

博士論文 (要約)

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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1. Introduction

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.¹ 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.² On the other hand, tricarbonyl rhenium(I) ($[\text{Re}(\text{CO})_3]^+$) unit is well-known to show an electron deficient property, and its complexes have been investigated over recent decades, due to their significant photochemical or electrochemical properties.^{3,4} Based on their electronic features, recently, our laboratory reported tetra-*tert*-butylated Pc complexes with one or two $[\text{Re}(\text{CO})_3]^+$ units (**Re₁Pc**, **Re₂Pc** in Figure 1).⁵ The incorporation of $[\text{Re}(\text{CO})_3]^+$ unit(s) red-shifted the π - π^* -dominated, sharp Q absorption bands, enabling **Re₂Pc** to work as the NIR absorber. Also, the combination of the $[\text{Re}(\text{CO})_3]^+$ unit(s) and Pc ligand stabilized the HOMO energy level, which increases the tolerance toward oxidation. Furthermore, in the case of **Re₂Pc**, the easy demetallation reaction from **Re₂Pc** to **Re₁Pc** occurred in polar coordinative solvents, because the $[\text{Re}(\text{CO})_3]^+$ units significantly bulged from the Pc plane, which makes the Pc ring unusually distorted. These characteristic properties of the RePc complexes motivated me to prepare novel stable Re TAP derivatives and investigate them in details.

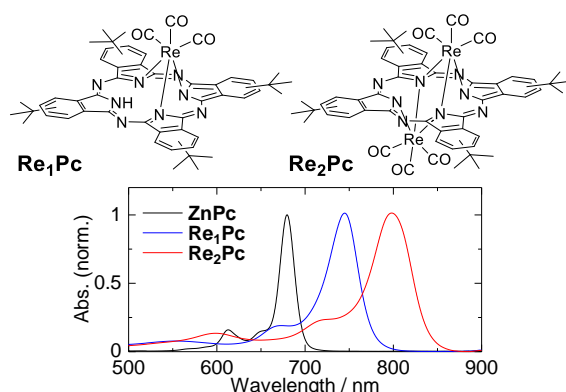
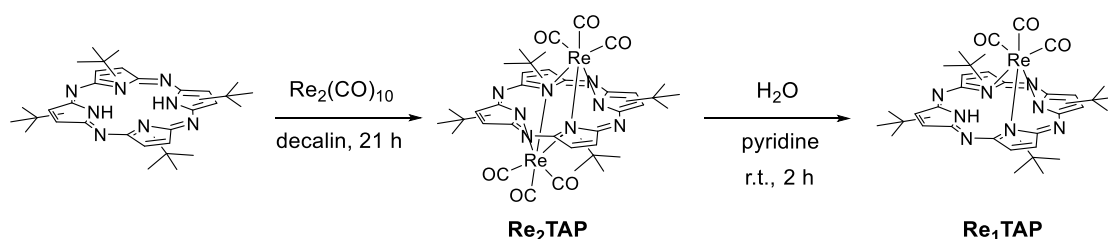


Figure 1. Electronic absorption spectra in the Q band region for **Re₁Pc** and **Re₂Pc**.

In this paper, tricarbonyl rhenium TAP derivatives were synthesized, and their reactivities, spectroscopic and photochemical properties were investigated from the viewpoint of the combination of the $[\text{Re}(\text{CO})_3]^+$ unit(s) and TAP ligand. To control electronic properties, photochemical properties and stability in Pc analogues has been investigated by the comparison between the RePc and ReTAP complexes.

2. Syntheses and demetallation reactions

Syntheses **Re₂TAP** was synthesized by heating a decalin solution containing a mixture of $\text{Re}_2(\text{CO})_{10}$ (Re source) and H_2TAP (Scheme 1). In contrast, **Re₁TAP** was selectively synthesized through the demetallation reaction of **Re₂TAP** only in pyridine. Also, an octabutoxylated Pc complex with two $[\text{Re}(\text{CO})_3]^+$ units (**Re₂ObPc** in Figure 2), which has no isomer in terms of the substitution pattern of the Pc ring, was synthesized, and its X-ray single-crystal structural analysis was successfully performed, as shown in Figure 2. In **Re₂ObPc**, the Pc skeleton is distorted, because two $[\text{Re}(\text{CO})_3]^+$ units, which are coordinated with three of the four pyrrole



Scheme 1. Syntheses of **Re₂TAP** and **Re₁TAP**.

nitrogen atoms, are located on different sides of the Pc plane.

