

# 学位論文の要約

題目 Studies on Control of Proton–Electron Coupling and Functionalization Based on Metal–Organic Complexes

(金属-有機錯体を基盤としたプロトン–電子カップリング制御ならびに機能性発現に関する研究)

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## 序論

Proton plays a vital role in electrochemical systems, such as ionic conductivity and redox processes. Among them, proton conduction as a special case of ionic conduction has been extensively studied in fuel cells, sensors, and supercapacitors. It is usually carried out through two conventional conduction media, i.e., H<sub>2</sub>O and ammonia. The new medium is rarely reported due to the harsh experimental conditions and/or technical limitations. In addition, for redox processes, proton is a hard acid that can form covalent bonds and reconstruct  $\pi$ -conjugated systems, affecting proton–electron coupling. To date, among the numerous metal complexes, most synthetic approaches focus on the introduction and control of proton–electron coupling through the selection of metal ions. Compared to redox-active metal ions, redox-active ligands are more promising for controlling the proton–electron coupling in metal complexes, because their chemical modification is expected to have a drastic effect not only on the Lewis acidity/basicity but also on redox properties. Furthermore, the geometric isomerization in metal complexes has been a subject of intense research, which affects proton–electron coupling by controlling electronic behavior through isomeric transformations. This thesis aims to investigate the proton conduction behavior of metal-organic frameworks using a new proton mediator and to declare the control of proton–electron coupling through ligand-driven redox processes and metal–ligand isomeric transformations.

## 1. CO<sub>2</sub> Mediated Proton Conductive Metal–Organic Frameworks

The CO<sub>2</sub> mediated proton conduction was investigated based on a diamine-appended MOF, Mg<sub>2</sub>(dobpdc)-mmen (dobpdc<sup>4-</sup> = 4,4'-dioxidobiphenyl-3,3'-dicarboxylate; mmen = *N,N'*-dimethylethylenediamine), under high CO<sub>2</sub> pressure. Firstly, I studied the proton conductivity

between  $\text{Mg}_2(\text{dobpdc})$  and  $\text{Mg}_2(\text{dobpdc})\text{-mmen}$  under ambient conditions by changing relative humidity and temperature. The experimental results indicate that the proton conductivity of diamine-appended MOF ( $\text{Mg}_2(\text{dobpdc})\text{-mmen}$ ) is 4 orders of magnitude higher ( $4.31 \times 10^{-5} \text{ S cm}^{-1}$ ) than that of the  $\text{Mg}_2(\text{dobpdc})$  ( $2.92 \times 10^{-9} \text{ S cm}^{-1}$ ) at 298 K and 95% relative humidity (RH). The proton conductivity was also estimated in the  $\text{CO}_2$  atmosphere based on the altering current (AC) impedance measurements. The observation of the change in proton conductivity after injecting  $\text{CO}_2$ ,  $1.16 \times 10^{-12} \text{ S}\cdot\text{cm}^{-1}$  at 0.3 bar and  $2.20 \times 10^{-11} \text{ S}\cdot\text{cm}^{-1}$  at 10 bar, elucidates that the effect of  $\text{CO}_2$  during the proton transfer processes.

## **2. Strong Proton–Electron Coupling in $\pi$ -Planar Metal Complex with Redox-Active Ligands**

I focused on a metal complex bearing a redox-active *o*-iminothiosemiquinonate ( $\text{itsq}^{1-}$ ) ligand as a possible candidate for strong PCET systems. This N,S-donor ligand can promote the reconstruction of the  $\pi$ -conjugated system upon protonation, because of the expanded orbital on sulfur atoms. In relation, the sulfur atom has a stronger  $\sigma$  and  $\pi$  donating ability than nitrogen, which stabilizes the complexation with a metal ion and improves the electron reservoir properties of the complex. Optical and electrochemical measurements demonstrated strong proton–electron coupling in the complex, which was manifested as significant acidity-sensitive reduction potential. Theoretical calculations predicted that proton–electron coupling in the complex, which was evaluated from the energetic shift of LUMO by protonation, was more pronounced than that in a conventional nickel(II) complex with redox-inactive ligands.

## **3. Isomerization-controlled Proton–Electron Coupling in $\pi$ -Planar Metal Complex**

I demonstrated the first example of the control of the proton–electron coupling based on the geometrical configuration in a  $\pi$ -planar platinum complex,  $\text{Pt}(\text{itsq})_2$  ( $\text{itsq}^{1-}$ : *o*-iminothiosemiquinonate). Kinetic experiments based on  $^1\text{H}$  NMR spectroscopy demonstrated the isomeric transformation from the *cis* to *trans* forms in organic solvents, which was supported by the simulated potential energy curve. Theoretical calculations revealed that the isomeric change in the ligands while keeping the components has a drastic effect on proton–electron coupling compared to the component substitution while keeping the geometrical structure of the ligands.