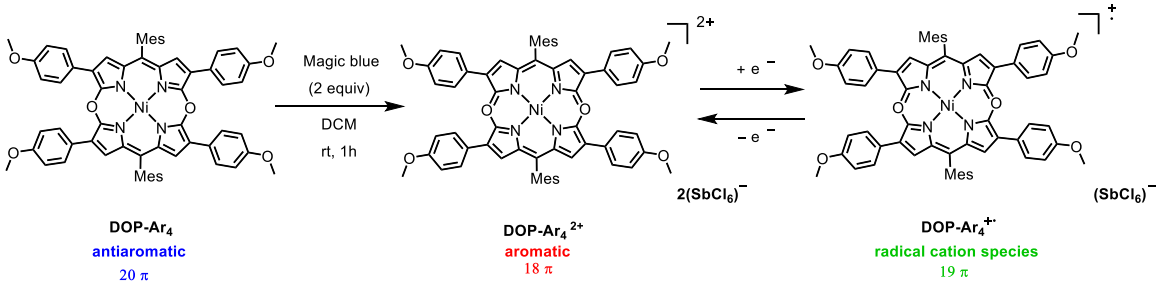
Synthesis of Tetraaryl-Substituted 5,15-Dioxaporphyrin and its Oxidation to the Aromatic Dication

([1]*Graduate School of Engineering, Kyushu University,* [2]*Advanced Research Support Center (ADRES), Ehime University*) ○ Jiping Hao,[1] Shigeki Mori,[2] Hiroyuki Furuta,[1] Soji Shimizu[1]

Keywords: 5,15-Dioxaporphyrin; Antiaromatic; Aromatic Dication; Redox Chemistry

Heteroatom-containing porphyrin analogs have been attracting attention because antiaromatic conjugated systems can be generated as stable forms. Among such heteroatom-containing porphyrin analogs, we have synthesized 5,15-dioxaporphyrin (DOP) for the first time by a nucleophilic aromatic substitution reaction of a nickel bis(α,α'-dibromodipyrrin) complex with benzaldoxime, followed by an intramolecular annulation of the α-hydroxy-substituted intermediate.[1] In our previous work, a redox reaction of DOP to transform the 20π-antiaromatic neutral state to the 18π-aromatic dication was investigated. However, due to the reactivity at the β-pyrrolic positions of the radical cation, a β,β-linked dimeric product was obtained. In this work, to prevent the dimerization reaction upon oxidation and investigate redox behaviors of DOP, tetraaryl-substituted DOP (DOP-Ar_4) was synthesized by bromination of DOP and Suzuki-Miyaura coupling reactions.

The neutral DOP-Ar_4 was oxidized with two molar equivalents of tris(4-bromophenyl)ammoniumyl hexachloroantimonate (Magic blue) in CH_2Cl_2 at room temperature for one hour to provide a dication species. The aromatic nature of the dication species was confirmed by the down-field shifts of the β-pyrrolic protons. We also obtained the 19π radical cation species during the oxidation process. Therefore, the neutral DOP-Ar_4 can be oxidized stepwise from a 20π antiaromatic state to a 19π radial cation and further to an 18π aromatic dication. Structures of all these states were characterized by single crystal X-ray diffraction analysis. In this presentation, the synthesis of DOP-Ar_4 and its redox behaviors will be reported.



Scheme 1. Redox reactions of DOP-Ar_4

1) A. Nishiyama, M. Fukuda, S. Mori, K. Furukawa, H. Fliegl, H. Furuta, S. Shimizu, *Angew. Chem. Int. Ed*. **2018**, *57*, 9728.