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学 位 論 文 題 目 Construction of Nanoscale Coordination Systems by

Accumulating Metal-Containing Macrocycles

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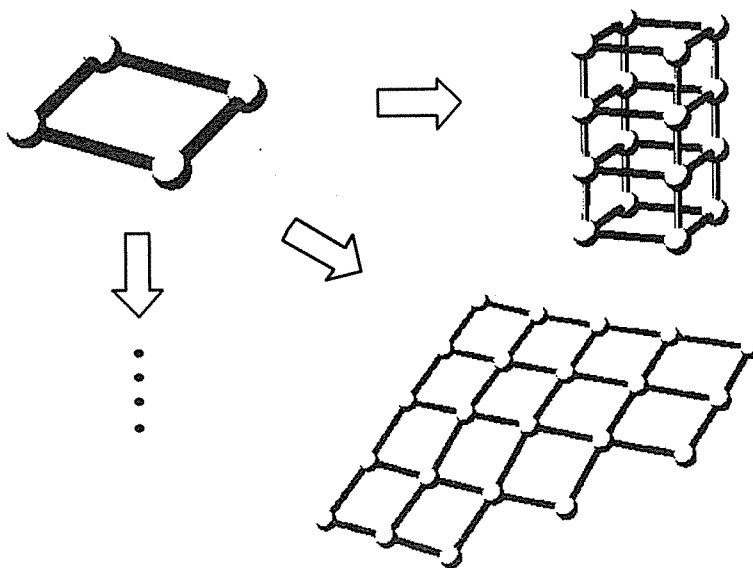
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This thesis describes the studies on the construction of various finite and infinite molecular architectures by accumulating metal-containing macrocyclic subunits.

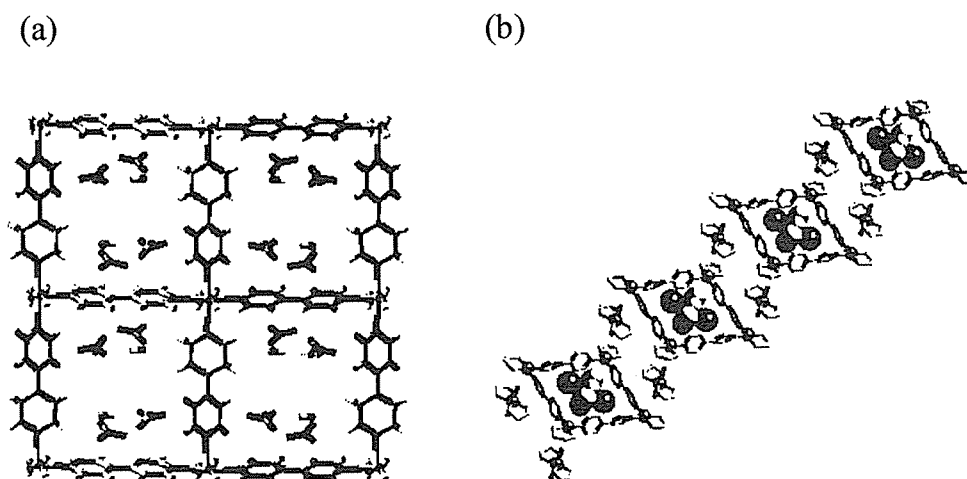
Macrocycles can bind small molecules in their cavities and have played an important role in the development of host-guest chemistry, molecular recognition chemistry, and supramolecular chemistry. Recently, macrocyclic frameworks have been constructed quite efficiently through *molecular self-assembly* which is featured by spontaneous generation of highly ordered structures from well-designed small components under thermodynamic conditions. Although a variety of metal containing macrocycles have been constructed by this method, further accumulation of the self-assembled macrocycles have been never investigated. Thus, the author paid his special attention to the concept of "*assembly of assembly*", where self-assembled structures self-assemble into more complex systems, and designed the accumulation of macrocyclic complexes into higher ordered structures. As described in [Chapter 1](#), the construction of such hierarchical assembled systems by the accumulation of macrocyclic units is his basic concept throughout the work in this thesis (Figure 1).



**Figure 1.** The accumulation of macrocyclic units into higher ordered structures: the authors basic concept throughout the thesis.

