

論文の内容の要旨

論文題目 Syntheses, Reactivities, Spectroscopic and Photochemical Properties of Tricarbonyl Rhenium Tetraazaporphyrin Derivatives

(トリカルボニルレニウムテトラアザポルフィリン誘導体の合成、反応性、分光学的および光化学的性質)

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Phthalocyanines (Pcs), one of the tetraazaporphyrin (TAP) derivatives, have found uses in various fields, such as dyes, pigments, photoconducting materials and photosensitizers, owing to not only their diverse electronic and optical properties but also their excellent coordination behaviors. In addition, their absorption in the red or near-infrared (NIR) region, which corresponds to a biological window, has attracted considerable attention from the viewpoint of biological applications, such as photodynamic therapy. On the other hand, tricarbonyl rhenium(I) unit, ($[\text{Re}(\text{CO})_3]^+$), is well-known to show an electron deficient property, its complexes haven investigated in catalysis over recent decades. Based on their diverse electronic and optical properties, it is very interesting to combine the Pc ligand and tricarbonyl rhenium ($[\text{Re}(\text{CO})_3]^+$) unit from the viewpoint of preparing functional molecules. Recently, our laboratory reported the study of tetra-*tert*-butylated Pc complexes with one or two $[\text{Re}(\text{CO})_3]^+$ units (**Re₁Pc** and **Re₂Pc**). It showed that compared to ZnPc, the introduction of $[\text{Re}(\text{CO})_3]^+$ unit(s) produced a remarkable red shift of the Q band and improved the tolerance of the phthalocyanine ring to oxidation. As a consequence, **Re₂Pc** can work as the NIR absorber, while **Re₁Pc** can work as a photo CORM upon red light irradiation. For **Re₂Pc**, the easy demetallation reaction from **Re₂Pc** to **Re₁Pc** occurred in polar coordinative solvents. The stability of complex is important when considering the applications in the biological system. For **Re₁Pc**, further studies on the excited state properties are required to understand the CO-releasing behavior and to design stable CORMs. These characteristic properties of the RePc complexes motivated me to prepare novel stable Re TAP derivatives and investigate them in details.

In this study, to prepare novel functional Pc-based molecules, tricarbonyl rhenium TAP derivatives were synthesized, and their reactivities, spectroscopic and photochemical properties were investigated.

Chapter 1 introduced the concepts about carbon monoxide, CO-releasing molecules, phthalocyanine complexes, tricarbonyl rhenium complexes, rhenium phthalocyanine complexes and the aim of this study.

Chapter 2 explained the basic theory required for interpretation and analysis of the spectroscopic and photochemical properties of tricarbonyl rhenium TAP derivatives.

Chapter 3 summarized the results of syntheses. First Re complexes (**Re₁TAP**, **Re₂TAP** and **Re₂ObPc**) were synthesized. **Re₂TAP** was selectively synthesized by heating a decalin solution containing a mixture of Re₂(CO)₁₀ (Re source) and H₂TAP. In contrast, **Re₁TAP** was selectively synthesized through the demetallation reaction of **Re₂TAP** only in pyridine. Also, an octabutoxylated Pc complex with two [Re(CO)₃]⁺ units (**Re₂ObPc**), which has no isomer in terms of the substitution pattern of the Pc ring, was synthesized for X-ray single-crystal structural analysis.

The X-ray single-crystal structural analysis of **Re₂ObPc** was successfully performed. In **Re₂ObPc**, the Pc skeleton is distorted, because two [Re(CO)₃]⁺ units, which are coordinated with three of the four pyrrole nitrogen atoms, are located on different sides of the Pc plane.

Re₁TAP and **Re₂TAP** were fully characterized by fourier transform infrared (FT-IR) spectra, ¹H and ¹³C{¹H} NMR spectra, elemental analysis and electrospray ionization-high resolution mass spectrometry. The isomer types of **Re₁TAP** and **Re₂TAP** were considered based on NMR spectra analyses.

