

論文 / 著書情報
Article / Book Information

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Title(English)	Stereo-Directed Construction and Host Capability of Multiple Anthracene Nano-Assemblies
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種別(和文)	論文要旨
Type(English)	Summary

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 (工学)
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要旨 (英文 800 語程度)

Thesis Summary (approx.800 English Words)

There are a wide variety of natural and artificial molecules in the world. These molecules have diverse stereo and regiostructures, which often determine the key factor of their characteristic properties and reactivities. Therefore, to regulate stereo and regiochemistry of molecules and molecular assemblies is one of the prime subjects for the development of functional organic materials. Through this thesis, I challenged to develop novel molecular capsules composed of highly stereocontrolled amphiphilic compounds with multiple polyaromatic panels for the purpose of exploring relationship between the host-guest behaviors and the stereochemistry of the amphiphiles. To make stereoregulated amphiphiles for host frameworks, I focused my attention on the combination of atropisomer and anthracene panels. As new stereoregulated amphiphiles, I designed three types of concaved amphiphilic compounds having multiple anthracene rings connected by *meta*-phenylene spacers with two hydrophilic groups, which are readily accessible to obtain water-soluble rigid atropisomers. These amphiphiles provide concave hydrophobic surfaces defined by the polyaromatic panels and convex hydrophilic surfaces so that they generate capsular assemblies through hydrophobic effects and aromatic-aromatic interactions in aqueous solutions. The capsular assemblies provide confined cavities surrounded by polyaromatic panels and thereby could encapsulate various aliphatic and aromatic molecules.

I prepared tape-shaped amphiphilic molecules composed of three anthracene rings linked by two phenylene spacers with peripheral hydrophilic sulfonate groups. The tape-shaped compounds have two atropisomers (i.e., *cis* and *trans* isomers) due to sterically restrict rotation about the anthryl-phenyl bonds by the *ortho*-substituents. The *cis*-atropisomer with a large concave aromatic framework gave rise to a dimeric capsule with diameters of approximately 3 nm in an aqueous solution, as confirmed by NMR, MS, and AFM analyses. In sharp contrast, the *trans*-isomer afforded only oligomeric aggregates with diameters in the range of 5-12 nm. The dimeric capsule encapsulated quinone derivatives to form vibrant host-guest charge transfer (CT) complexes. Emission intensity from the fluorescent capsule was modulated depending on the nature of the encapsulated guest molecules.

A supramolecular capsule with fluorescent frameworks composed of U-shaped complementary subunits was developed. An amphiphilic U-shaped amphiphile was stereoselectively synthesized from the isomeric mixtures and the dimeric capsule was spontaneously and quantitatively formed through hydrophobic aromatic-aromatic interactions in an aqueous solution. The capsule provides a confined cavity encircled by multiple anthracene fluorophores and thereby various non-fluorescent natural monoterpene compounds (*e.g.*, menthone, menthol, and *p*-menthane) could be encapsulated in the cavity through hydrophobic effects. The emissive intensity and color tone of the capsule were altered depending on the encapsulated monoterpene compounds, which were mapped into a 3D graph. Therefore, I demonstrated that the present capsule acts as a fluorescent supramolecular probe and decodes the structural information of monoterpene molecules into fluorescent signals distinguished by the 3D map.

To demonstrate the rigidity and flexibility effects on host frameworks, tribranched anthracene amphiphiles with two types of cores were designed. I succeeded in the stereoselective preparation of a tribranched amphiphile with an *ortho*-substituted 1,3,5-triphenylbenzene derivative and three anthracene panels. The stereocontrolled bowl-shaped amphiphile formed a dimeric capsule in water. The dimeric capsule possesses stereocontrolled, flexible polyaromatic frameworks and thereby efficiently encapsulated several perylene compounds in an aqueous solution through simple grinding protocols, as confirmed by UV-vis and DLS analyses. Notably, the encapsulated, π -stacked perylene molecules exhibited an unusual Y-type excimer emission in aqueous solutions at room temperature. In contrast, an analogous assembly without the *ortho*-substituents on the amphiphile showed E-type excimer emission from the encapsulated perylene stack under same conditions. In short, the *ortho*-substituents on the central benzene core are essential for the formation of the well-defined capsular structure and the characteristic host-guest emissive properties.

Through above works, I established the design and stereoselective synthetic methods of new polyaromatic amphiphiles, which intrinsically possess multiple stereoisomers. Moreover, I developed molecular capsules through self-assembly of the stereo-controlled amphiphiles and revealed the effects on stereoregulation of the amphiphiles for the resultant assembled structures and host-guest interactions. These results would contribute to design, construction, and function for various novel nano-architectures, which would further progress supramolecular chemistry.

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。

Note: Thesis Summary should be submitted in either a copy of 2000 Japanese Characters and 300 Words (English) or 1 copy of 800 Words (English).

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