Photochemical Hydrogen Evolution from Alkaline Water Catalyzed by Co-NHC Complexes

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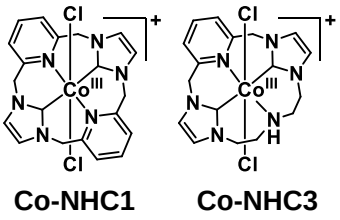
In order to realize overall water-splitting reaction ($2H_2O + 4h\nu \rightarrow 2H_2 + O_2$) on the basis of molecular systems, it is crucial to ensure sufficient driving force for both H_2 and O_2 evolution reactions (HER and OER). We have previously studied on molecular photosystems in which HER is 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.



A large amount of H_2 (TON = 40000 at pH = 12.8) evolved when using a $[Ru(bpy)_3]^{2+}$/ascorbate photochemical system in the presence of a newly synthesized **Co-NHC3** catalyst for HER even under highly alkaline conditions (Figure 1). Furthermore, it was found that **Co-NHC3** is more durable than **Co-NHC1**. More interestingly, as the pH increased, sustained evolution of H_2 took place in larger amounts (pH < 12.8). We are now carefully investigating the factors correlating with this unusual pH response toward the catalytic activity. In the presentation, we will show the overall picture for photocatalytic cycle of HER by **Co-NHC3** and **Co-NHC1**.

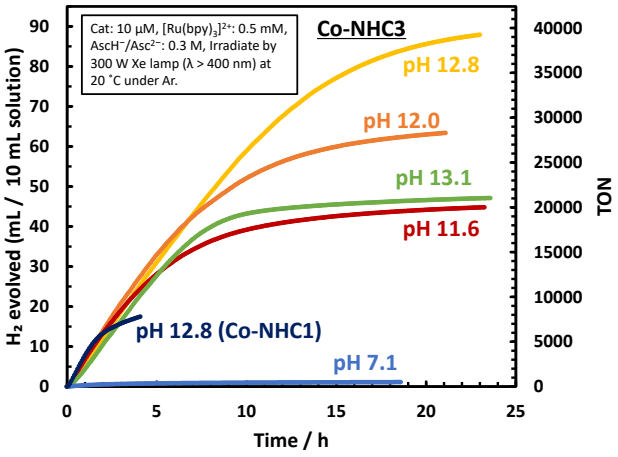


Figure 1. Photochemical H_2 Evolution from Alkaline Water Catalyzed by Co-NHC complexes.

1) Kawano, K.; Yamauchi, K.*; Sakai, K.* *Chem. Commun.* **2014,** *50*, 9872-9875, 2) Yatsuzuka, K.; Yamauchi, K.*; Kawano, K.; Ozawa, H.*; Sakai, K.* *Sustainable Energy Fuels* **2021,** *5*, 740-749.