Chapter 4 studied the reactivities of Re complexes from the viewpoint of tolerance to demetallation reaction and tolerance to oxidation reaction. To confirm the stability in demetallation reaction, **Re₂TAP** was examined in polar solvents with different coordinating abilities such as pyridine, acetonitrile, and methanol. Here, the TAP ligand is expected to suppress the demetallation reaction in polar solvents, because compared with the Pc ligand, the absent fused benzo-rings stabilized the LUMO energy level of the TAP ligand, which can enhance the π-back donation between the Re ion and TAP ligand. As expected, the demetallation reaction of **Re₂TAP** was relatively inert and occurred only in pyridine by the removal of only one [Re(CO)₃]⁺ unit, which was in contrast to the stability of **Re₂Pc** in polar solvents: the demetallation reaction of **Re₂Pc** can occur even in acetonitrile and methanol, whose coordinating abilities are relatively weak. Also, the rate of the reaction with pyridine was much slower for **Re₂TAP** → **Re₁TAP** than for **Re₂Pc** → **Re₁Pc**. Notably, in pyridine, the demetallation reaction of **Re₂TAP** → **Re₁TAP** occurred, while that of **Re₁TAP** → **H₂TAP** was not observed.

Density functional theory (DFT) calculations were performed in order to theoretically understand the demetallation reactions. Here, the model complexes, i.e., **Re₁TAP'**, **Re₂TAP'**, **Re₁Pc'** and **Re₂Pc'**, in which *tert*-butyl groups were replaced with hydrogens, were employed, and the reliability of their optimized structures was confirmed by comparing with the X-ray single-crystal structural analyses of **Re₂ObPc** and di-nuclear Re(I) tricarbonyl tetraphenylporphyrin. In the demetallation of di-nuclear Re(I) complexes, **Re₂TAP'** was shown to be more stable and less prone to lose one [Re(CO)₃]⁺ unit than **Re₂Pc'**, in terms of the Gibbs free energies (ΔG⁰) calculated for the demetallation reactions, the bond lengths of Re-N, and the deviation of the Re ion from the mean plane of the four *meso*-nitrogen atoms. Further, the demetallation reactions that occurred only in the di-nuclear complexes, but could not proceed in the mono-nuclear complexes were explained by the favorable formation of σ-type bonding and the electrophilicity of Re ion

in the mono-nuclear complexes. Thus, the demetallation reaction in polar solvents can be suppressed by the TAP ligand.

To confirm the tolerance to oxidation of **Re₂TAP** and **Re₁TAP**, singlet oxygen (¹O₂) was used as the oxidant for bleaching the absorption of target complexes. Compared to **ZnPc**, tolerance to oxidation was greatly improved by the combination of [Re(CO)₃]⁺ unit(s) and TAP ligand, no spectral changes were observed in **Re₂TAP** and **Re₁TAP**. On the other hand, comparing the experimental results of ReTAP with that of RePc, significant difference of tolerance to oxidation was not seen. Tolerance to oxidation of Re complexes will be discussed in detail in the next chapter.

Chapter 5 investigated the electronic properties of ReTAP complexes and compared to that of RePc complexes. To evaluate the electrochemical properties, cyclic voltammetry (CV) measurements for **Re₁TAP** and **Re₂TAP** were performed. Compared to the conventional **ZnTAP** without the electron deficient [Re(CO)₃]⁺ unit(s), both the first oxidation and the first reduction potentials shift to the positive side with an increase in the number of [Re(CO)₃]⁺ units in the order of **ZnTAP** < **Re₁TAP** < **Re₂TAP**.

Electronic absorption spectra of **Re₁TAP**, **Re₂TAP**, and **ZnTAP** were measured. Compared with **ZnTAP**, the Q absorption band shifts to the lower energy side and broadens with the introduction of [Re(CO)₃]⁺ unit(s) to the TAP ligand. This red-shift due to the introduction of the [Re(CO)₃]⁺ unit(s) is consistent with the experimental results of the RePc complexes, but the broadening is characteristic of the ReTAP complexes, which suggests the possibility of MLCT contribution to the Q band.

The molecular orbital (MO) energies were calculated to theoretically analyzing the electronic properties. In **Re₁TAP'** and **Re₂TAP'**, the HOMO is predominantly TAP-centered a_{1u}-like π orbital (a_{1u}'), while the HOMO-1 mainly originates from the d orbital on the Re ion. The LUMO and LUMO+1 correspond to the TAP-centered e_{gy}- and e_{gx}-like π* orbitals (e_{gy}', e_{gx}'), respectively. Based on the MO analyses, the first oxidation and reduction potentials are assigned to the redox events of the TAP ring for both **Re₁TAP** and **Re₂TAP**. In the TAP complexes, owing to the introduction of [Re(CO)₃]⁺ unit(s), both the first oxidation and the first reduction potentials shift to the positive side, which is consistent with the trend for the stabilization of the HOMO and LUMO energy levels, respectively. Based on the Pc → TAP change, the large positive shift in the first oxidation potential is observed, which is consistent with the stabilization of the HOMO energy level. The significant positive shift of the first oxidation potential, particularly in **Re₂TAP**, indicates that these ReTAP complexes are stable and show tolerance to oxidation, which was experimentally confirmed to be inert to singlet oxygen. Thus, the combination of the [Re(CO)₃]⁺ unit(s) and TAP ligand is useful for controlling redox properties.

