPyP)** was discussed in terms of the multi-electron chargeable character, where **Co(*p*TMPyP)** was confirmed to bind CO_2 after at least four-electron reduction according to electrochemical studies. On the other hand, compared with **Co(*p*TMPyP)**, substantial improvement in TON_{CO} (4000) together with Sel_{CO2} (90%) for **Co(*o*TMPyP)** could be achieved. Note that this TON_{CO} by **Co(*o*TMPyP)** is among the highest values reported thus far within the group of fully earth abundant photocatalytic systems in water.

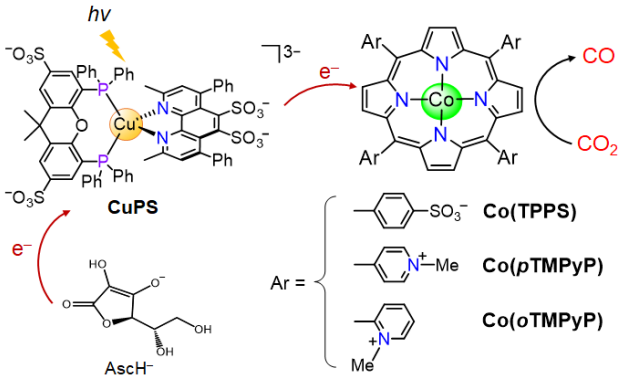

Figure 1. Earth-abundant photocatalytic systems for CO_2 reduction focused in this study.

Finally, the mechanisms of two different type multi-electron chargeable cobalt porphyrin catalysts, **Co(*p*TMPyP)** and **Co(*o*TMPyP)**, were successfully elucidated based on the electrochemical and density functional theory (DFT) studies, as shown in **Figure 2**. The H_2 evolution path is strongly inhibited by the active intermediate of **Co(*o*TMPyP)** possessing a low-spin d^7 Co^{II} center due to its mismatch in forming an effective molecular orbital (MO) association with a $1s(H^+)$ orbital. To the best of the knowledge, this is the first catalyst example avoiding the standard path relying on a filled d_{z2} orbital in binding CO_2. Instead, both π- and σ-type frontier MO associations are formed by two degenerated $\pi^*(CO_2)$ orbitals using a filled d_{xz} and a half-filled d_{z2} orbital. However, in the case of **Co(*p*TMPyP)**, highly electron charged intermediates show switching in configuration from $(d_{xz})^2(d_{z2})^1$ to $(d_{xz})^1(d_{z2})^2$, permitting the standard σ-type interaction of the $(d_{z2})^2$ pair with CO_2. Correlation between the multi-electron charging behaviors of cobalt porphyrins and the mechanism of photo- and electrocatalytic CO_2 reduction is rationalized by using the DFT results. The achievement made in this thesis sheds new light on strategies to rationally control the reaction rates and/or pathways based on the frontier MO engineering.

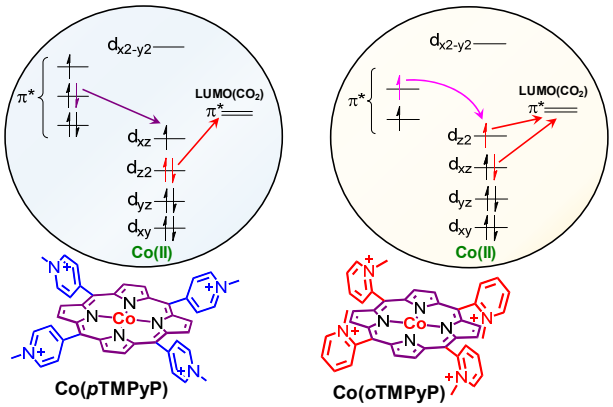

Figure 2. MO associations of **Co(*p*TMPyP)** and **Co(*o*TMPyP)**, respectively.