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Title(English)	Synthesis and Fluorescent Properties of Molecular Tubes with Covalently Linked Anthracene Rings
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論 文 要 旨

THESIS SUMMARY

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学生氏名： Student's Name	萩原　啓太	指導教員（主）： Academic Advisor(main)	吉沢　道人　准教授
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要旨（英文 800 語程度）
Thesis Summary（approx.800 English Words ）

Tubular nanostructures that delimit a one-dimensional space have potential applications for the selective inclusion, isolation, or transportation of ions and molecules. There are many examples of biological tubular assemblies (*e.g.* ion channels) and synthetic molecular tubes (*e.g.* carbon nanotube). However, it remains uncommon that molecular tubes provide both fluorescent properties and host capabilities. In this thesis, I designed and prepared novel molecular tubes with well-defined nanometer or subnanometer-sized cavities encircled by covalently linked multiple anthracene rings. These tubes provide both fluorescent properties from the anthracene frameworks and host capabilities for neutral organic molecules. Depending on the guest molecules, the host-guest complexes exhibited unusual fluorescent properties through host-guest interactions. There are five chapters relevant to the synthesis, host-guest properties, and fluorescent properties of the molecular tubes in this thesis.

In Chapter 1, I briefly introduced the definition of "tube" and the representative structures of natural channels and tubes and then synthetic macrocyclic and tubular molecules. In addition, I described the unique chemical and physical phenomena in the limited space of the synthetic tubes. I proposed new molecular tubes as target molecules in this thesis.

In Chapter 2, I succeeded in the preparation of a novel tubular structure containing four anthracene panels covalently linked by *meta*-phenylene and biphenylene spacers by sequential coupling reactions, transformation of peripheral functional groups, and dimerization of semi-rigid half-tube precursors using palladium catalyzed cross-coupling protocols. This tube was fully characterized by NMR spectroscopy, mass spectrometry, and single-crystal structure analysis. X-ray crystallographic analysis revealed that the tube has a rigid and fully aromatic columnar cavity with a diameter of ~1 nm and a length of 1 nm. The tube exhibited strong blue fluorescence from the anthracene frameworks. The obtained molecular tube provides well-defined tubular frameworks with an exterior surface, which can be rapidly modified by simple functionalization.

In Chapter 3, I prepared an aqueous molecular tube with four anthracene panels and peripheral eight hydrophilic sulfonate groups and elucidated the host-guest fluorescent properties in water. The water-soluble molecular tube was obtained by the straightforward synthetic route, which is 7-steps shorter than the route of the previous chapter. The obtained sulfonate-capped tube was highly soluble in water (>100 mM). The open-ended and 1-nm length cylindrical cavity of the tube facilitated quantitative encapsulation of two molecules of fluorescent coumarin dyes in water through the hydrophobic cavity through hydrophobic and aromatic-aromatic interactions. In combination with ESI-TOF MS analysis, a

UV-visible spectral titration study clearly illustrated the quantitative formation of the 1 : 2 host-guest structure. Interstingly, the bound coumarin dimers in a stacked fashion exhibited unusual excimer-like emissions in the confined space through efficient host-guest energy transfer. This chapter demonstrates that photoactive and water-soluble polyaromatic tubes have potential for exploring novel host-guest supramolecular structures and subsequent unique photophysical properties.

In Chapter 4, I designed and synthesized a water-soluble molecular tube containing three anthracene panels with twelve methoxy groups at the open ends. The tube provides a highly symmetrical tubular structure linked by three *meta*-biphenylene spacers with six hydrophilic groups for water-solubility. This new aqueous tube was synthesized by five-step reaction starting from arthraqionone derivatives and was highly soluble in water (>100mM) and in MeOH (>35 mM). The tube was characterized by NMR spectroscopy and mass spectrometry. The tube has a subnanometer-wide cavity and showed host capabilities for linear hydrocarbons and a π-conjugated biomolecule in water through hydrophobic effect and CH-π and π-π interactions. In addition, the guest-induced fluorescent enhancement of the tube was observed for the linear hydrocarbons. In this chapter, I described host-guest interactions within the molecular tube with the particular aim of developing unique fluorescent enhancement sensors and materials.

In Chapter 5, I described the conclusion of this thesis and proposals of the present molecular tubes. Through these works, I have established the design and synthetic routes of novel molecular tubes with cavities surrounded by large polyaromatic panels. Moreover, I have revealed the comprehensive relationship between the fluorescent properties and the host-guest interactions in the one-dimensional cavities of the tubes. These results would contribute to the development of supramolecular chemistry and supramolecular photochemistry. Finally, I described three proposals for the application of the molecular tubes. The first is the modulation of the emission color and the enhancement of the quantum yield of the tube by guest encapsulation. The second is the elongation of the molecular tubes by the covalent linkage of the tubes. The third is the creation of fluorescent transmembrane channel by the introduction of long alkyl chains at the open ends of the tube.