

Outline doctoral thesis

Thesis title: Design and Construction of Framework Catalysts for Hydrogen Evolution

水素発生反応に向けたフレームワーク触媒の設計と構築

The photocatalytic reduction of water molecule into dihydrogen is known as a promising way to provide a sustainable and environmentally friendly chemical energy. Therefore, several efforts have been made on the construction homogeneous systems using various combinations of molecular-based catalysts and photosensitizers. A great advantage of such homogenous systems is that we can understand their reaction mechanisms in detail based on well-established spectroscopic techniques. The nature of the systems allows us to precisely tune their structures/properties, which results in improved catalytic activities. However, these system are considered to have difficulty for practical application due to their moderate stability and low reusability, for which heterogeneous photocatalytic systems are rather advantageous. Based on the background, in this study, we aimed to develop novel molecular-based catalytic system, in which the advantages feature of homogeneous and heterogeneous system are integrated.

In this doctoral thesis, after the General Introduction, the development of a novel heterogeneous photocatalytic system for H₂ evolution is reported in Chapter 1. I propose that a heterogeneous photocatalytic system can be constructed by the supramolecular assembly of discrete molecules. In this system, a discrete catalyst module (CM), which contains metal complex-based catalytic centre (catalytic node) and intermolecular connection sites (molecular connector), can be assembled into an ordered structure through non-covalent interaction to afford a heterogeneous framework catalyst (FC). Unlike assembly driven by coordination bonding, known as coordination polymers, catalyst modules can easily be assembled/disassembled simply by changing solvents while maintaining the structure of the active sites. Therefore, my system can reveal two prominent features; (1) well-defined catalytic sites attributed to the molecular-based modules and (2) reusability and high durability based on the heterogeneous nature.

Based on the aforementioned strategy, I employed a Rh(II) dimer complex bearing 1,8-naphthalimide-based ligands, Rh₂(NIP)₄ (CM-1, HNIP = 3-(1,8-naphthalimido)-propanoic acid) as a catalyst module. The Rh(II) paddle-wheel moiety is expected to serve as catalytic center and is suitable for the construction of ordered structures due to its high (*D_{4h}*) symmetric structure. 1,8-Naphthalimide unit can serve both as a light-harvesting unit for the photocatalytic reaction and a functional moieties to

construct intermolecular interactions.

CM-1 was successfully synthesized by the ligand exchange reaction between **HNIP** and $\text{Na}_4[\text{Rh}_2(\text{CO}_3)_4]\cdot 3\text{H}_2\text{O}$, and characterized by several spectroscopic analysis techniques and elemental analysis. Subsequently, the self-assembly of **CM-1** to construct a framework catalyst (**FC-1**) was performed by the slow diffusion of CHCl_3 into a DMSO solution of **CM-1**. The single-crystal X-ray structure analysis of the obtained crystal reveals the formation of framework structure stabilized by the intermolecular π - π stacking interactions between the aromatic rings of the **NIP** ligands. The result clearly indicates that the framework catalyst (**FC-1**) can be constructed via the self-assembly of **CM-1**. I also investigated the photophysical properties of **CM-1** and **FC-1**, and it was found that the excellent light-harvesting property of 1,8-naphthalimide units are retained. Subsequently, electrocatalytic activity of **CM-1** and **FC-1** was examined by cyclic voltammetry. Cyclic voltammograms of **CM-1** and **FC-1** exhibited a large irreversible current attributed to the electrocatalytic H_2 evolution in the presence of acetic acid. Note that catalytic reaction did not proceed in the absence of acetic acid, indicating that the interaction between acetic acid and the Rh_2 centre generates the catalytically active $\text{Rh}_2\text{-H}$ species to promote catalytic hydrogen evolution both in solution and the solid state.

The photocatalytic activity of **FC-1** was consequently examined in an aqueous acetate buffer solution (pH = 5) containing EDTA-2Na (0.2 M) as a sacrificial electron donor. Upon light irradiation ($\lambda > 320$ nm), the production of H_2 linearly increased with time. The initial reaction rate (TOF) for 1 h was determined to be $67 \mu\text{mol g}^{-1}\text{h}^{-1}$ and the turnover number (TON) reached to 3.5 after 75 h. Several control experiments demonstrated that integration of the photosensitizer (1,8-naphthalimide moiety) and the catalytic centre (Rh(II) paddle-wheel unit) into the same molecule is crucial for photocatalytic H_2 production. I also investigated the stability and the reusability, and it was found that the catalytic activity of **FC-1** was maintained after 70 h of photoreaction, and the catalyst can be reused at least for three cycles without considerable loss of the activity. I also found that the intramolecular oxidative quenching of **NIP*** by the Rh_2 centre was a key step to generate the catalytically active $\text{Rh}_2\text{-H}$ species.

Chapter 2 describes the development of photo-active catalyst with visible-light absorbing dye moieties. I chose boron dipyrromethene dye (BODIPY; **BDP**), as a visible-light absorbing unit because the chromophore is known to exhibit intense absorption bands in yellow-green region and rich electrochemical properties. The new Rh(II) dimer complex bearing bodipy-based ligands, $\text{Rh}_2(\text{BDP})_4$ (**CM-2**, **HBDP** = 1,3,5,7-tetramethyl-8-(4-carboxyphenolic)-BODIPY acid) was successfully synthesized and characterized. I also succeeded in constructing a framework catalyst (**FC-2**) by the self-assembly of **CM-**

2 and the structure of **FC-2** was determined by the single-crystal structural analysis. Cyclic voltammetry and controlled-potential electrolysis of **CM-2** and **FC-2** confirmed the electrocatalytic activity of **CM-2** and **FC-2** for H₂ production.

I subsequently investigated the photocatalytic activity of **CM-2** for hydrogen evolution under visible light irradiation. Irradiation of visible light ($\lambda_{\text{exc}} > 370$ nm) to a solution of **CM-2** (0.1 mM) in THF/water containing BIH (1,3-dimethyl-2-phenyl-2,3-dihydro-1*H*-benzimidazole) as a sacrificial electron donor results in the generation of dihydrogen as confirmed by gas chromatography. Several control experiments were also conducted to further clarify the catalytic activity of **CM-2** in detail.

In Chapter 3, investigation of a framework catalyst by high energy X-ray measurements (HEXS) and pair distribution analysis (PDF) is reported. X-ray scattering results coupled with PDF analysis can reveal distances between neighbouring atoms of overall real space in solid-state. Therefore, a comparison of experimentally obtained scattering patterns with patterns calculated from coordinate model can provide the quantitative bond distances in the materials. In this study, I tried the analysis of **FC-1** by solid-state phase X-ray scattering technique and PDF analysis. By analysing the patterns, several distances in **NIP** light-harvesting moiety and the rhodium dimer catalytic centre were successfully determined. I also found the several spectral features reflecting the packing structure of **FC-1**. This outcome study demonstrates the opportunity to resolve the full inner and outer shell ligand structure for coordination complexes in solid-state.

Finally, I concluded that the novel approach to construct the catalytic system for hydrogen production was successfully developed by the self-assembly of catalyst modules via intermolecular non-covalent interactions.