

## 論文の内容の要旨

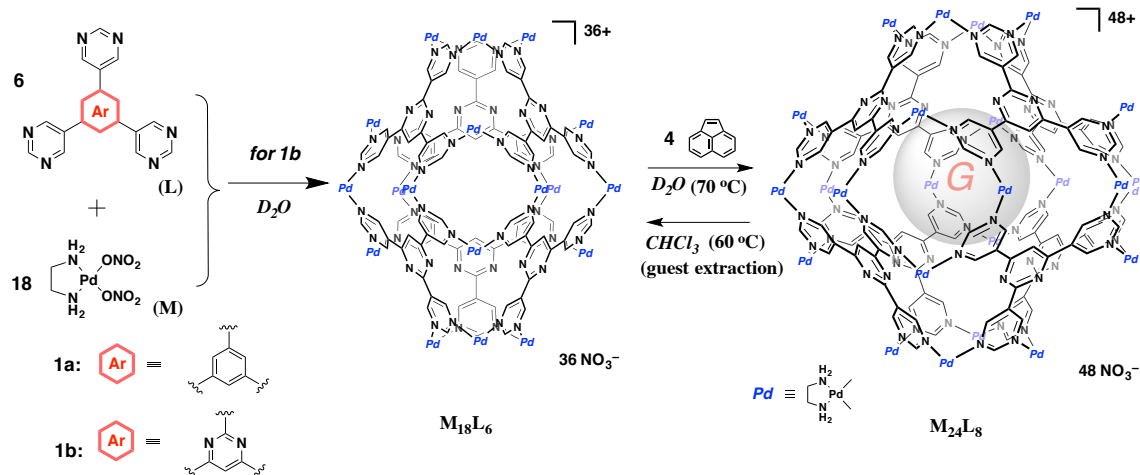
論文題目 **Functionalization of Self-Assembled Coordination Capsules via Ligand Design**

(配位子設計による自己組織化カプセル錯体の機能化)

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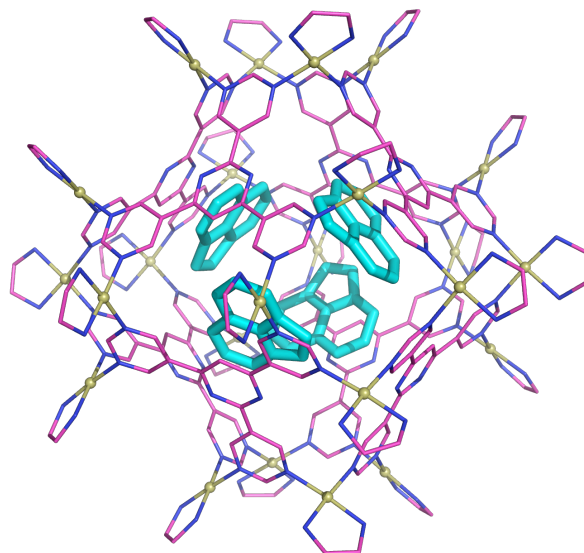
Supramolecular capsules can provide isolated environment for the entrapped guest molecules and render them some unique properties that are usually different from those in the external bulk solutions. Among many interactions used for constructing the supramolecular capsules (such as covalent bonding, hydrogen-bonding, ion pair interactions, *etc.*), the metal coordination self-assembly is most attractive to chemists, as the categories of metal ions and organic ligands are usually broad, and by rational design, many kinds of capsules with various properties could be constructed. Up till now, chemists have made much effort to construct self-assembled coordination capsules. However, the giant size and excellent molecular recognition abilities for those capsules have still been challenging. In this thesis, I would focus on the ligand design to control and tune the metal coordination capsules.

### 1. A self-assembled $M_{24}L_8$ capsule



Scheme 1  $M_{18}L_6$ – $M_{24}L_8$  capsule conversion by guest encapsulation and extraction.

