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Author(s)	Ruengsuk, Araya
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Form 3

Abstract of Thesis

Name (Araya Ruengsuk)	
Title	Supramolecular Architectures Based on Pillar[5]arene Derivatives （ピラー[5]アレーン誘導体を基盤とする超分子構造体）

Abstract of Thesis

Macrocyclic hosts have been a key player in the research field of supramolecular chemistry, and the creation and development of macrocycles with unique host-guest properties have received increasing attention, with expanding their applications in chemistry, biology, engineering, and nanotechnology. Recently, pillar[n]arenes, which are pillar-shaped macrocyclic molecules with a rigid cavity constructed from electron rich arenes, have become attractive candidates to study supramolecular host-guest chemistry and self-assembly because they can use a rigid central cavity to encapsulate guest molecules through CH-π interactions. However, synthesis of pillar[5]arenes, in particular, with highly functionalized structures and low-symmetrical structures, is still challenging. In this work, the post-functionalization of pillar[5]arenes was carried out, and the physical and chemical properties of the resulting pillar[5]arene derivatives, together with their supramolecular self-assembling behavior, were investigated.

Part I: Pertosylated pillar[5]arene: self-template assisted synthesis and supramolecular polymer formation.

The first research avenue in this thesis was the synthesis of the pertosylated pillar[5]arene (**1**), which is a functionalisable macrocyclic compound. The cyclization reaction of the ditosylate monomer afforded **1** in a high yield as a result of a tosylate self-templating effect. Single-crystal X-ray analysis revealed the five-fold symmetric structure of **1**, together with the formation of a linear polymeric structure that is stabilized by the intermolecular inclusion of tosylate arms into pillar[5]arene rings. Macrocycle **1** with tosylate groups acts as a reactive species instead of the corresponding macrocycle with halogen groups, allowing to produce a wide range of pillar[5]arene derivatives through post-synthetic modifications. This post-synthetic modification should lead to the creation of tailored macrocycles for specific applications.

Part II: Tosylate Self-Templating Selective Synthesis and Supramolecular Assembly of Tosylated Co-Pillar[4+1]arenes.

The innovative tosylate self-templating strategy, which can allow to construct unique supramolecular networks resembling pseudorotaxanes in the solid state, led to the successful creation of octatosylated copillar[4+1]arenes (**P[4]OTs[1]A**) in a high yield without producing a mixture of constitutional isomers or polymeric by-products. This method also facilitated the precise synthesis of mono-quinone functionalized pillararenes (**P[4]OTs[1]Bq**). Notably, the

incorporated mono-quinone exhibited not only unique electrochemical property but also temperature-dependent self-assembly behavior that was confirmed by VT NMR and SAXS techniques. Moreover, the degree of supramolecular self-assembly was supported by spectroscopic method, single crystal X-ray analysis, and FMO modeling calculations. This research highlighted the significant potential of tosylate groups to enhance the selectivity, efficiency, and functionalization of pillar[5]arene in the synthesis and self-assembly process.

Part III: Supramolecular Architectures Consisting of Cationic Pillar[5]arene Derivatives and Anionic Metal Complexes with D-Penicillamine.

In this chapter, pertosylated pillar[5]arene (**1**) was modified to pillar[5]arene with imidazolium side arms (**P[5]Imi**), which can work as a cationic building block for creating ionic supramolecular architectures. Treatment of the cationic pillar[5]arene with the anionic $\mathrm{Au^{I}_{3}Co^{III}_{2}}$ complex with D-penicillamine, $[\mathrm{Au_3Co_2(D\text{-}pen)_6}]^{3-}$ (**$[\mathbf{1\text{-}D}]^{3-}$**, $\mathrm{D\text{-}H_2pen}$ = D-penicillamine), afforded a metallosuparmolecular compound **$(\mathbf{P[5]Imi})_3[\mathbf{1\text{-}D}]_{10}$** (**$[\mathbf{1\text{-}D}]^{\mathbf{Imi}}$**) through a co-crystallization process. The creation of a porous ionic framework *via* the electrostatic interaction between the cationic **P[5]Imi** and anionic **$[\mathbf{1\text{-}D}]^{3-}$**species was confirmed by single crystal X-ray analysis using synchrotron radiation. Notably, only the *Sp* configuration of cationic pillar[5]arene was incorporated into the framework upon the crystallization with the optically active $\mathrm{Au^{I}_{3}Co^{III}_{2}}$ complex with D-pen. This result demonstrated that porous supramolecular ionic compounds created via the co-crystallization of chiral cationic/anionic pillar[5]arenes and chiral anionic/cationic metal complexes can show a unique mutual chiral recognition between cationic and anionic species.