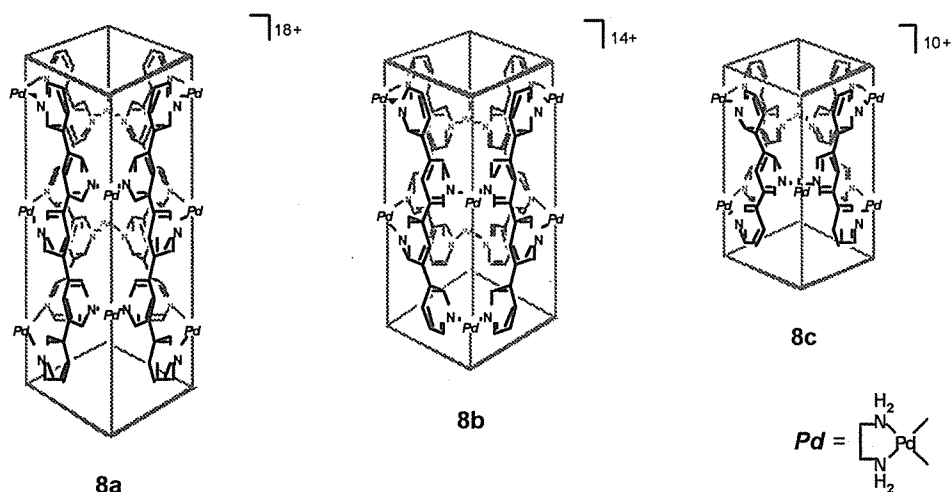
Among many metal-containing macrocycles,  $M_4L_4$  (M: metal, L: ligand) square complexes, in which metal provides 90 degree at every corner of the square, are one of the simplest and hence well-studied macrocyclic coordination compounds. He first examined infinite accumulation of

the square motif by combining  $\text{Cd}(\text{NO}_3)_2$  and 4,4'-bpy (4,4'-bpy = 4,4'-bipyridine) as described in Chapter 2. As a result, the variation of M:L ratios and concentrations led to the formation of two-dimensional  $\{[\text{Cd}(4,4'\text{-bpy})_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O} \cdot 2\text{NO}_3\}_n$  (1), one-dimensional  $\{[\text{Cd}(4,4'\text{-bpy})_3(\text{H}_2\text{O})_2] \cdot 2(4,4'\text{-bpy}) \cdot 2\text{NO}_3 \cdot 4.5\text{H}_2\text{O}\}_n$  (2), and zero-dimensional  $[\text{Cd}_2(4,4'\text{-bpy})_5(\text{NO}_3)_2(\text{H}_2\text{O})_4] \cdot 4\text{H}_2\text{O} \cdot 2\text{NO}_3$  (3). Complex 1 possesses a non-interpenetrated fused square grid network in which the square cavities are occupied by water molecules and nitrate ions (Figure 2a). The structure of the framework is similar to that of a guest-encapsulated square grid complex, which is previously reported, except shortened interlayer distance. The one-dimensional polymer 2 and zero-dimensional structure 3 forms two-dimensional networks with the assistance of O-H...N hydrogen bonds. Whereas the square grid is a two-dimensional extension of a square structure within a plane, he also designed the three-dimensional extension of a square motif along its vertical direction. Thus, in Chapter 3, the formation of  $\cdots\text{Pt}(\text{II})\cdots\text{Br}\text{-Pt}(\text{IV})\cdots$  mixed-valence complexes was utilized for the assembly of square compounds,  $[(\text{en})\text{M}(4,4'\text{-bpy})]_4(\text{NO}_3)_8$  ( $4 \cdot (\text{NO}_3)_8$ ; **a**: M = Pt(II), **b**: M = Pd(II)), into higher ordered infinite complexes. The reaction of  $4^{8+}$  with cationic Pt(IV) complex,  $[\text{PtBr}_2(\text{en})_2]^{2+}$  ( $5^{2+}$ ), afforded a 1:3 complex  $4\mathbf{a} \cdot (5)_3^{14+}$ . Crystallographic analysis of this complex showed that two moieties of  $5^{2+}$  bridged at the cis corner of  $4\mathbf{a}^{8+}$  making a stair-like infinite network, whereas another moiety of  $5^{2+}$  was accommodated in the cavity of  $4\mathbf{a}^{8+}$  (Figure 2b). On the other hand, complexation of  $4\mathbf{b}$  with anionic Pt(IV) complex,  $\text{PtX}_6^{2-}$  ( $6^{2-}$ ; **a**: X = Cl, **b**: X = Br), afforded a 1:4 complex  $4 \cdot (6)_4$ . UV-vis observations suggested the formation of a linear tube structure, in which each corner of  $4^{8+}$  is bridged by the linear X-Pt-X motif of  $6^{2-}$ .



