

Development of Earth-Abundant Molecular Systems for Efficient Photocatalytic CO₂ Reduction in Fully Aqueous Media

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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)			
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論 文 審 査 の 結 果 の 要 旨

To mitigate the global warming and climate change, substantial efforts have been made to diminish atmospheric CO₂ emissions. The light-driven conversion of CO₂ to value-added chemicals and fuels is among the most promising approaches towards this issue. A great number of homogeneous molecular systems are well-developed with respect to photocatalytic CO₂ reduction reaction (CO₂RR). From a practical and sustainable view, the development of environmental-friendly and earth-abundant photochemical reduction systems by avoiding the use of organic solvents is one of the most crucial targets. However, the earth-abundant homogeneous molecular catalytic systems for efficient photocatalytic CO₂RR in fully aqueous media have not been widely studied so far. In this context, this candidate has attempted to develop photosystems free of precious metals for CO₂ reduction only in aqueous solutions. Moreover, the mechanisms of photoinduced CO₂RR were well-interpreted by electrochemical combined with computational studies.

In Chapter 1, a water-soluble heteroleptic copper(I) complex (**CuPS**) with four hydrophilic sulfonate groups is firstly found and investigated by photophysical and electrochemical properties. Interestingly, because of steric hindrance surrounding to Cu center, **CuPS** could preserve the long-lived emission property (1.1 μs) even in a fully aqueous phase. In addition, **CuPS** is highly stable in water, although it remains a need to improve durability under the photocatalytic conditions since it gradually forms a more favorable homoleptic bisdiimine copper(I) species upon light illumination. Therefore, further efforts should be focused on exploring more stable copper photosensitizers over long-term irradiation in water.

In Chapter 2, this newly water-soluble **CuPS** has been successfully demonstrated as a photosensitizer for CO₂RR. Moreover, by employing this **CuPS** in combination with cationic cobalt porphyrin catalyst, **Co(pTMPyP)**, tethered to four *para-N*-methylpyridinium moieties possessing multi-electron chargeable character, an efficient, selective, and non-noble molecular-based photocatalytic aqueous system is achieved with a high turnover number (TON_{CO} = 2680) and selectivity (Sel_{CO₂} = 77%) for CO₂-to-CO conversion.

In Chapter 3, further examinations on two more positively charged cobalt porphyrin catalysts, namely **Co(TMAPP)** and **Co(oTMPyP)**, are carried out in **CuPS**-driven photocatalytic system for CO₂-to-CO conversion in purely aqueous media. An important finding is that substantial improvement in Sel_{CO₂} (90%) and TON_{CO} (4000) can be achieved by **Co(oTMPyP)** catalyst, which possesses *ortho-N*-methylpyridinium

substituents. Notably, such catalytic performance is among the highest values reported thus far within the group of earth-abundant photocatalytic systems used for CO₂RR in water.

In Chapter 4, the mechanisms of two different multi-electron chargeable cobalt porphyrin catalysts (*i.e.*, **Co(*p*TMPyP)** and **Co(*o*TMPyP)**) are successfully clarified based on electrochemical and DFT studies. The computed reduction potentials show good consistence with experimental results of both catalysts, and the computational results directly support the assignments of each reduction process of **Co(*p*TMPyP)** and **Co(*o*TMPyP)**. Note that the H₂ evolution path is strongly inhibited by the active intermediate of **Co(*o*TMPyP)** possessing a low-spin d⁷ Co^{II} center due to its mismatch in forming an effective MO association with a 1s(H⁺) orbital. This is the first catalyst example avoiding the standard path relying on a filled d_{z²} orbital in binding CO₂. Instead, both σ- and π-type frontier MO associations are formed by two degenerated π*(CO₂) orbitals using a filled d_{xz} and a half-filled d_{z²} orbital. In the case of **Co(*p*TMPyP)**, however, 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 CO₂. Correlation between the multi-electron charging behaviors of cobalt porphyrins and the mechanism of photo- and electrocatalytic CO₂ reduction is rationalized using the DFT results. This work certainly sheds new light on the strategies to rationally control the reaction rates and/or pathways based on the frontier MO engineering.

As described above, this candidate has successfully advanced the new strategies to develop highly active photocatalytic CO₂ reduction systems based on the unique multi-electron transfer processes together with the use of unprecedented types of rate-determining mechanisms. These achievements are expected to provide a high impact to the artificial photosynthesis community and the related fields. Based on these achievements together with the results of the PhD Thesis Defense, the Degree Committee concluded to approve the candidate for the award of the degree of Doctor of Science.