Quantitative Self-Assembly of [2]Catenanes and Cages Possessing Transition Metals in Their Backbones

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Chapter 5. A Thermally Switchable Molecular Lock. The Guest-Templated Synthesis of a Kinetically Stable Nano-Sized Cage

Chapter 1

General introduction

Chemists always admire the beauty and complexity of biological structures and ask themselves why such structures, e.g., double helix of DNA and 3D folding proteins, appear spontaneously in nature.[1] Recent understanding on self-organization phenomena in biology have led chemists to recognize that weak interactions play an important role to generate such structures. Inspired by the biological phenomena, chemists have paid their significant attention to the weak interactions such as hydrogen bonding, hydrophobic interactions, and van der Waals interactions, and began to develop a new strategy for constructing well-organized and highly complex structures. The rapid developments in these days led a new concept of molecular self-assembly,[2] which is termed for the spontaneous generation of well-defined structures through assembling of small molecules under a well-organized set of conditions.

Interlocking molecules as represented by [2]catenanes (*catena* = chain in Latin, Figure 1) are good target for studying weak interactions (Figure 1) because these covalently separated but mechanically linked rings have never been prepared efficiently without utilizing weak interactions for the preorganization of interlocked frameworks. Namely, the catenane synthesis is a lesson for understanding weak interactions. Fascinated by their unique and challenging structures, the author of the thesis was motivated to study the efficient synthesis of catenanes and related compounds through molecular self-assembly.[3]

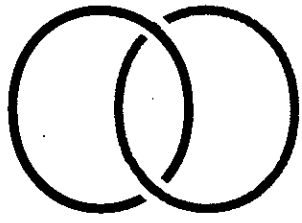


Figure 1. Topology of a [2]Catenane

Of many weak interactions, the author paid his attention to metal-coordination because, during the last decade, coordination bonds have been showing remarkable potential to induce the self-assembly of well-defined discrete strutures such as helices,[4] macrocycles,[5] cages,[6] grids,[7]

tubes,[8] capsules,[9] and so on. Accordingly, this thesis describes the studies on the highly efficient self-assembly of catenanes by the incorporation of transition metals in their backbones.

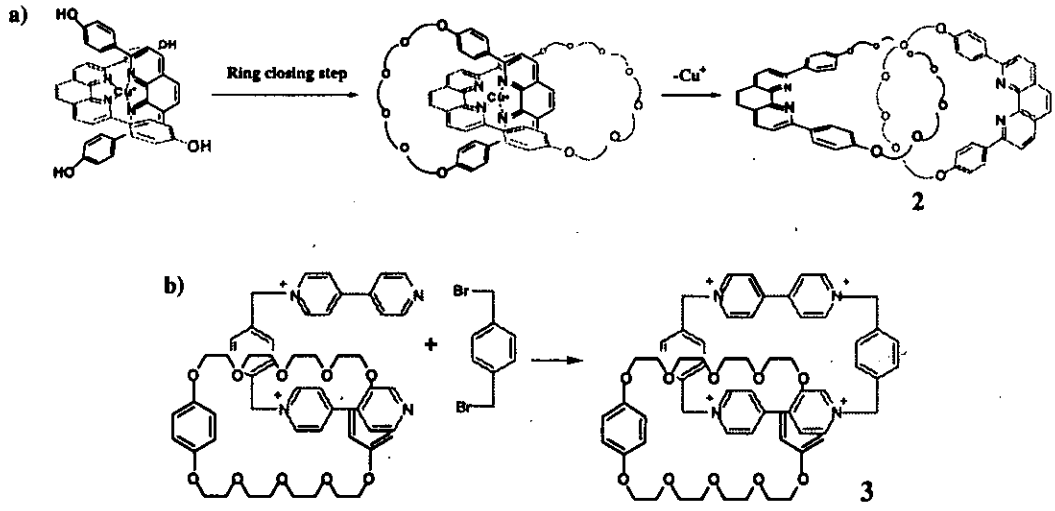
1-1 Development of catenane synthesis

The first synthesis of a catenane was reported by Wasserman, who examined the acyloin condensation of a long α,ω-dicaboxylic ester in the presence of a C_{34} macrocycle (Scheme 1).[10] He obtained catenane **1**, but the yield was quite poor (< 0.01%) because threading the macrocycle on the diacid chain is statistical.

