

学位論文の要約

題目 Study on Synthesis and Physical Properties of Dinuclear Platinum Complexes
 (白金二核錯体の開発ならびに物性に関する研究)

氏名 王 鹏皓 (Wang Penghao)

序論

Solid proton/proton-electron-mixed conductors play a pivotal role in diverse applications such as energy storage and fuel cells. Additionally, proton-electron-mixed conductors have also proven their importance as essential materials for hydrogen separation. Over a long period, inorganic metal oxides, and organic polymers have been extensively explored as candidates. However, to effectively design advanced proton/proton-electron-mixed conductors, a major challenge lies in clarifying the relationship between the conduction and structural characteristics due to poorly understood due to their undefined structures and conducting mechanisms. Dinuclear platinum complexes are emerging as a promising platform to study structure-property relationship because of their high designability and well-defined structures. The judicious design or choice of components have yielded notable dinuclear platinum complexes with proton/proton-electron mixed conduction, particularly through controlling the pK_a/pK_b of organic ligands and incorporating cationic π -conjugated molecules. Therefore, the purpose of this thesis is to create new incredible dinuclear platinum complexes and study their unique physical properties especially in terms of conducting behavior.

1. Proton Conduction in Paddlewheel-Type Dinuclear Platinum(III) Complex System Including Neutral and Protonated 1,2,4-Triazole

We present the first approach to simultaneously incorporate neutral trz moieties with active Lewis basic sites into metal complex anions and $Htrz^+$ cations as their counterparts. We utilized paddlewheel-type dinuclear Pt (III) complex anions, in which the Pt_2 units coordinate with four squarate (sq^{2-}) ligands at the equatorial positions and two trz ligands at the axial positions. As expected, sq ligands can assist in the formation of proton-conducting pathways in the crystal. Two complexes, $(Htrz)_2[Pt_2(sq)_4(trz)_2] \cdot 3(H_2O)$ and $(Bu_4N)_2[Pt_2(sq)_4(trz)_2] \cdot 3(H_2O)$, were synthesized from the precursor, $(Bu_4N)_4[Pt_2(sq)_4] \cdot 1.5(H_2O)$ with Pt(II)-paddlewheels with no axial ligands, to

investigate the effect of hydrogen-bonding interactions between neutral and protonated trz species on proton conduction. A crystallographic study revealed that in contrast to $(\text{Bu}_4\text{N})_2[\text{Pt}_2(\text{sq})_4(\text{trz})_2] \cdot 3(\text{H}_2\text{O})$, $(\text{Htrz})_2[\text{Pt}_2(\text{sq})_4(\text{trz})_2] \cdot 3(\text{H}_2\text{O})$ is the first structurally defined solid with infinite hydrogen-bonding networks, including neutral and protonated trz in a 1:1 stoichiometric ratio. The two species are directly connected via effective $\text{N}-\text{H} \cdots \text{N}$ hydrogen bonds to facilitate fast proton transfer between high-proton affinity bases. Consequently, the proton conductivity of $(\text{Htrz})_2[\text{Pt}_2(\text{sq})_4(\text{trz})_2] \cdot 3(\text{H}_2\text{O})$ was more than three orders of magnitude higher than that of $(\text{Bu}_4\text{N})_2[\text{Pt}_2(\text{sq})_4(\text{trz})_2] \cdot 3(\text{H}_2\text{O})$ under the same conditions.

Molecule-based Proton-electron Mixed-conducting Metal with the Highest Ambipolar Conductivity

We prepared an ET-based proton-electron mixed-conducting cation radical salt, $(\text{ET})_4[\text{Pt}_2(\text{pop})_2(\text{Hpop})_2] \cdot \text{PhCN}$ (**1**) (ET: bis(ethylenedithio)tetrathiafulvalene; pop^{2-} : $\text{P}_2\text{H}_2\text{O}_5^{2-}$), by the electrooxidation of ET in the presence of protonated paddlewheel Pt(II) dimers, $[\text{Pt}_2(\text{pop})_2(\text{Hpop})_2]^{2-}$. Crystallographic study revealed that the salt has a layered structure, constructed by layers of cationic ET molecules and layers with protonated Pt-dimer complex anions. The salt shows metallic electronic conduction, which arises from the $(\text{ET})_2^{\bullet+}$ layers, with a high σ_e value ($1\text{--}2 \text{ S cm}^{-1}$ at room temperature). The metallic state was further corroborated by magnetic susceptibility measurement and band structure calculation. The salt also shows superprotonic conduction ($\sigma_{\text{H}} = 2.1 \times 10^{-2} \text{ S cm}^{-1}$ at room temperature under dried conditions), which relies on the one-dimensional (1D) hydrogen-bonding network of protonated paddlewheel-type Pt-dimer complex anions, $[\text{Pt}_2(\text{pop})_2(\text{Hpop})_2]^{2-}$. Infinite hydrogen-bonding networks formed by the $\text{pop}^{2-}/\text{Hpop}^-$ ligands coordinated to Pt ions in a paddlewheel manner are responsible for the Grotthuss-type proton conduction with a low E_a value (0.15 eV). Among the structurally-defined PEMCs, the salt prepared in this study displays the highest room-temperature σ_{amb} value of $2.1 \times 10^{-2} \text{ S cm}^{-1}$, even under dried conditions.