Conclusions

This study proposed three practical methods to design and fabricate pillar[5]arene derivatives by the modification of tosylate substitutions. First, pillar[n]arene was developed to novel pertosylated pillar[5]arene that can be functionalized by the employment of tosylate groups as a self-templating strategy. The synthetic approach of this compound demonstrated not only the self-templation of pendent tosylate substituents but also their role as effective leaving groups in post-synthetic modifications, which enables the creation of tailored macrocycles for specific applications. Second, tosylate monomers on pillar[5]arene were modified through co-cyclization, resulting in the creation of tosylated-copillar[5]arene derivatives. This method facilitated the precise synthesis of mono-quinone functionalized pillararenes, allowing to study their electrochemical properties and self-assembly behaviors at different temperatures. Third, pertosylated pillar[5]arene was modified to its cationic form via the post-synthetic method. The cationic form was found to be used as a building block for the construction of ionic supramolecular architectures in combination with an anionic multinuclear complex, exhibiting a unique chiral recognition event in the solid state. The achievements presented in this thesis provided effective methods for the design and synthesis of new class of pillar[5]arenes, which can enhance the selectivity, efficiency, and functionalization in self-assembly processes.

論文審査の結果の要旨及び担当者

氏　名　(　Araya Ruengsuk　)

論文審査担当者		(職)	氏　名
大阪大学	主 査	教授	吉成　信人
	副 査	教授	石川　直人
	副 査	教授	舩橋　靖博
	副 査	名誉教授	今野　巧
Mahidol University	副 査	Associate Professor	Thanthapatra Bunchuay
	副 査	Associate Professor	Ekasith Somsook
	副 査	Associate Professor	Jonggol Tantirungrotechai
	副 査	Associate Professor	Preeyanuch Sangtrirutnugul

論文審査の結果の要旨

Araya Ruengsuk は、タイ国マヒドン大学に在籍するとともに、部局間協定にもとづく Double Degree Program (DDP)により本部局の統合理学特別コースに在籍しており、コチュテルの合意にしたがって博士論文審査を進めた。提出された博士論文のタイトルは「Supramolecular Architectures Based on Pillar[5]arene Derivatives (ピラー[5]アレーン誘導体を基盤とする超分子構造体)」であり、トシル基を導入したピラー[5]アレーン分子の合成と、その誘導体合成や超分子構造形成について調査したものである。

第一のトピックは、トシル基を導入したヒドロキノン前駆体を用いて縮合反応を行うことにより、10 個のトシル基を置換基としてもつピラー[5]アレーン分子が合成され、擬ロタキサン構造形成による超分子鎖状構造が形成されることを示したことである。第二のトピックは、トシル基をもつ前駆体とメトキシ基をもつ前駆体を 4:1 の化学量論比で混合した場合には、共環化反応が進行し、8 個のトシル基と 2 個のメトキシ基をもつ、混合置換基ピラー[5]アレーンが選択的に得られたことである。この分子は、メトキシ基の脱保護により、大きな温度依存色調変化を示すベンゾキノン誘導体へと変換可能であることも明らかにした。第三のトピックは、10 価の正電荷をもつカチオン性ピラー[5]アレーン誘導体を D-ペニシラミンをもつアニオン性金属錯体とイオン結晶を構築した際に、D-ペニシラミンのキラル誘導によってピラー[5]アレーンの一方の鏡像体のみが選択的に結晶中に取り込まれたことである。

この論文に対して、それぞれの部局で予備審査を行い、双方ともに本審査を受けるに値するものと認めた。マヒドン大学では 2024 年 8 月 6 日にて予備審査が行われ、大阪大学の審査委員もオンライン形式で出席した。さらに本部局では、2024 年 8 月 8 日に、化学専攻Ａコースの教授全員が参加した博士論文公聴会がオンライン形式で開催された。博士論文公聴会の終了後、大阪大学とマヒドン大学の合同審査委員会をオンライン形式で開催し、博士論文の内容および公聴会における発表内容と質疑応答に基づいて評価を行なった。その結果、本論文は学位論文として十分価値あり、双方の大学から博士号を授与するに値すると認められた。