Molecular Catalysis of Co-NHC Complexes in Hydrogen Evolution from Water

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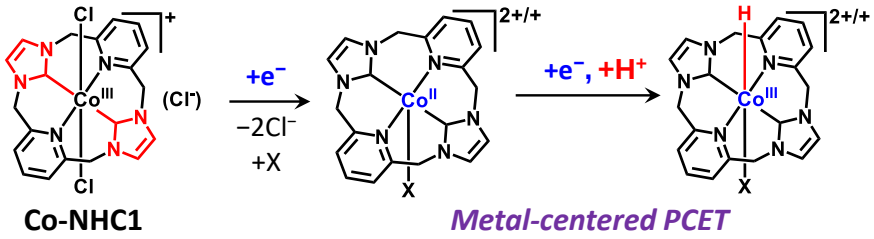
Artificial photosynthesis based on splitting water into H_2 and O_2 with solar energy has attracted recent years. In order to realize the overall water-splitting reaction based on molecular systems, it is crucial to develop highly active molecular catalysts for both hydrogen and oxygen evolution reactions (HER and OER). In this context, we have focused on molecular catalysis for H_2 evolution from water by employing a photochemical system comprising of EDTA, $[Ru(bpy)_3]^{2+}$, electron relay and the catalyst, where one-electron-reduced species of methylviologen MV^{2+} (i.e., MV^{+}•) only has a driving force (DF) of 150 meV for HER at pH 5.0. Within these studies, we succeeded in demonstrating that a macrocyclic cobalt-NHC complex **Co-NHC1** serves as a catalyst for HER using MV^{+}• as a reductant via the metal-centered PCET process.[1] This is the first example of the 1st row transition metal complex showing the catalysis in this system. Upon changing the electron mediator, we have improved the photosystem which shows 70 times higher rate of HER compared with that of MV^{2+}.[2] On the other hand, we have recently conducted the detailed analyses on the homogeneous electrocatalysis of **Co-NHC1** in aqueous media. Importantly, the turnover frequency (TOF) of HER catalyzed by **Co-NHC1** has turned out to be extremely high even in neutral media, in which some other cobalt-based molecular catalysts have been previously examined under the similar conditions.[3] Our recent finding includes the development of the highly efficient molecular system based on new cobalt-NHC complexes in photochemical H_2 evolution from alkaline water, which will be discussed in the presentation.



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. 3) Wang, J.-W.; Yamauchi, K.; Huang, H.-H.; Sun, J.-K.; Luo, Z.-M.; Zhong, D.-C.*; Lu, T.-B.*; Sakai, K.*, *Angew. Chem. Int. Ed.* **2019**, *58*, 10923-10927.