

Studies on synthesis, structure, and optical properties of tetrathiaporphyrin and isophlorin derivatives

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論 文 名： Studies on synthesis, structure, and optical properties of tetrathiaporphyrin and isophlorin derivatives
(テトラチアポルフィリン及びイソフロリン誘導体の合成、構造、並びに光学的性質に関する研究)

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論 文 内 容 の 要 旨

In this thesis, synthesis, structure, optical and redox properties, and electronic structure of tetrakis(pentafluoropheny)tetrathiaisophorin-dioxide ($S_4F_{20}TPPO_2$) are reported. $S_4F_{20}TPPO_2$ was synthesized by oxidation of tetrakis(pentafluoropheny)tetrathiaisophorin ($S_4F_{20}TPP$) with dimethyldioxirane (DMD). X-ray structural analysis revealed the di-sulfoxide structure with nonplanarity of $S_4F_{20}TPPO_2$, which was reflected by the significantly blue-shifted band compared to the corresponding band of $S_4F_{20}TPP$, and a weak tail of absorbance that extends out to 700 nm and no detectable Q band. There is almost no magnetic circular dichroism (MCD) intensity in the 500-700 nm region with weak Gaussian-shaped Faraday B_0 term in the 300-500 nm region, similar to that of $S_4F_{20}TPP$. Cyclic voltammogram (CV) shows an increase in HOMO energy level with the LUMO energy level intact, which is reflected in blue shifted absorption of $S_4F_{20}TPPO_2$. Nuclear-independent chemical shift (NICS) calculations indicated that the aromaticity of $S_4F_{20}TPPO_2$ is even more decreased than that of the parent $S_4F_{20}TPP$. Based on NICS values, 1H NMR data, absorption and MCD spectra, we can conclude that $S_4F_{20}TPPO_2$ is nonaromatic.

We also isolated the trioxide of the $S_4F_{20}TPP$ as a minor oxidized product and revealed its structure to have the $-S-O-O-O-S-$ moiety based on 1H - and ^{13}C NMR spectra and mass spectrum. Furthermore, an alternative synthetic route to $S_4F_{20}TPP$ was achieved. We also examined the synthesis of stable and readily soluble tetrathiaporphyrin dication (18π) species by replacing pentafluoropheny group at *meso* position with 3, 5-bis(*tert*-butyl)phenyl group, whose reactivity and optical and redox properties are in progress.