Demetallation reactions 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 $[\text{Re}(\text{CO})_3]^+$ 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** \rightarrow **Re₁TAP** than for **Re₂Pc** \rightarrow **Re₁Pc**. Notably, in pyridine, the demetallation reaction of **Re₂TAP** \rightarrow **Re₁TAP** occurred, while that of **Re₁TAP** \rightarrow **H₂TAP** was not observed (Scheme 1).

Theoretical calculations 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.⁶ In the demetallation of di-nuclear Re(I) complexes, **Re₂TAP'** was shown to be more stable and less prone to lose one $[\text{Re}(\text{CO})_3]^+$ unit than **Re₂Pc'**, in terms of the Gibbs free energies (ΔG^0) 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.

3. Electronic properties of the ReTAP complexes

Electrochemical properties To evaluate the electrochemical properties, cyclic voltammetry (CV) measurements for **Re₁TAP** and **Re₂TAP** were performed, and the results are summarized in Figure 3a. Compared to the conventional **ZnTAP** without the electron deficient $[\text{Re}(\text{CO})_3]^+$ unit(s), both the first oxidation and the first reduction potentials shift to the positive side with an increase in the number of $[\text{Re}(\text{CO})_3]^+$ units in the order of **ZnTAP** < **Re₁TAP** < **Re₂TAP**.

Electronic absorption spectra Electronic absorption spectra of **Re₁TAP**, **Re₂TAP**, and **ZnTAP** are shown in Figure 3b (top). Compared with **ZnTAP**, the Q absorption band shifts to the lower energy side and broadens with the introduction of $[\text{Re}(\text{CO})_3]^+$ unit(s) to the TAP ligand. This red-shift due to the introduction of the $[\text{Re}(\text{CO})_3]^+$ 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.

Theoretical calculations The molecular orbital (MO) energies are shown in Figure 3a. In **Re₁TAP'** and

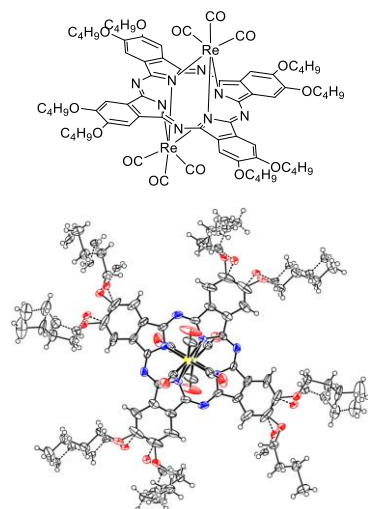


Figure 2. A crystal structure of **Re₂ObPc**.

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'** (Figure 3b, bottom). 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 (Figure 3a). Thus, the MLCT characteristics can contribute to the Q bands of the ReTAP complexes, while the π-π* characteristics are isolated in the RePc complexes.