**Figure 2.** (a) Crystal structure of two-dimensional polymer 1. (b) Crystal structure of stair-like infinite network  $4\mathbf{a} \cdot (5)_3$ .

One of the most interesting structures derived from macrocyclic units is tubular assemblies. In fact, tubular polymers, which are capable of ion transportation and catalysis, have been constructed by linking macrocyclic compounds. However precise control of lengths have been unrealized yet. In [Chapter 4](#), coordination nanotubes, which possess very stable and discrete frameworks, were constructed by linking oligo(3,5-pyridine)s (pentakis: **7a**, tetrakis: **7b**, tris: **7c**) with a cis-protected Pd(II) building block, (en)Pd(NO<sub>3</sub>)<sub>2</sub> (Figure 3). This transformation was in fact accomplished with the remarkable template effect of biphenyl derivatives. Thus, the reaction of **7** with (en)Pd(NO<sub>3</sub>)<sub>2</sub> first resulted in the formation of uncharacterizable products. However, the addition of sodium 4,4-biphenylenedicarboxylate to the solution induced the smooth assembly of nanotubes **8a-8c** wherein four molecules of **7** were held together with six to ten Pd(II) units. A nanotube structure templated by a guest was confirmed by an X-ray crystallographic analysis.

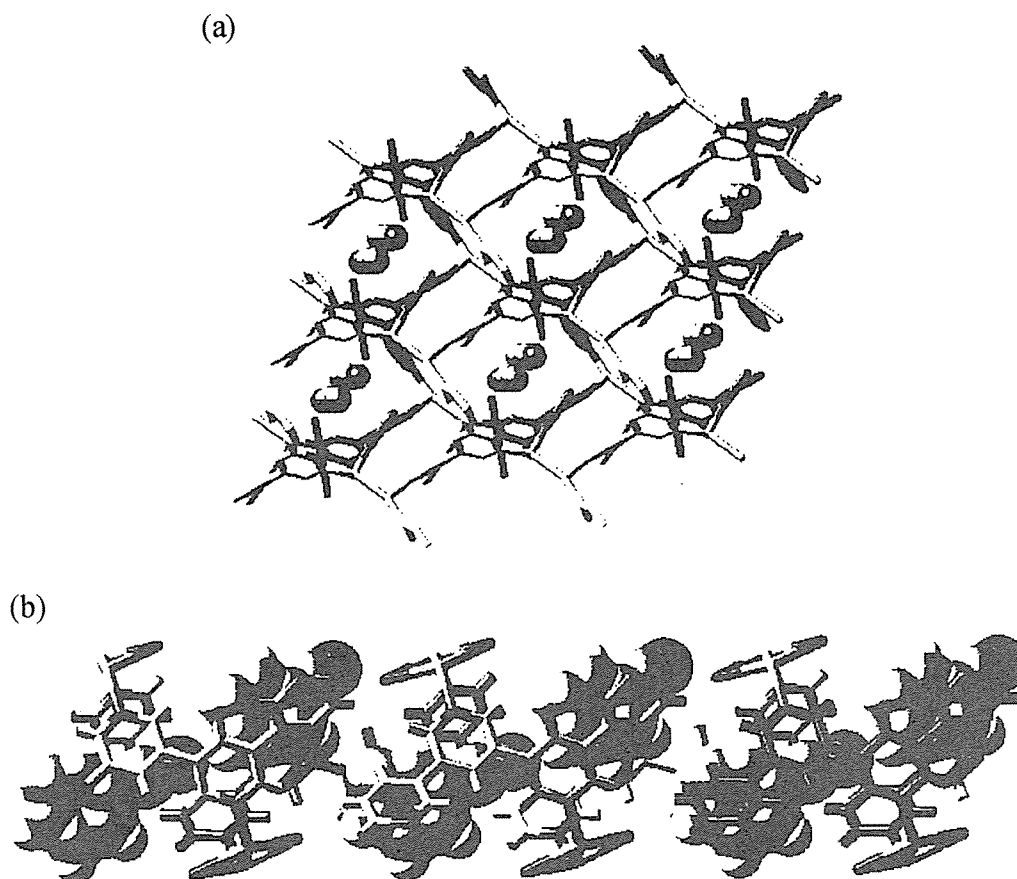


**Figure 3.** Coordination nanotubes **8a-c**.

The dynamics of guest molecule accommodated in the coordination tubes **8a** and **8c** was investigated in [Chapter 5](#) by variable temperature NMR measurements at different host-guest ratios. As the results, guest molecules are found to shuttle in the tube without flipping at low temperatures, but intermolecularly exchange at elevated temperatures. Coordination nanotube **8b** for which structural isomers can be considerable was isolated as a single isomer by recrystallization. The structure of a isomer was confirmed by X-ray crystallography. This single isomer slowly turned into an equilibrium mixture of two structural isomers in aqueous media.

