学 位 論 文 内 容 の 要 旨

博士の専攻分野の名称　博士（工学）　氏名　孫　宇華

学 位 論 文 題 名

Synthesis and Strain Analysis of Contracted Porphyrin-related Macrocycles

（環縮小ポルフィリン類縁体の合成と歪み解析）

Porphyrin and related compounds are important functionalized macrocycles because of their attractive conjugation structure and coordination ability. The macrocyclic skeleton of porphyrin and calix[4]pyrrole which consisting of 4 pyrrole units and 4 *meso* carbons is considered as the optimal size. While reducing number of pyrrole subunits and/or *meso* carbon subunit from the optimal size will cause the increase of ring strain because the resulting rigid structure can't release strain energy well by adjusting conformation. The unique structures and properties induced by ring strain make it another factor besides conjugation and coordination that can functionalize molecules. However, such ring strain effect also makes the synthesis of contracted analogues become more difficult and always requires novel well-designed synthetic methodologies to overcome the ring strain. In this sense, the research for contracted porphyrin-related macrocycles still at the infancy stage that remain subjects worth exploring. Therefore, the objective of this thesis is investigating novel contracted porphyrin related macrocycles to further reveal the effect of ring strain on synthetic process and properties for the development of new synthetic methodology and new strain-induced functionalization.

This thesis consists of 6 chapters. The content contains investigation for calix[2] type macrocycle, [2.2](2,5)pyrrolophane type macrocycle and tetrapyrrole-fused cyclooctatetraene skeleton.

In chapter 1, the general background of porphyrin and related macrocycles as well as the unique ring strain effect for contracted analogues was was introduced. Then, the objective and overview of this thesis were also mentioned.

In chapter 2, the applicability of ring tightening approach using cyclic ketone precursors for highly strained calix[2] type macrocycle was investigated. The two promising precursors, cyclic tetraketone and furanophane, were synthesized successfully from a 4-step synthetic route and their ring strain state was investigated by their single crystal structures with deformation and conformation analysis. But treatment with several Paal-Knorr conditions for neither cyclic tetraketone nor furanophane, target calix[2]pyrrole or calix[2]furan macrocycles was not generated. Comparing with successful synthesis of less strained calix[3]pyrrole and calix[3]furan macrocycles obtained from same strategy, aromatic ring formation was regarded can't overcome the increased ring strain due to the ring contraction effect. A further theoretical calculation of destabilization energy indicated an insurmountable energy increase in these process that it seems unfavorable for conventional thermal reaction condition.

In chapter 3, the utilization of StrainViz which is an important local energy analysis was explored for novel contracted porphyrin related compound analysis and design. The character of StrainViz which is an important local energy analysis was revealed with the comparison with the result from conventional homodesmotic reaction method by analyzing several

calix[3]pyrrole derivatives. Then, the unobtained compound in chapter 2, highly strained calix[2]pyrrole, was investigated with simulated structure by StrainViz method for intuitive understanding its strain energy distribution. Later, a novel [2.2](2,5)pyrrolophane type macrocycle was designed as redox-driven flexible π conjugation system. The several isomers of the new core were evaluated by StrainViz method for distinguishing difference between different linkage mode with the visualization of strain energy distribution and a suitable structure was selected for actual synthesis.

In chapter 4, the synthesis and property investigation of designed [2.2](2,5)pyrrolophane type macrocycle, so called cyclo[4]pyrrole, was furnished. A 5-step route combined carbonyl related reaction was conducted to provide key linear terpyrrole precursor with 14% yield. The final cyclization step was furnished by Suzuki-Miyaura coupling that successfully provided the target compound with 25% yield. In addition, an alternative synthetic route with terpyrrole-diketone precursor were also explored while the cyclo[4]pyrrole was not found. The high strain state of cyclo[4]pyrrole, which was detailed researched by single crystal structure and StrainViz method, was regareded as one of the reason prevent ring tighting approach worked. Further, UV-Vis absorption spectroscopy, fluorescence emission spectroscopy, and cyclic voltammetry were conducted for the optoelectronic properties investigation. In particular, the two reversible oxidation processes exhibited in cyclic voltammetry was further investigated using *in situ* absorption spectroscopy and computational chemistry methods. The results shown that oxidation not only changes the electronic structure, but also causes conformational changes due to ring filpping. The unique ring strain energy change accompanying the electron energy change in redox process was considered to be the cause of its unique spectral absorption. Because in the dication state, the closed-shell state and the open-shell triplet state were regarded to have a very small energy difference and they can be converted through ring filpping.

In chapter 5, another situation of four pyrrole direct connected with less ring strain was considered. A feasible synthetic route was proposed for the elusive cyclic tetrapyrrole with cyclooctatetraene core and the skeleton was evaluated by calculation in advance. A promising bipyrrole precursor was furnished in multiple steps under mild reaction conditions which is a novel synthetic strategy for 2, 3'-bipyrrole synthesis. And the preliminary attempt for the followed homocoupling of bipyrrole indicated well-designed reaction condition are required to overcome the steric hindrance.

Chapter 6 summarized the work in this thesis and described some perspectives for future.

Based on these results, the authors further revealed ring strain effect on synthesis and property of contracted porphyrin related macrocycles. The novel developed synthetic methodology and macrocycles in this thesis can provide valuable insights for the future synthesis and application.