

# Studies on Metalloporphyrin Isomers: Synthesis, Structures, and Properties of Metal Complexes of N-Confused/N-Linked Porphyrins

マウリヤ ヨゲシュ クマール

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氏 名 : マウリヤ ヨゲシュ クマール

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### 論 文 内 容 の 要 旨

Corroles, one of the important family of porphyrinoids, are contracted tetrapyrrolic macrocycles containing a direct pyrrole-pyrrole linkage that resemble the skeletal structure of corrin. The characteristic feature of corroles is an ability to coordinate metal ions with unusual higher oxidation states, which allowed us to apply to catalysts. To date, researchers have made tremendous efforts to elucidate the structure-property relationships of the metallo-corroles. However, the studies of bona fide metalloporphyrin isomers are still in its infancy in analogy with the porphyrin derivatives.

In this thesis, the author described the wide scope of metalloporphyrin analog chemistry, that is N-confused/N-linked corroles and their metal complexes. The intriguing photophysical properties and redox reactivities of the metal complexes of these corrole mutants have been investigated, which arose from the special coordination environment with an inner carbon donor in the confused pyrrolic ring of the respective macrocycles. The findings presented in this thesis would provide an important basis for the future applications, such as sensors, emitters, and catalysts.

Chapter 1 outlines a brief overview of the chemistry of porphyrinoids, mainly focusing on the fundamental structural properties, reactivities, and the potential application of corroles and metalloporphyrins. The important question why the high-valent metal corrole complexes can be a competent example for a wide variety of applications has been discussed, while a combination of some specific metal ions with redox-active corrole ligands gave rise to a varied degree of ligand noninnocence character. In this aspect, core modifications of the corrole skeleton with “N-confusion” approach can provide a new redox chemistry for carbacorroles and their metal complexes toward unique catalytic activities. This chapter also shed light

on the class of covalently linked corrole dimers which can be considered as an example for biomimetic models and can be promising candidates for optoelectronic devices using the distinct near-infrared phosphorescent properties.

In Chapter 2, a concept of symmetry modulation of  $\pi$ -HOMO (b1) orbital of the corroles by N-confusion approach was implemented to stabilize the distinct high valent copper species using the aforementioned NNNC coordination environment with a strong  $\sigma$  donating ability of the inner carbon atom. This peculiar core-modified corrole framework indeed enabled to stabilize the high valent organocopper(III) species predominantly as inferred from the complementary spectroscopic means; X-ray crystallography, variable temperature NMR, XPS, XANES, and UV-vis absorption. The meticulous tuning of the orbital energies of Cu  $d_{x^2-y^2}$  and the  $\pi$ -carbacorrole (b1) debilitates its interaction in the electronic structures, and the ground singlet Cu(III) structures were thus verified by DFT calculations. Furthermore, these organocopper corroles demonstrated unique redox reactivity to give a new  $\pi$ -laminated dimeric architecture via an oxidative inner carbon-carbon bond formation adjacent Cu(III) center.

In Chapter 3, utilizing a facile synthetic strategy for covalently linked corrole dimers that the author established, a series of conformationally stable chiral chromophores have been developed based on the novel corrole isomers. These face-to-face dimeric corroles possessing different ground electronic structures display unique chirality structures (e.g., stereogenic centers and axial chirality) with extraordinary high geometric stabilities, which can be regarded as mimetic model platforms for photosynthetic reaction centers, dimeric chlorophylls.

In Chapter 4, the author describes the synthesis of a series of iridium(III) complexes of the corrole analogs possessing various *para*-substituted pyridine axial ligands as novel near-infrared emitting materials at wavelength beyond 900 nm. The comparative studies have been made with the iridium corrole congeners to understand how the N-linked mutation affects the photophysical properties. Moreover, various axial pyridine ligands on the complexes were utilized to control the inherent stability and solubility in organic solvents and subsequently can tune their photophysical properties.

In Chapter 5, the author summarized the findings and perspectives of the future works. These metal complexes of carbacorrole analogs obtained by the N-/Neo-confusion modification can be utilized for various applications in catalysts, chiral recognition sensors and NIR-responsive devices.

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