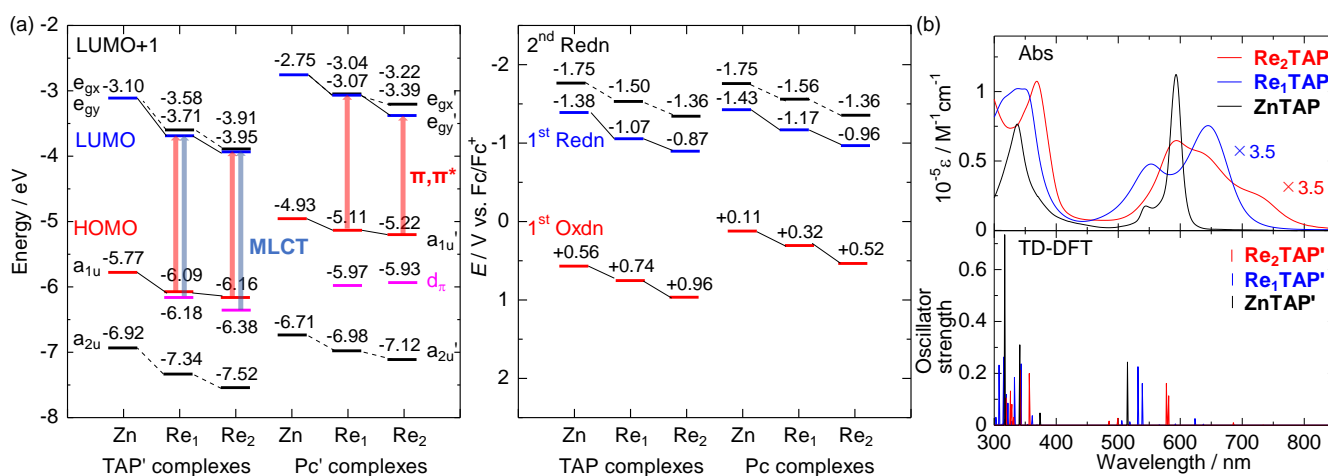


Figure 3. (a) Energy plot of the calculated frontier orbitals of optimized TAP' (Zn, Re₁, Re₂) and Pc' (Zn, Re₁, Re₂) complexes and the electrochemical results of TAP (Zn, Re₁, Re₂) and Pc (Zn, Re₁, Re₂) complexes. For Zn complexes, the HOMO is the a_{1u} orbital and the LUMOs are the e_g orbitals. For Re complexes, the HOMO is the a_{1u}' orbital and the LUMOs are the e_g' orbitals. (b) Electronic absorption spectra of **Re₂TAP** (red), **Re₁TAP** (blue), and **ZnTAP** (black) in toluene and calculated electronic transitions of the excited singlet states of the model complexes (**Re₂TAP'**, **Re₁TAP'**, and **ZnTAP'**) based on TD-DFT.

4. Photochemical properties of the RePc complexes

Photochemical CO release 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.

Photophysical properties 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 (Figure 4a). 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 state, respectively. For **Re₁Pc**, the S_1 and T_1 lifetimes were 2.7 ps and ~ 90 ns, respectively. The excited-state properties are summarized in Figure 4b.

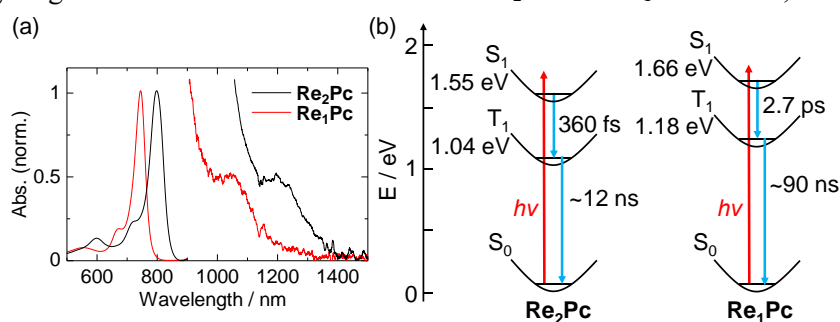


Figure 4. (a) Electronic absorption spectra in the red/NIR regions for **Re₂Pc** (red) and **Re₁Pc** (black) in CHCl_3 . (b) The excited-state properties of **Re₂Pc** and **Re₁Pc**.

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 μs) 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).⁷ This indicates that the ultrafast intersystem crossing occurs in the RePc complexes, which can be explained by the efficient spin-orbit coupling owing to the out-of-plane displacement of the $[\text{Re}(\text{CO})_3]^+$ unit(s). Thus, based on the very short S_1 lifetime, the dissociation of CO is considered to occur from **Re₁Pc** in the T_1 state.

5. Conclusion

In conclusion, tricarbonyl Re TAP derivatives were synthesized and their demetallation reactions, electronic properties and photochemical properties were investigated. The combination of the $[\text{Re}(\text{CO})_3]^+$ 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 $[\text{Re}(\text{CO})_3]^+$ 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.

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[Publication] M. Wang, K. Murata, K. Ishii, *Chem. Eur. J.* accepted. DOI: 10.1002/chem.202005042R5