In the electronic absorption spectra, in contrast to the sharp Q bands of the RePc complexes, which are attributable to the π-π* character, the significant broadening of the Q bands was observed for the ReTAP complexes. To identify the characteristic spectroscopic properties, TD-DFT calculations were performed for **Re₁TAP'** and **Re₂TAP'** as well as **ZnTAP'**. The broadening of the Q bands can be explained by the change in the a_{1u}' orbital energy level: the Pc → TAP change stabilizes the a_{1u}' orbital energy, which

becomes comparable in energy to the d_{π} orbitals of the Re ions. Thus, the MLCT characteristics can contribute to the Q bands of the ReTAP complexes, while the $\pi-\pi^*$ characteristics are isolated in the RePc complexes.

Chapter 6 investigated photochemical and photophysical properties of Re complexes. As CO has been linked to therapeutic benefits, photochemical CO-releasing molecules (CORMs) have been developed as potential therapeutic agents. Since the red light can deeply penetrate living tissues, it is important to design CORMs based on the use of red light. The photodissociation of CO from **Re₁Pc** was found upon red light irradiation in the presence of molecular oxygen and coordinative solvent, such as pyridine and acetonitrile. On the other hand, in the case of **Re₁TAP**, the dissociation of CO was not observed under the similar condition. Thus, **Re₁Pc** was shown to work as the CORM upon red light irradiation, although the existence of pyridine causes the demetallation of **Re₂Pc** and **Re₂TAP**. Therefore, the photophysical properties of the RePc complexes were investigated.

Electronic absorption spectra were measured for the highly concentrated solutions of **Re₂Pc** and **Re₁Pc**, in order to observe the spin-forbidden singlet-triplet transitions. The absorption bands corresponding to the lowest excited triplet (T_1) state energy were successfully observed around ~ 1190 and ~ 1050 nm for **Re₂Pc** and **Re₁Pc**, respectively. TD-DFT calculations indicated that the lowest excited singlet (S_1) and T_1 states mainly originated from the $\pi-\pi^*$ characters for **Re₂Pc** and **Re₁Pc**. Further, the excited-state lifetimes were measured by transient absorption spectroscopy. In the case of **Re₂Pc**, the excited-state lifetimes were 360 fs and ~ 12 ns for the S_1 and T_1 states, respectively. For **Re₁Pc**, the S_1 and T_1 lifetimes were 2.7 ps and ~ 90 ns, respectively.

It is noteworthy that the excited-state lifetimes of the RePc complexes are much shorter than those (S_1 : several ns, T_1 : several 100 μ s) of the conventional Pcs, i.e., H_2Pc and $ZnPc$. In particular, the T_1 lifetimes (~ 12 ns and ~ 90 ns) of the RePc complexes are shorter than that of an IrPc complex (760 ns). This indicates that the ultrafast intersystem crossing occurs in the RePc complexes, which can be explained by the efficient spin-orbit coupling (SOC) owing to the out-of-plane displacement of the $[Re(CO)_3]^+$ unit(s). Due to the very short S_1 lifetime, the dissociation of CO is considered to occur from **Re₁Pc** in T_1 state. Based on these experimental results, new SOC and CO-releasing mechanism were proposed.

Chapter 7 summarized the results of this study. In conclusion, tricarbonyl Re TAP derivatives were synthesized and their demetallation reactions, electronic properties and photochemical properties were investigated. The combination of the $[Re(CO)_3]^+$ unit(s) and TAP ligand was found to be efficient for not only improving the tolerance to demetallation reaction but also controlling electronic properties, such as the first oxidation potentials and the electronic absorption spectra, which are correlated with the tolerance to oxidation and the admixture of MLCT and $\pi-\pi^*$ characters. Also, the combination of the $[Re(CO)_3]^+$ unit(s) and Pc ligand was found to enable **Re₁Pc** to work as the CORM upon red light irradiation, which will be applicable to biological environments, and new SOC and CO-releasing mechanism were proposed. Thus, this study is useful for preparing novel functional Pc-based molecules.