

論文 / 著書情報
Article / Book Information

題目(和文)	溶液 / 固体状態の芳香環カプセルの揮発性有機化合物に対する特異機能
Title(English)	Unusual Functions of Solution/Solid-state Polyaromatic Capsules toward Volatile Organic Compounds
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Category(English)	Doctoral Thesis
種別(和文)	論文要旨
Type(English)	Summary

(博士課程)
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論文要旨

THESIS SUMMARY

系・コース： Department of, Graduate major in	応用化学 応用化学	系 コース	申請学位 (専攻分野)： Academic Degree Requested	博士 Doctor of	(工学)
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要旨 (英文 800 語程度)

Thesis Summary (approx.800 English Words)

Volatile organic compounds (VOCs), which are organic compounds with high volatility under ambient temperature and pressure, are categorized into two types: synthetic VOCs and natural VOCs, including monoterpenes. Both synthetic and natural VOCs are familiar to us yet simple, efficient, selective, and tight binding and separation methods have seldom been established so far, because of the similarity of their structures and physical properties.

There have been many reports on the binding of VOCs by synthetic host compounds in solution and in the solid state. 〇 Several host compounds show high binding selectivity depended on the shape and size of the cavities. However, their high reusability toward VOC binding and catalytic reactivities toward monoterpenes have been rarely accomplished. The majority of the host compounds are used either in solution or in the solid state, because of their poor solubility, low stability, and weak host-guest interactions. The development of host compounds with high VOC binding abilities both in solution and in the solid state is expected to generate novel nanoflasks capable of recognizing, preserving, and converting various VOCs.

In this doctoral thesis, I revealed the novel host functions of coordination-driven M_2L_4 polyaromatic capsules as host compounds toward VOCs in water and in the solid state. The capsules, with isolated cavities surrounded by eight anthracene panels, could bind benzene various derivatives and monoterpenes not only in the inner cavities but also outer spaces between them, through the hydrophobic effects and, $CH-\pi$, $\pi-\pi$, and hydrogen-bonding interactions. These multiple and effective host-guest interactions led high binding selectivity of polyaromatic capsules toward the VOCs. The encapsulated benzene derivatives and monoterpenes showed unusual properties in the polyaromatic cavities, which can't be observed both in solution and in the solid state without the capsules. In addition, an isotropically expanded capsule was synthesized through the simple ligand extension and the host function was studied. *In chapter 1*, the general introduction of the binding and conversion of VOCs by various host compounds, host abilities of polyaromatic capsules, and the purpose of this research are described.

In chapter 2, the binding ability of solid-state polyaromatic capsules toward benzene derivatives is described. The finite capsule solids bound several molecules of xylene isomers, especially *o*-xylene, over toluene and benzene at ambient temperature and pressure within 1 hour, revealed by 1H NMR analysis. TG-DTA and 1H NMR analyses clarified the capsule solids can suppress the volatilization of benzene derivatives through efficient $CH-\pi$ and $\pi-\pi$ interactions between the host polyaromatic panels and the guests. The stable capsule solids showed high

binding reusability without changes in the capability and efficient adsorption ability toward diluted *o*-xylene vapor.

In chapter 3, the selective encapsulation of cyclic monoterpenes by a polyaromatic capsule in water is discussed. ¹H NMR, ESI-TOF MS, and X-ray crystallographic analyses demonstrated that the capsule can bind one molecule of various cyclic monoterpenes in a quantitative fashion and recognize menthone with high selectivity, derived from multiple host-guest interactions, in water at room temperature. Encapsulated menthone formed ternary host-guest complexes with π -conjugated cyclic monoterpenes and displayed unusual thermal isomerization from a stable chair conformer to unstable diaxial-type chair and boat conformers, supported by ¹H NMR, ESI-TOF MS, and DFT studies. Volatilized monoterpene was also bound by the capsule solid with high selectivity for menthone. ¹H NMR studies revealed that the capsule largely suppressed the volatilization of bound monoterpenes even at elevated temperature in water as well as in the solid state.

In chapter 4, the encapsulation of linear monoterpenes by solution- and solid-state polyaromatic capsules is described. The capsule recognized citronellal from a mixture of linear and/or bicyclic derivatives in water and in the solid state. ¹H NMR and ESI-TOF MS analyses and DFT calculations revealed that the capsule can extract *p*-menthane-3,8-diols, with high equatorial-stereoselectivity, from a reaction mixture obtained by the acid-catalyzed cyclization of citronellal in water. Furthermore, the acid-loaded capsule solid promoted catalytic cyclization-dimerization of vaporized citronellal and gave *p*-menthane-3,8-diols citronellal acetal in 330% yield, with product/stereo-selectivity, based on the capsule under ambient conditions, analyzed by NMR, GC-MS and DFT studies. The capsule solid could be reused at least 5 times with enhanced conversion.

In chapter 5, the synthesis of an isotropically expanded, polyaromatic capsule and its binding properties are discussed. The self-assembly of two metal ions and four bispyridine ligands bearing three anthracene panels afforded a spherical M₂L₄ capsule with 1.9 nm in a diameter and 1600 Å³ in volume, supported by NMR, DLS, AFM, and DFT studies. ¹H NMR, ESI-TOF MS, and UV-vis analyses demonstrated that the expanded capsule encapsulates one molecule of a fullerene family (e.g., Sc₃N@C₈₀, C₇₀, and C₆₀), up to four molecules of planar aromatics (1-methylpyrene and coronene), and one or two molecules of large dyes (Cu-phthalocyanine and Zn-tetraphenylporphyrin) under aqueous conditions. Unusual pairwise encapsulation of two planar aromatics and one large dye was observed in the expanded cavity.

In chapter 6, the summary and perspectives of this thesis are described.

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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