Fujita's group previously (*Nature* **1999**, 398, 794–796.) reported a huge  $M_{18}L_6$  hexahedral capsule self-assembled from a triangular exo-hexadentate ligand **1a** with the ethylenediamine protected palladium (II) the (en)Pd(NO<sub>3</sub>)<sub>2</sub> (M). Though this capsule had a very large inner cavity, it showed no guest encapsulation behavior. To enhance the interactions between the ligands and electron-rich guest molecules, here I redesigned the ligand by replacing the benzene ring with a pyrimidine core, and synthesized an electron deficient planar ligand **1b**. After the ligand **1b** and Pd(II) metal M were mixed in 1:3 molar ratio in water and stirred for 24 h at 70 °C, a



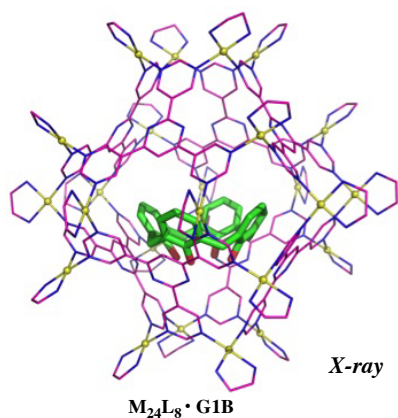
**Figure 1** X-ray structure of  $M_{24}L_8 \cdot 4(\text{acenaphthylene})$

highly symmetrical ( $D_{3h}$ )  $M_{18}L_6$  hexahedral capsule was quantitatively formed as confirmed by NMR and crystallographic analysis. When excess acenaphthylene was suspended to this solution (70 °C, 24 h), the capsule structure was dramatically changed. Single crystal X-ray analysis clearly revealed the formation of  $M_{24}L_8$  octahedral capsule encapsulating four molecules of acenaphthylene (Figure 1). The  $M_{24}L_8$  capsule had a giant inner cavity volume (923 Å<sup>3</sup>, calculated by VOIDOO), suggesting that larger molecules could be encapsulated. Then the big guest molecule calix[4]arene (**G1B**) was examined, and in that case, one molecule was encapsulated within the  $M_{24}L_8$  capsule, which was characterized by NMR measurements, elemental analysis and crystallographic analysis (Figure 2). Thus, by simple ligand design, I successfully created an electron-deficient  $M_{18}L_6$  hexahedral capsule of which the guest encapsulation ability was much improved, and after guest encapsulation, it could convert into a giant  $M_{24}L_8$  octahedral capsule that could encapsulate very large guest molecules.

## 2. Guest recognition behavior and capsular effects of $M_{24}L_8$ capsules

The guest encapsulation behavior was further tested and two types of guests were found to be suitable for encapsulation. Type **A** molecules were those with similar sizes as acenaphthylene, and type **B** were those molecules bearing phenol parts. Interestingly, some similar guests even with a small difference could not be encapsulated into the  $M_{24}L_8$  capsules. For example, **G2B** could be encapsulated, while **G3B** was failed (Figure 2). This giant  $M_{24}L_8$  capsule had good capsular effects. It could protect the entrapped acenaphthylene guest from extraction by organic solvent (CDCl<sub>3</sub>) at

room temperature, which was quite different from the supramolecular cages with big windows in which the inside guests could be quickly extracted into the organic solvent. Only at elevated



	Guest	Capsule-capsule conversion
G1B		Yes
G2B		Yes
G3B		No

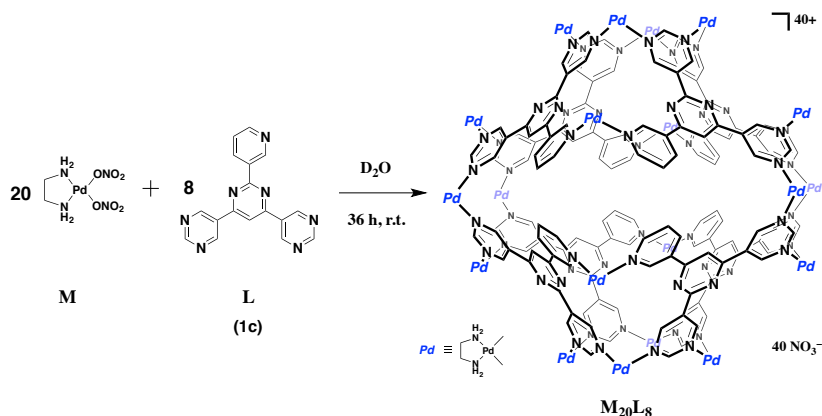
temperature (60 °C) the guest acenaphthylene within this  $M_{24}L_8$  capsule could be released into the  $CDCl_3$  phase,

**Figure. 2** X-ray structure of  $M_{24}L_8 \cdot G1B$  and the guest recognition behavior of the  $M_{24}L_8$  capsule.

was then quickly converted from the  $M_{24}L_8$  octahedral back into the  $M_{18}L_6$  hexahedral capsules (scheme 1). Additionally, the  $M_{24}L_8$  capsule could selectively control the *syn*-[2+2] dimerization of acenaphthylene within the cavity after UV photo-irradiation, suggesting the good capsular effects of this octahedral capsule.

