H_2 Evolution and CO_2 Reduction Reactions Catalyzed by Cobalt-based Molecular Catalysts

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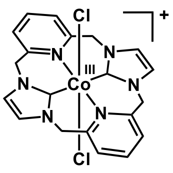
Artificial photosynthesis based on splitting water into H_2 and O_2 with solar energy has attracted recent years. In order to realize overall water-splitting reaction ($2H_2O + 4h\nu \rightarrow 2H_2 + O_2$) on the basis of molecular systems, it is crucial to ensure sufficient driving force for both H_2 and O_2 evolution reactions (HER and OER). We have previously studied on molecular photosystems in which HER is driven by oxidative quenching of $[Ru^*(bpy)_3]^{2+}$, but the reaction rates and turnover numbers were relatively low when **Co-NHC1** and other molecular catalysts were employed [1,2]. On the other hand, the reductive quenching of $[Ru^*(bpy)_3]^{2+}$ provides large driving force for HER but insufficient driving force for OER in the acidic to neutral pH range. In this study, we focus on a new strategy to maintain the driving force for both HER and OER by carrying out the reductive quenching process of $[Ru^*(bpy)_3]^{2+}$ under highly alkaline conditions.



Co-NHC1

A large amount of H_2 (turnover number = 40000 at pH = 12.8) evolved when using a $[Ru(bpy)_3]^{2+}$/ascorbate photochemical system in the presence of a newly synthesized new Co-NHC catalyst for HER even under highly alkaline conditions (Figure 1). Furthermore, it was found that the new catalyst is more durable than **Co-NHC1**. More interestingly, as the pH is increased, sustained evolution of H_2 takes place in larger amounts (pH < 12.8). On the other hand, the turnover frequency (TOF) of **Co-NHC1** has been also determined by conducting the electrochemical studies. Importantly, the TOF in the aqueous phosphate buffer solution (pH = 7) was estimated as tens of million s^{-1}.

Furthermore, we recently reported that some cobalt porphyrin compounds serve as efficient molecular catalysts in photochemical CO_2 reduction to CO even in aqueous media with high selectivity (**Sel$_{CO2}$** = 74-90%) (Figure 1) [3,4]. The mechanism of CO_2 reduction by cobalt porphyrins will be also discussed in detail.

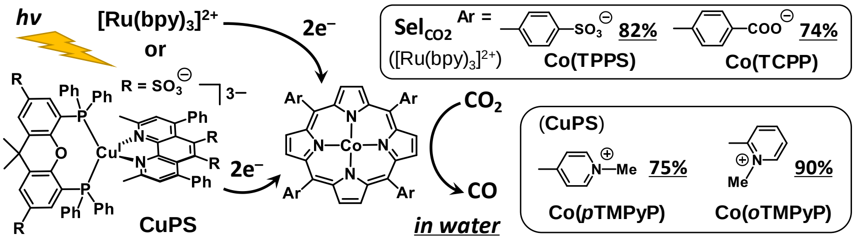


Figure 1. Photochemical CO_2 reduction catalyzed by cobalt porphyrins.

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[2] K. Yatsuzuka, K. Yamauchi*, K. Kawano, H. Ozawa*, K. Sakai*, *Sustainable Energy Fuels* **2021**, *5*, 740.

[3] A. Call*, M. Cibian*, K. Yamamoto, T. Nakazono, K. Yamauchi, K. Sakai*, *ACS Catal.* **2019**, *9*, 4867.

[4] A. Call*, M. Cibian, K. Yamauchi*, K. Sakai*, *Sustainable Energy Fuels,* **2022**, *6*, 2160.