

# 学位論文の要約

題目     Studies on Subporphyrins and Their Analogues  
          (サブポルフィリンとその類縁体に関する研究)

氏名     吉田 康太

## General Introduction

Subporphyrin is a genuine ring-contracted porphyrin that consists of regularly connected three pyrrole rings and three methine carbon atoms. Subporphyrins have been extensively studied owing to its intriguing properties such as curved  $14\pi$ -electron conjugated systems, bowl-shaped structure, and bright fluorescence, which are highly tunable by peripheral modifications. In this thesis, the author explores peripherally functionalized subporphyrins possessing attractive properties based on their bowl-shaped structures and pyrrole-modified subporphyrins, where one of the pyrrole units is replaced by a cyclic or acyclic unit.

## $\beta$ -Mono- and $\beta$ -Hexasulfanylated Subporphyrins

$\beta$ -Mono- and  $\beta$ -hexasulfanylated subporphyrins were synthesized by  $S_NAr$  reactions of  $\beta$ -mono- and  $\beta$ -hexachlorinated subporphyrins with various thiols under basic conditions.  $\beta$ -Hexasulfanylsubporphyrins show more perturbed absorption spectra than that of  $\beta$ -monosulfanylsubporphyrin probably due to the proper arrangements of sulfanyl substituents for effective interaction with the subporphyrin core. While the obvious interaction of  $\beta$ -unsubstituted subporphyrin with  $C_{60}$  was not observed in toluene- $d_8$ ,  $\beta$ -tris(1,4-benzodithiino)subporphyrin captures  $C_{60}$  in a 1:1 ratio with an association constant of  $857 \pm 58 \text{ M}^{-1}$  at 25 °C in toluene- $d_8$ .

## $\beta$ -Sulfinylsubporphyrins: Observation of Diastereomeric Interconversions as Evidence for Bowl Inversion

$\beta$ -(4-methoxyphenylsulfinyl)subporphyrins were synthesized and separated into two diastereomers in order to observe the bowl inversion of subporphyrin. The interconversions between *B*-phenyl diastereomers did not occur even at 140 °C in tetrachloroethane- $d_4$ , indicating that neither the bowl inversion of subporphyrin nor the pyramidal inversion of the sulfur atom occurred under such conditions. On the other hand, the interconversions between *B*-methoxy diastereomers occurred in protic solvents such as methanol- $d_4$  and ethanol- $d_5$ , and were accelerated with trifluoroacetic acid. These experimental results suggest that the bowl inversion of subporphyrin proceeds via an  $S_N1$ -type mechanism, which includes the formation of subporphyrin borenium cation as a key intermediate.

### ***syn*- and *anti*- $\beta,\beta$ -(1,4-Dithiino)subporphyrin Dimers Capturing Fullerenes in a Different Way**

*B*-(4-Methoxyphenyl) *syn*- and *anti*- $\beta,\beta$ -(1,4-dithiino)subporphyrin dimers were prepared and their complexation behaviors with C<sub>60</sub> and C<sub>70</sub> were examined. The complexation behaviors of *anti*-dimer with C<sub>60</sub> and C<sub>70</sub> could not be investigated because of facile precipitation of crystals of a 1:1 complex. On the other hand, *syn*-dimer captured C<sub>60</sub> in a 1:1 manner with an association constant of  $(1.9 \pm 0.2) \times 10^6 \text{ M}^{-1}$  in toluene, which is the highest value among those of bowl-shaped fullerene receptors reported to date. In addition, *syn*-dimer formed a 2:1 complex with C<sub>70</sub> in toluene, and the association constants are  $K_1 = (1.6 \pm 0.5) \times 10^6$  and  $K_2 = (1.8 \pm 0.9) \times 10^5 \text{ M}^{-1}$ . Structural analysis of 1:1 complexes of *syn*-dimer with C<sub>60</sub> and C<sub>70</sub> suggested that the *syn*-dimer could change its cavity size by taking advantage of the conformationally flexible fused 1,4-dithiine unit.

### **Subchlorophin: Pyrrole-Modified Subporphyrin Bearing an Aldimine Unit**

Subchlorophin, where two  $\beta$ -carbon atoms in one of three pyrrole units are missing, was synthesized from subporphyrin. Subchlorophin takes a bowl-shaped structure, and shows an intermediate diatropic ring current between those of subporphyrin and subchlorin, roughly subchlorin-like absorption spectrum, and significantly enhanced fluorescence with the smallest Stokes shift compared to those of subporphyrin and subchlorin. Electrophilic aromatic substitution reactions at the  $\alpha$ -positions of subchlorophin were examined, and consequently nitration with Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O and Ac<sub>2</sub>O proceeded with high regioselectivity. Further modifications provided  $\alpha$ -(arylethynyl)subchlorophins, which showed perturbed absorption and fluorescence spectra depending on aryl groups. This result indicates the effective interaction between the subporphyrin core and the aryl groups through the ethynyl bridge.

### **Subporpholactone, Subporpholactam, and Imidazolosubporphyrin: Pyrrole-Modified Subporphyrin Bearing a Non-Pyrrolic Cyclic Unit**

New pyrrole-modified subporphyrins bearing a non-pyrrolic cyclic unit, subporpholactone, subporpholactam, and imidazolosubporphyrin were synthesized. They showed attenuated diatropic ring currents as compared with that of subporphyrin and subporphyrin-like absorption and fluorescence spectra. Reaction of imidazolosubporphyrin with (pentamethylcyclopentadienyl)iridium(III) dichloride dimer gave imidazolosubporphyrin-Ir<sup>III</sup> complex bearing a 6-membered iridacycle, and this complex reacted with diphenylacetylene, to afford different products depending on added salts. When potassium hexafluorophosphate was added, two isomeric imidazolosubporphyrinylidene-Ir<sup>III</sup> complexes bearing a carbene adjacent to the outer nitrogen atom of the imidazole segment were obtained. To the best of our knowledge, these are first examples of porphyrinoids bearing a carbene in their  $\pi$ -electronic frameworks.