# SUMMARY OF Ph.D. DISSERTATION

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Title

Synthesis and Molecular Function of Cyclic Imine Oligomers


Abstract

Cyclophanes with an aromatic cavity have been used for the construction of biomimetic molecular recognition processes. Nowadays, aiming at the construction of such a biomimetic molecule recognition, free functional control by outside environmental stimulation is expected. Not using conventional cyclophanes based on a synthetic cavity control, I focused my attention on the redox active aromatic imine macrocycles to control the cavity by outside stimulation. The rigid π-conjugated macrocycles based on aromatic rings and imine bonds with various cavity structures were prepared and elucidation of the molecular accumulation structure and redox properties was attended.

The synthesis of the cyclophanes, which had phenylazomethine frames on the cyclic main chain, these structural characteristics, and basics properties are described in Chapter1 and Chapter2. There was a limitation in the macrocyclic composition as a high dilution condition was required, and the yields were low, but highly preferential formation of macrocycles was obtained by a simple technique based on a normal polycondensation condition by devising steric effects due to the substituted groups and composition methods.

The synthetic method to obtain only macrocycles from two kinds of polycondensation types is described and from a cyclic 3mer to a 20mer are isolated, and the structures are described in Chapter3. The correlation among the polycondensation types, the imine geometrical isomerism, and the shape of the macrocycles are described in detail based on an X-ray crystal structure analysis. In addition, the electrochemical response was measured by electrospectrochemical method. The reversible and stable redox activation was achieved by adding a Lewis acid or a proton to the cyclophanes, and during the redox process, the change in the cavity structure was elucidated. Furthermore, the wide derivatives of the macrocycles were clarified such as the cyclic accumulation complex by a hybrid with metal ions and reductants of the cyclphanes.

In Chapter4, an example is introduced in which the imine macrocycles are used as a redox-driven molecular module. A paraphenylenediamine was selected as the molecular module that is able to fix and release the free rotation axis in a paraphenylene, and cyclic quinine-imines were synthesized. The open and close mechanisms in the cavity based on the anisotropy in the cyclic frame and structural change by the redox were clarified by electrochemical measurements and an X-ray crystal structure analysis. In addition, the inclusion of a guest was controlled in an All-or-None manner by opening and closing the cavity. This is the first successful example of the molecule gate construction with cyclophanes controlled by an outside stimulation.

In Chapter5, an example is described in which the pheylazomethine bonds are applied to the development of environmental friendly engineering plastics having hydrolysis properties and a high thermal stability. A polyamideazomethines were prepared by introducing azomethine backbones into the main chain of a polyamide that is a representative of engineering plastics. Their thermal stability and decomposition properties were investigated by thermogravimetric analysis and spectrochemical analysis. It was clarified that the prepared polymers had a high thermal stability and decomposition properties. A novel technique to balance the high thermal resistance and decomposition properties that allowed chemical recycling was proposed.

In this study, the basic properties of the cyclophanes having an aromatic imine backbone in the cyclic main frame such as the molecular structure, and the redox process were elucidated, and their utility as a redox-driven molecular module was demonstrated.