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論文 / 著書情報 Article / Book Information

題目(和文)	 多環芳香族骨格を有するポリカチオン性三次元ナノ構造体の構築	
Title(English)	Construction of Polycationic Nanostructures with Well-Defined Polyaromatic Cavities	
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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10215号, 授与年月日:2016年3月26日, 学位の種別:課程博士, 審査員:吉沢 道人,穐田 宗隆,小坂田 耕太郎,豊田 真司,今岡 享稔	
Citation(English)	Degree:, Conferring organization: Tokyo Institute of Technology, Report number:甲第10215号, Conferred date:2016/3/26, Degree Type:Course doctor, Examiner:,,,,	
学位種別(和文)	 博士論文	
Category(English)	Doctoral Thesis	
Type(English)	Summary	

論文要旨

THESIS SUMMARY

専攻:	化学環境学	重攻	申請学位(専攻分野): 博士 (丁学)
Department of			Academic Degree Requested Doctor of
学生氏名:	午崎 晃亚		指導教員(主): 吉沢 道人
Student's Name			Academic Advisor(main)
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要旨(英文800語程度)

Thesis Summary (approx.800 English Words)

In a history of supramolecular chemistry, a variety of three-dimensional nanostructure with well-defined cavities have been designed and synthesized by using neutral organic frameworks. However, the incorporation of cationic moieties into the neutral frameworks of hollow structures has been seldom explored so far.

In this thesis, I developed new methods to construct polycationic nanostructures with polyaromatic panels. I utilized bent bispyridine ligands containing polyaromatic lings such as an anthracene and an acridinium panel. By using bent bispyridine ligands, I designed and prepared novel polycationic nanostructures with well-defined cavities. In addition, I revealed the function of the polyaromatic nanospace.

A synthesis of polyaromatic molecular bowl was accomplished by the use of two bent anthracene-embedded bispyridine ligands linked by two methylene spacers. The bowl-shaped structure was confirmed by NMR, ESI-TOF MS, and X-ray crystallographic analyses. The bowl provides a ~1 nm-sized hemi-spherical cavity surrounded by four anthracene panels and includes two dicationic (Lewis acidic) bis-pyridinium moieties. The molecular bowl has high water solubility because of the cationic units, and they bound carbonyl compounds through hydrophobic and hydrogen bonding interactions.

A polyaromatic molecular tube was prepared by using Zincke reaction of a diamino anthracene dimer and a Zincke salt of the bis-pyridine ligand. The X-ray single crystal analysis revealed that the tube has a 1 nm-sized cylindrical cavity encircled by four anthracene panels. Interestingly, the tube bound a variety of long hydrocarbons in aqueous solutions, and selectively bound branched and/or unsaturated hydrocarbons even without coordinative groups.

The quantitative formation of polycationic capsular and tubular structures was realized by using a new bent bispyridine ligand containing two acridinium rings as a cationic moiety. The cationic ligand was prepared in three-step reactions. The 2:1 combination of the ligand and Pd(II) ions led to the quantitative formation of a dodeca-cationic M_2L_4 molecular capsule. On the other hand, mixing a 1:1 ratio of the ligand and Pd(II) ions resulted in the selective formation of deca-cationic M_2L_2 molecular tube. The two structures were interconvertible by addition of the ligands or metal ions.

An $M_{3}L_{4}$ double capsule, two capsular molecules linked in close proximity, was prepared by self-assembly of metal ions and new W-shaped tripyridine ligands. The W-shaped ligand is containing four anthracene panels linked by two *meta*-phenylene spacers. Simple combination of Pd(II) ions and the W-shaped ligand led to the quantitative formation of the $M_{3}L_{4}$ double capsule. The product provides two 1 nm-sized cavities fully covered by eight anthracene panels, and these cavities are located at a close distance. This double capsule encapsulated one or two neutral molecules in each cavity.

Through above works, I developed new synthetic methods for polycationic nanostructures with well-defined cavities encircled by multiple polyaromatic panels. The resultant structures showed distinctive properties due to their frameworks and shapes. These results would contribute to the development of a new methodology to design and construct functional three-dimensional nanostructures.

備考 : 論文要旨は、和文 2000 字と英文 300 語を 1 部ずつ提出するか、もしくは英文 800 語を 1 部提出してください。

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