### 3. A self-assembled $M_{20}L_8$ octahedral capsule

As the  $M_{24}L_8$  octahedral capsule could only encapsulate some certain aromatic guests, and nonaromatic guests were not suitable because of lacking host-guest  $\pi-\pi$  interaction to stabilize the entropy-unfavored  $M_{24}L_8$  framework, here I further designed a new ligand **1c** by replacing one external



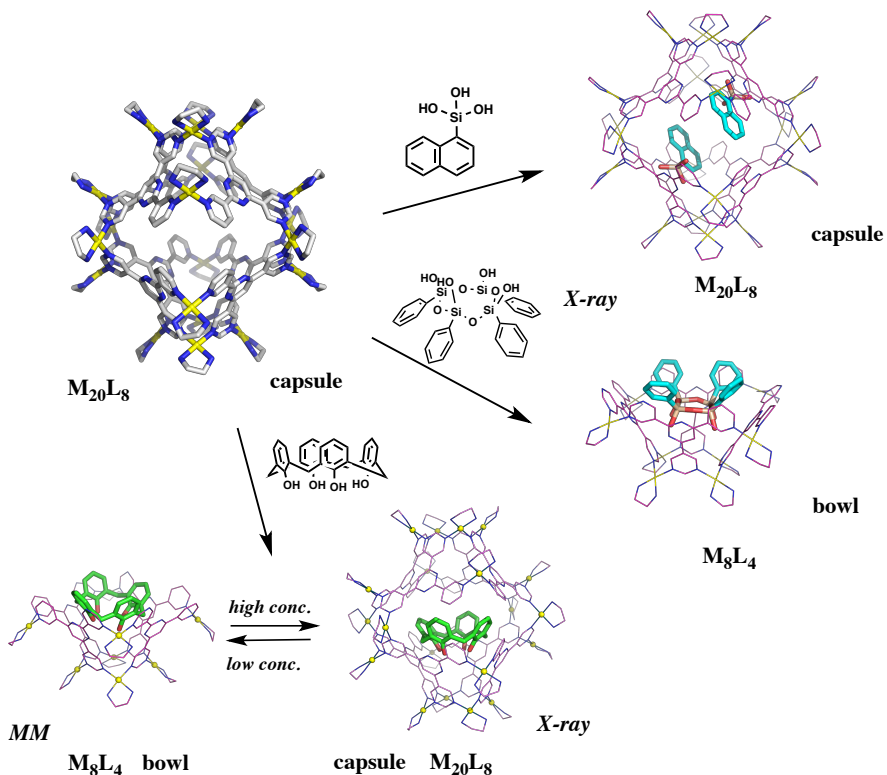
**Scheme 2** Self-assembly of the  $M_{20}L_8$  octahedral capsule

3,5-pyrimidyl ring on **1b** with 3-pyridyl group. After the ligand **1c** and  $Pd^{II}$  were mixed in 2:5 molar ratio in water at room temperature for 36 h, a symmetric ( $D_{2h}$ )  $M_{20}L_8$  octahedral capsule was formed, as confirmed by the  $^1H$  NMR spectrum and X-ray crystal analysis (Figure 3). From the crystal structure, two suitable pores (5 Åx6 Å) and some clefs could be observed, suggesting that this capsule was flexible and some linear guests might be suitable for encapsulation by this capsule. The nonaromatic aliphatic guest 1,6-dibromohexane and the gold complex

chloro(trimethylphosphine)gold(I) were found suitable for encapsulation.

Additionally, this capsule showed unique capsule–bowl conversion either by guest control or concentration control. The  $M_{20}L_8$  octahedral capsule could split into two  $M_8L_4$  bowls triggered by the big guest molecule all-*cis* tetraphenylcyclotetrasiloxanolate.

And the octahedral framework was maintained when the guest was naphthalene-substituted trisilanol. When the guest was calix[4]arene, the capsule–bowl conversion showed concentration-dependent effect. At



**Figure 3 Unique capsule feature:  $M_{20}L_8$  capsule– $M_8L_4$  bowl conversion.**

diluted concentration the  $M_8L_4$ •calix[4]arene bowl was formed; on the other hand, at high concentration, the bowl was switched into the  $M_{20}L_8$ •calix[4]arene octahedral capsule. This concentration-dependent conversion was also revisable. Finally, the  $M_{20}L_8$  octahedral capsule could co-encapsulate calix[4]arene and ferrocene guest molecules within the cavity, further supporting the giant volume and good guest recognition ability of this  $M_{20}L_8$  octahedral capsule.