論文 / 著書情報
Article / Book Information

題目(和文)	アントラセン環に囲まれた配位ナノ空間の特異なホスト機能
Title(English)	Unique Host Functions of Coordination Nanocavities Surrounded by Anthracene Rings
著者(和文)	山科雅裕
Author(English)	Masahiro Yamashina
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Category(English)	Doctoral Thesis
種別(和文)	論文要旨
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（博士課程）
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論 文 要 旨

THESIS SUMMARY

専攻： Department of	化学環境学　専攻	申請学位（専攻分野）： Academic Degree Requested	博士 Doctor of　（　工学　）
学生氏名： Student's Name	山科　雅裕	指導教員（主）： Academic Advisor(main)	吉沢　道人
		指導教員（副）： Academic Advisor(sub)	穐田　宗隆

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

The functions of organic and coordinative nanospaces have recently received much attention because of their synthetic designability, accessibility and adjustability. As mentioned above, unique properties and reactivities within synthetic molecular hosts have attracted considerable attention in the field of organic, biological, physical, and material chemistry. Whereas a variety of *organic* and *coordinative nanospace* have been synthesized, most of the cavity frameworks are composed of aliphatic units and/or small aromatic rings. Coordination molecular hosts bearing organic ligands with extended polyaromatic panels remain uncommon. Thus, I presumed that molecular capsules with large *coordinative nanospace* encircled by *polyaromatic frameworks* could generate novel guest behaviors through efficient host-guest interactions.

Through this thesis, I challenged to investigate unique host-guest phenomena within enclosed polyaromatic nanocavities for the purpose of exploring unusual molecular recognition and photophysical properties. As a polyaromatic nanospece, I employed M_2L_4 coordination molecular capsules, which have a large cavity (~1 nm in diameter and ~580 $Å^3$ in volume) surrounded by eight anthracene rings tightly. It has been revealed that the Pd(II)- or Pt(II)-linked capsules can encapsulate simple, hydrophobic, and rigid organic compounds such as fullerene C_{60}, corannulene, and pyrene through effective hydrophobic effects and aromatic-aromatic interactions between host frameworks and guest molecules. However, unusual guest recognition, conformation, structure, properties, and reactivities have not been explored so far in the nanospace.

The selective recognition of male sex hormones over female ones was successfully demonstrated by using the Pt(II)-linked polyaromatic capsule in water. Competitive binding experiments revealed that the capsule preferentially binds male hormones through multiple CH-π interactions between the hormones and the capsule frameworks. Furthermore, fluorescent detection of steroid hormones was achieved by using a host-guest complex with a fluorescent dye.

I disclosed that sucrose, a highly hydrophilic disaccharide, was successfully encapsulated in the well-defined cavity of the Pt(II)-linked polyaromatic capsule in water. Through the efficient host-guest interactions, the capsule displayed selective and excellent host capability for sucrose with a binding constant (K_a) of 2.9×10^3 M^{-1} at ambient temperature.

Unlike previous coordinative host-guest systems, highly emissive host-guest complexes (up to Φ_F = 50%) were successfully prepared upon encapsulation of various fluorescent dyes (*e.g.*, BODIPY and coumarin derivatives) by the Pt(II)-linked coordination capsule in water. Picosecond time-resolved spectroscopy elucidated the photophysical behaviors of the obtained complexes. Notably, the emission color of the fluorescent the host-guest complex containing the BODIPY derivative could be readily modulated upon pairwise encapsulation with planar aromatic molecules.

The well-known and widely used radical initiators such as AIBN (2,2'-azobisisobutyronitrile) and its derivatives were successfully stabilized toward external stimuli through encapsulation within the Pd(II)-linked nanocapsule with polyaromatic frameworks. The encapsulation process occurred quantitatively by hydrophobic host-guest interactions in aqueous solution at room temperature. The encapsulated initiators within the capsule were significantly stabilized against light irradiation (580 times) and heat (645 times). The safely stored initiators could be used for usual olefin polymerization in organic solvent through spontaneous release of the initiators.

Oligo(ethylene oxide)s (OEO) are well-known highly hydrophilic compounds but were quantitatively enclathrated in the hydrophobic cavity of the Pt(II)-linked polyaromatic nanocapsule in water. The hydrophilic long-chain compounds were quantitatively enclathrated in the hydrophobic cavity of the capsule. Depending on the length of OEOs, the bounded molecules formed coiled or pseudo-rotaxane-shaped conformations. In addition, selective encapsulation of oligo(ethylene oxide)s was demonstrated by using the capsule.

Anisotropic expansion of the spherical M_2L_4 coordination capsule through the elongation of the ligand led to a new $M_2L'_4$ capsule. The expanded capsule provides an elliptical cavity encircled by polyaromatic frameworks with large openings and thereby could encapsulate elliptical fullerene C_{70} and monofunctionalized fullerene C_{60} in high yields. In addition, selective formation of a new $M_2L_2L'_2$ capsule occurred by mixing the original M_2L_4 and expanded $M_2L'_4$ capsules in a 1:1 ratio upon addition of C_{60} or mono-functionalized C_{60} as a template molecule.

Through above works, I have developed new chemical functions and phenomena within polyaromatic nanocapsules through effective host-guest interactions. I realized that the isolated cavities fully encircled by polyaromatic frameworks capable of (i) encapsulating various organic molecules, (ii) showing high molecular recognition capability, (iii) inducing unusual fluorescent properties, and (iv) stabilizing reactive chemical reagents toward light and heat, which cannot be achieved by previous molecular cages and capsules. These results would greatly progress host-guest chemistry and also contribute to the design of a new type of molecular sieves, sensors, probes, and reactors and the investigation of their further developments and applications.