Studies on Reactivities of Antiaromatic 5,15-Dioxaporphyrin toward Creation of its Molecular Assemblies

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論 文 名　：Studies on Reactivities of Antiaromatic 5,15-Dioxaporphyrin toward Creation of its Molecular Assemblies（分子構造体構築を指向した反芳香族性 5,15-ジオキサポルフィリンの反応性に関する研究）

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論 文 内 容 の 要 旨

Porphyrin is a group of macrocyclic compounds composed of four pyrrole subunits interconnected at their *α*-positions via methine bridges. According to Hückel's rule, porphyrin exhibits aromatic properties due to its planar structure and 18π-electron conjugated system. Porphyrins are versatile in various fields, including biology, medicine, materials science, and catalysis. Furthermore, in life processes, such as oxygen transportation and photosynthesis, porphyrin and its derivatives also play indispensable roles. Therefore, the study of porphyrin and its derivatives have been attracted considerable attention.

In comparison to regular porphyrin and its analogues, antiaromatic porphyrin analogues have been limited. However, owing to the unique reactivities and properties arising from their inherently narrow HOMO–LUMO energy gap, the synthesis and properties of antiaromatic porphyrin analogues have been intensively investigated.

The difficulty in the synthesis of antiaromatic porphyrin analogues lies in their low stability. Recently, as one of the synthetic strategies, heteroatom-substitution has been developed. Based on this strategy, in the author's group, air-stable 20π antiaromatic 5,15-dioxaporphyrin (DOP), which has oxygen atoms at two opposite *meso*-positions instead of carbon atoms, was synthesized for the first time. In the previous studies in the author's laboratory, much effort has been devoted to the synthesis of DOP with various kinds of aryl substituents and central metal ions, whereas its reactivities and functionalization have not been well investigated. Therefore, in this thesis study, the author focuses on such aspects of DOP chemistry, and the creation of its molecular assemblies has also been attempted.

Chapter 1 provides a general introduction to porphyrin and its analogues, with a primary emphasis on the synthesis of antiaromatic porphyrins, especially highlighting the air-stable 20π antiaromatic heteroporphyrins. The following three research motivations of this thesis are also presented: 1) the synthesis and properties of various metal complexes of DOP; 2) the investigation of its redox properties; and 3) the creation of its antiaromatic nanobarrel.

In Chapter 2, a ring-opening reaction of DOP to 1,9-dipyrrins with Grignard reagents was

investigated. The author optimized the reaction scope of Grignard reagents and revealed that less-sterically hindered aryl Grignard reagents, such as phenyl and para-substituted phenylmagnesium bromides, successfully produced the desired 1,9-diaryldipyrrin products. However, when alkyl, ethynyl, and 2-thienylmagnesium bromides as well as the sterically hindered mesitylmagnesium bromide were used, no reaction occurred, and unreacted DOP was recovered. The resulting 1,9-diaryldipyrrin products were fully characterized by NMR spectroscopy and single-crystal X-ray diffraction analysis.

In Chapter 3, to investigate the redox properties of DOP, tetraaryl-substituted DOP (DOP-Ar_4) was designed and concisely synthesized by bromination and subsequent Suzuki-Miyaura coupling reactions. Air-stable DOP-Ar_4 was oxidized with Magic Blue in a stepwise manner from a 20π neutral state to a 19π radical cation and further to an 18π aromatic dication. Notably, when an excess amount of Magic Blue was used, dipyrrindione was obtained as a ring-opened product. Aromaticity of the dication species was confirmed by the downfield chemical shifts of β-pyrrolic protons in the ^{1}H NMR spectrum. The NICS and ACID calculations also supported the observed conversion from the antiaromatic neutral state to the aromatic dication state. The electronic structures of each oxidation state were also revealed by absorption spectral changes upon oxidation and theoretical calculations. Structures at all the oxidation states were characterized by single-crystal X-ray diffraction analysis and ^{1}H NMR spectroscopy.

In Chapter 4, by using $B_2(Epin)_2$ as a boron source, a facile approach to construct tetraborylated DOP as a key building block for molecular assemblies has been established. With tetraborylated DOP in hand, the author envisioned the synthesis of antiaromatic DOP nanobarrel via consecutive cross-coupling reactions at multiple sites. However, the subsequent Suzuki-Miyaura coupling reactions with 2,6-dibromopyridine or 1,3-dihalobenzenes was not proceed. To solve this problem and synthesize the antiaromatic nonobarrel, a new boron-masking synthetic strategy was then investigated and is still under investigation.

Overall, in this thesis, the author extensively examined the reactivities of NiDOP towards nucleophiles and oxidants. The application of Grinard reagents led to a ring-opening reaction, resulting in the formation of 1,9-diaryldipyrrins. Furthermore, the author successfully employed Magic Blue as an oxidant to transform NiDOP from its 20π antiaromatic state to an 18π aromatic dication state. Additionally, the author obtained tetraborylated NiDOP, which serves as a key building block for the antiaromatic nanobarrel synthesis. The project involving the synthesis of antiaromatic nanobarrel is currently in progress.

As a future prospect, the author believes that further study of the unique air-stable 20π antiaromatic NiDOP will enrich the oxaporphyrin chemistry and lead to the discovery of new properties, which are distinctive from those found in normal porphyrins.