論文 / 著書情報
Article / Book Information

題目(和文)	オルト架橋アントラセン二量体を活用した芳香環ナノカプセルの機能開発
Title(English)	Development of Functional Polyaromatic Nanocapsules Featuring ortho-Anthracene Dimers
著者(和文)	岸田夏月
Author(English)	Natsuki Kishida
出典(和文)	学位:博士(工学), 学位授与機関:東京工業大学, 報告番号:甲第12733号, 授与年月日:2024年3月26日, 学位の種別:課程博士, 審査員:吉沢 道人,河野 正規,大塚 英幸,稲木 信介,澤田 知久
Citation(English)	Degree:Doctor (Engineering), Conferring organization: Tokyo Institute of Technology, Report number:甲第12733号, Conferred date:2024/3/26, Degree Type:Course doctor, Examiner:,,,,
学位種別(和文)	博士論文
Category(English)	Doctoral Thesis
種別(和文)	論文要旨
Type(English)	Summary

（博士課程）
Doctoral Program

論 文 要 旨

THESIS SUMMARY

系・コース： Department of, Graduate major in	応用化学 系 応用化学 コース	申請学位（専攻分野）： Academic Degree Requested	博士 （ 工学 ） Doctor of
学生氏名： Student's Name	岸田 夏月	審査員主査： Chief Examiner	吉沢 道人

要旨（英文 800 語程度）
Thesis Summary (approx.800 English Words)

Living organisms provide various nanoarchitectures with high complexity and excellent functions. The majority of these biostructures are constructed by assembly from subunits, composed of simple building blocks, through non-covalent interactions. For example, enzymes and ion channels, formed from peptide assemblies comprising amino acid building blocks, exhibit efficient binding and selective recognition abilities toward molecules and ions in their cavities, respectively. Inspired by such biological systems, numerous artificial nanostructures with well-defined cavities have been prepared using simple aliphatic- and/or aromatic-based units. The obtained macrocyclic, cage-shaped, and capsular compounds have shown intriguing host capabilities toward synthetic and biological molecules. Particularly, well-defined cavities surrounded by polyaromatics show efficient host abilities through π-electron-based interactions and the hydrophobic effect. Based on the above background, I focused on the preparation of new polyaromatic nanostructures for the development of novel host functions, utilizing a bent polyaromatic framework as a novel building block, and the investigation of their host properties in aqueous media.

In this thesis, I designed a building block comprising an anthracene dimer with an *ortho*-phenylene spacer. The two anthracene panels are arranged in a dihedral angle of 60° and efficiently interact with the CH and CH_3 groups of guests in a sandwich fashion, unlike previously reported the *meta*-anthracene dimers with 120° in a dihedral angle. Additionally, the anthracene panels can undergo intramolecular [4+4] photo-cycloaddition, inhibiting interactions with guest molecules, which is impossible in the case of the *meta*-dimers. By assembling these *ortho*-anthracene dimers, I aimed to prepare new coordination and micellar capsules with polyaromatic cavities.

Chapter 1 is the introduction of this thesis. I introduce previously reported nanostructures with various building blocks and their characteristic properties and host functions. In addition, I propose the aim of this thesis.

Chapter 2 is concerned with the design and preparation of a novel coordination capsule from two metal ions and four bispyridine ligands including the *ortho*-anthracene dimer. The capsule has a well-defined spheroidal cavity with diameters of 1.5 × 1.0 nm fully encircled by a polyaromatic framework. One large planar or bowl-shaped molecule (e.g., porphine and sumanene) is quantitatively bound by the capsule. The bound bowl-shaped

molecules are compressed by the capsule framework upon the cavity-induced compression effect. Temperature-dependent ^{1}H NMR analyses reveal that the activation energy of the inversion decreases largely upon encapsulation.

Chapter 3 is concerned with the detailed studies of the binding capability of the spheroidal capsule toward planar polyaromatics and metal complexes. In the spheroidal cavity, one molecule of large and medium-sized polyaromatic molecules (e.g., coronene and pyrene) is exclusively bound from mixtures bearing the same number of aromatic CH groups. Theoretical studies reveal that multiple host-guest CH-π interactions (up to 32 interactions) are the predominant driving force for the observed selectivity. In addition, one molecule of planar metal complexes (e.g., bis(acetylacetonato) Cu(II)) is quantitatively bound by the capsule. The ESR and theoretical studies demonstrate the isolation capability of the capsular framework and an unusual polar environment in the polyaromatic cavity.

Chapter 4 is concerned with the preparation of a water-soluble spheroidal capsule by attaching hydrophilic side chains onto the outer surface of the capsule. The capsule quantitatively encapsulates various monosaccharide derivatives (e.g. permethylated α-D-glucose and α-D-galactose). Competitive binding studies reveal that permethylated β-D-glucose is selectively encapsulated by the capsule. Notably, the resultant host-guest complexes show the Cotton effect attributed to the capsular frameworks, indicating that the guest-induced helicity control of the host and selectively recognizes pentamethylated D-glucose through multiple CH-π interactions water.

Chapter 5 is concerned with the design and preparation of a novel photoresponsive micellar capsule by self-assembly of amphiphiles comprised of the *ortho*-anthracene dimer and two hydrophilic groups in water. The micellar capsule quickly and quantitatively disassembles by conversion of the amphiphiles to closed forms upon photo-irradiation. Regeneration of the nanocapsules is demonstrated by light irradiation or heating of the closed amphiphiles. A wide rang of hydrophobic molecules (e.g., Nile red, Cu(II)-phthalocyanine, and fullerene C_{60}) are captured by the capsule and released by UV light irradiation. This feature can furthermore be utilized to switch the fluorescence of encapsulated coumarin guests through their controlled release.

Chapter 6 is the conclusion of this thesis.