To extend molecular nanotubes into solid tubular materials, in [Chapter 6](#), the formation of the coordination polytubes were examined by combining **7b** and a transition metal (CuI). The X-

ray crystallographic analyses showed that two types of non-interpenetration networks were induced by non-aromatic and aromatic guest molecules in the reaction media. A non-aromatic guest  $\text{CH}_3\text{CN}$  induced two-dimensional polytube  $[\mathbf{7b} \cdot (\text{Cu}_2\text{I}_2)] \cdot 2\text{G} \cdot \text{H}_2\text{O}$  (**9**,  $\text{G} = \text{CH}_3\text{CN}$ ) with an accessible porosity of 32% (Figure 4a). On the other hand, Aromatic guests such as nitrobenzene or cyanobenzene induced three-dimensional polytube structures  $[\mathbf{7b} \cdot (\text{Cu}_2\text{I}_2)] \cdot 2\text{G}$  (**10a**:  $\text{G} =$  nitrobenzene, **10b**:  $\text{G} =$  cyanobenzene) with large accessible porosity of 48% (Figure 4b). The cavities of **9** and **10** were occupied by guest molecules. Thermogravimetric (TG) analysis, IR spectroscopy, and powder X-ray diffraction analysis of **10b** before and after guest removal showed that the polytube framework is kept even after guest removal.



**Figure 4.** (a) Crystal structure of the 2D-polytube **9**. (b) Crystal structure of 3D-polytube **10b**.

## 論文の審査結果の要旨

環状化合物はその内部空孔での分子認識に基づきさまざまな機能が発現する。青柳君は自己集合によって生成した物質がさらに高次構造へと組織化する「集合体の集合体」という概念に焦点を定め、配位結合を介して自己集合した環状化合物が有限および無限高次構造体へ組織化する系を研究した。まず、遷移金属と有機配位子からなる大環状四核錯体を基本骨格として、環状構造をその平面方向に集積化させることにより二次元格子状の高分子錯体をつくった。X線結晶構造解析の結果、この錯体は二次元格子が積層したシート構造を有しており、積層シートを貫いてチャンネルが形成されていることがわかった。このような化合物には配位結合性のゼオライト様化合物としての機能が期待できる。一方、大環状四核錯体の基本構造を垂直方向へ集積化させることで、階段状あるいはチューブ状の高分子錯体を合成することにも成功した。またこの概念を拡張し、あらかじめ一次元につなげた素子を環化させ、配位結合性チューブ型錯体を合成した。このチューブ構造は内部に棒状のゲスト分子を取り込むことで安定に存在する。実際にチューブ錯体の自己集合は棒状の有機分子を鋳型に用いることで、高効率で達成された。チューブ内に取り込んだ分子の動的挙動も観測した。例えば、棒状のゲスト分子は、低温ではチューブ内で一次元的なシャトル運動のみが許容されるが、高温ではゲストのチューブ外への脱出を経て、分子軸の反転が可能となる。このようなチューブ構造の特性やゲストの特異的な動的挙動を利用することで、分子の選択的通過、形状選択的触媒等の応用が可能となる。さらに同様のチューブ構造を2次元あるいは三次元に集積化することによって細孔構造を持つ物質（ポリチューブ）の合成にも成功した。

以上の研究成果は3報の論文（一報は投稿中）としてまとめられており、提出論文は学位を与えるに相応しいものとなっていると判定した。

また、面接による試験は、出願者に学位論文の内容を約1時間で発表してもらい、その後、論文内容全体について1時間半にわたって質疑応答を行った。本学位論文では「集合体の集合体」という概念に基づいた環状構造の錯体の集積化が主題となっており、特に論文後半ではチューブ構造の構築に主眼が置かれている。質疑応答では、とりわけ溶液（水）中で得られる安定なチューブ錯体に関して、その自己集合過程、熱力学挙動、さらにはチューブ内に取り込まれたゲスト分子の動的挙動等に関し活発な論議が展開された。いずれの質疑に対しても適確な応答があり、研究の展開力や考察力、さらには討論に関して十分な能力を持ち合わせていると判定された。

本論文は英語で書かれており、既に発表されている3報の論文（英文）を中心に英語力を審査し、語学力に何等問題はないと判定された。

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