1

Scheme 1. First catenane synthesis by Wasserman

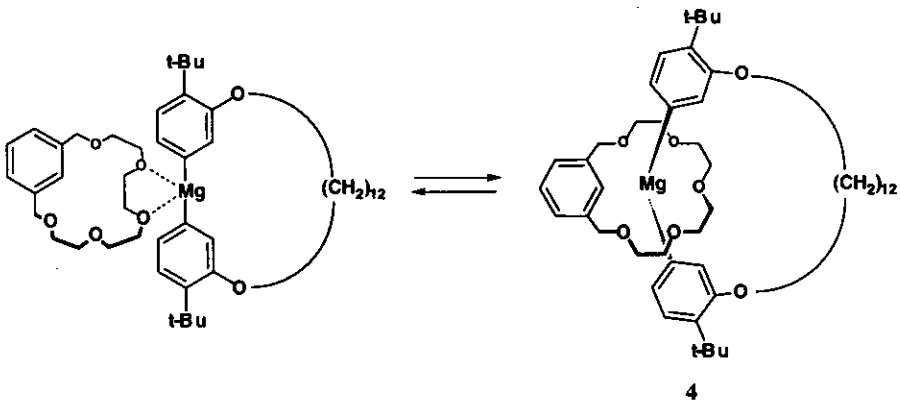
Nonstatistical synthesis has been explored since the middle 1980s due to the development of templating and self-assembly. Thus, molecular self-assembly around the tetrahedral geometry of Cu(I) was first applied to the templated synthesis of catenane **2** in 1983 (Scheme 2a).[11] An organic rectangular molecular box containing quaternary alkylated 4,4'-bipyridine showed remarkable ability to bind electron rich aromatic systems through the efficient aromatic contact, and catenane **3** was prepared in 70% isolated yield (Scheme 2b).[12]



2 **3**

Scheme 2. a) Strategic catenane synthesis by template procedures with copper(I) b) Strategic catenane synthesis by charge transfer interactions

The first inorganic catenane **4** was first reported in 1993 which involved carbon-magnesium bonds (Scheme 3).[13] Because the carbon-magnesium bond momentarily dissociates, reversible threading of the crown ether ring by an organo-magnesium ring was observed.

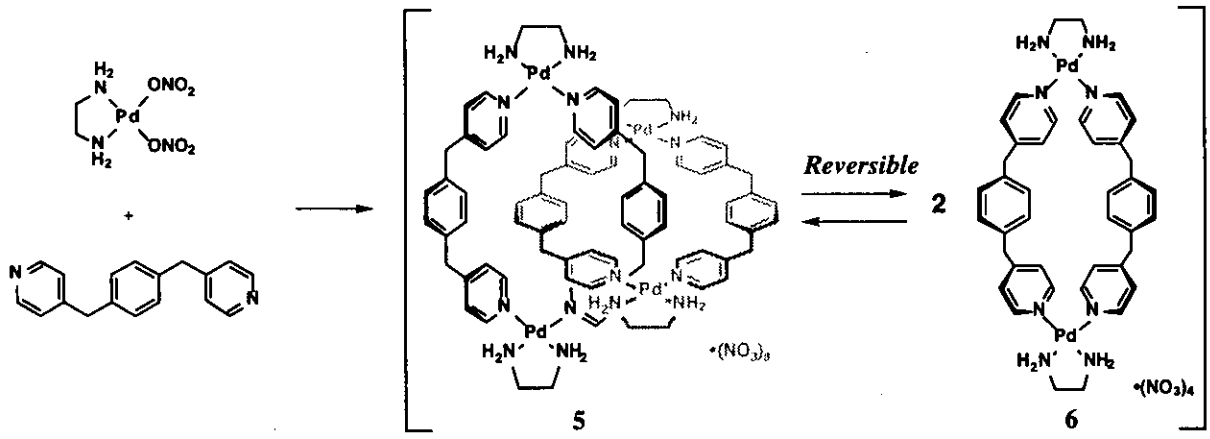


4

Scheme 3. Magnesium-mediated catenane **4**

1-2 Metal-incorporated self-assembling [2]catenane

The author's study on catenane synthesis started based on his previous finding that transition metal-containing catenane **5** self-assembles quantitatively from Pd(II) ions and pyridine-functionalized organic ligands. The detailed study on this phenomenon is discussed in **Chapter 2**.



