Synthesis and Properties of N-Fused Porphyrin Rhodium and Iridium Complexes

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論 文 名　：Synthesis and Properties of N-Fused Porphyrin Rhodium and Iridium Complexes（N−フューズポルフィリンロジウムおよびイリジウム錯体の合成と物性）

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論文内容の要旨

N-fused porphyrin (NFP) is an endocyclic fused porphyrin analogue with an unusually narrow HOMO-LUMO energy gap, which exhibits distinct near-infrared absorption bands up to 1100 nm. Moreover, NFP serves as a versatile mono-anionic tridentate N3 donor ligand, which can bind various metal centers tightly. Nevertheless, despite its fundamental properties and applications, studies on N-fused porphyrins metal complexes remain largely unexplored.

In this thesis, the author has highlighted the metal-coordination chemistry of the internally fused porphyrinic analogue NFP, primarily focusing on the rhodium and iridium complexation. In particular, the unique metallation-induced cyclooctadiene isomerization and oxidative NFP ring cleavage and the fundamental optical/redox properties of the NFP complexes were examined. The NIR chromophore coordinated to the catalytically active metal ions such as rhodium and iridium ions provides a vast opportunity to probe into intriguing light-responsible catalytic properties.

In Chapter 1, the author presents a brief overview of the porphyrin family, primarily focusing on the molecular design strategies for developing NIR absorbing dyes based on the modified tetrapyrrolic systems, e.g., N-confused porphyrins (NCP) and its fused analogues, NFPs. Unlike conventional porphyrin ligands, exploitation of the metal coordination of the NFPs is worthwhile because the specific asymmetric ligand environment aids unprecedented structural transformations and provides photofunctional opt materials.

In Chapter 2, the author has disclosed a novel synthetic methodology for oxidative ring cleavage of the chemically stable NFP macrocycles. The rigid NFP skeleton is regioselectively cleaved into an N-fused bilatrienone analogue, benefitting from the iridium-dioxygen active species' coordination mode and

reactivity. Due to the NFP-ring cleavage, the N-fused bilatrienone gave in-plane octahedral coordination in the organoiridium complex (**Ir-3**), formerly not observed in regular NFP complexes. In contrast, the diverse coordination behavior of the NFP was also revealed that κ^1,η^3-isomerized (cyclooctadiene) C_8H_{12}-bound organoiridium species (**Ir-1**) were formed under an inert atmosphere. Upon varying the orientations κ^1,η^3-C_8H_{12} units, the NFP-iridium sandwich complex, **Ir-1**, shows the presence of discrete mixed isomers (**Ir-1a** and **Ir-1b**) in a 1:1 stoichiometric ratio.

In Chapter 3, the author has discussed the coordination behavior and the stability of novel rhodium-cyclooctadiene sitting-atop complexes with the NFP, achieving the first κ^1,η^3-isomerized cyclooctadiene-bound complexes. The corresponding sandwich complex (**Rh-1-Br**) was formed using a C21-brominated NFP derivative. The rhodium center in the complex was capped by a κ^1,η^3-C_8H_{12} ligand and undergo a facile rotation to form the corresponding isomers gradually at ambient temperature based on the ^{1}H NMR spectroscopic analysis and DFT calculations. Furthermore, the isolated single isomer species is subjected to partial debromination upon prolonged heating.

In Chapter 4, the author has established a facile approach to π-expanded cyclopentadiene sandwich rhodium complex, e.g., $[Cp^*RhCl_2]_2$. This was met by a rhodium(III)-chloride coordination to the NFP core, yielding the binuclear rhodium(III) complex (**Rh-2**) with a terminal and bridging μ-chloride ligands. In the case of the double-decker iron(II) complex showing the inter-chromophore solid interactions, the severely broad absorption features have been reported. The current μ-chloride sandwich RhNFP dimer, **Rh-2,** minimized the orbital interaction between the intra-ligands, which may show higher light-harvesting ability for photocatalytic activity.

Finally, in Chapter 5, the author has summarized all the findings and added perspectives about the future work. In particular, the due perspective on NIR-based photocatalytic or photovoltaic applications based on the aforementioned 4d and 5d metal ions incorporated NFP-metal complexes are discussed. The design principles evaluated anticipate promising applications in various catalytic/photocatalytic applications.

〔作成要領〕

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