Scheme 4. Quantitative catenane formation from pyridine-based ligands and Pd(II) metal centers

The X-ray crystal structure of [2]catenane **5** indicates that interactions between aromatic rings are quite important for [2]catenane formations. If the monomer frameworks have appropriate cavity with ca. 3.5 Å surface-to-surface distance, the two monomers are spontaneously interlocked into [2]catenanes with the aid of efficient CH-π and hydrophobic interactions. The [2]catenane

interesting point is that the [2]catenane structures are formed from two pre-formed ring compounds **6**, which takes place via transmetallation processes. The mechanistic aspect is also discussed in this **Scheme 2**,

1-3 Doubly interlocking [2]catenane

A [2]catenane is a topological isomer of two molecular rings. A more complex isomer in this family is a doubly interlocking [2]catenane in which two rings interlock each other with four crossing points (Figure 2c). The author realized the quantitative synthesis of a doubly interlocking [2]catenane, as discussed in **Chapter 3**, by combining template and self-assembly strategies, which have recently undergone on explosive development, making possible the synthesis of many fascinating and complex structures using only relatively simple procedures. The author's approach for doubly interlocking catenanes which have only been described recently[14] is to combine the two methods, based on coordination chemistry, "template" and "self-assembly" strategies. In the template strategy, copper(I) complexes have been used as precursors, affording simple to topologically very complex catenanes.

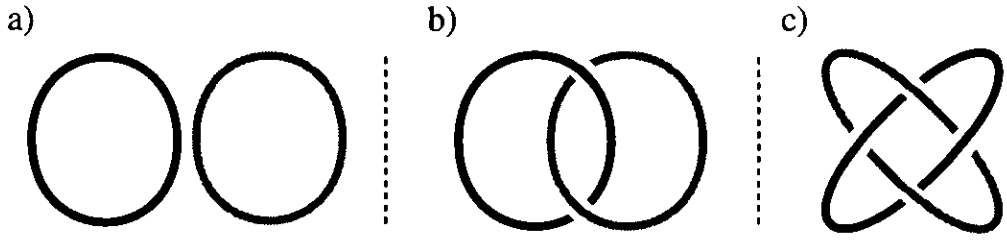
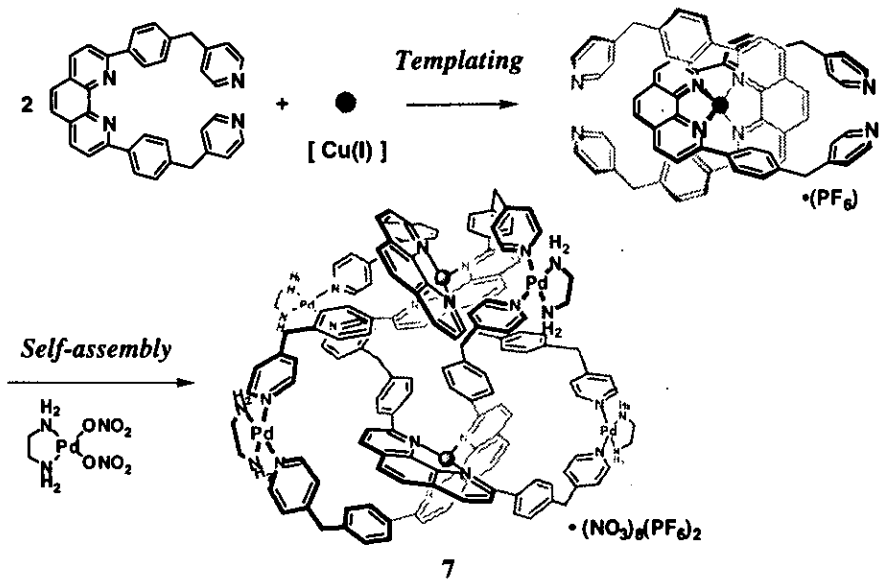


Figure 2. Topological isomers of two rings: a) two separate rings b) [2]catenane c) doubly interlocking catenane

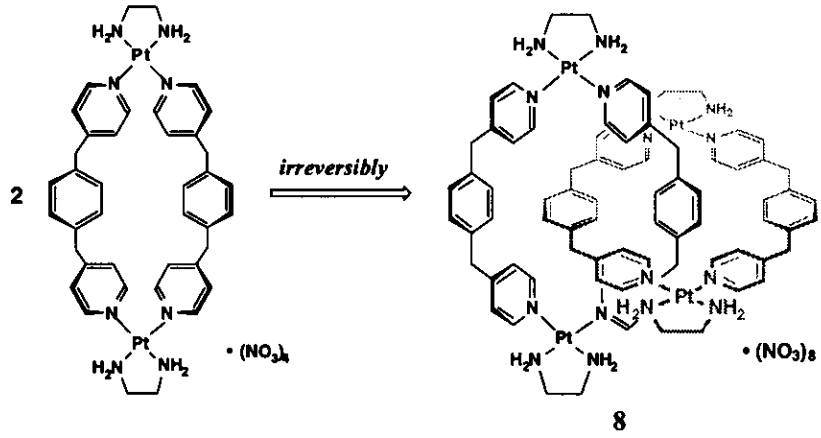
. The ligand used here contains a central 1,10-phenanthroline site attached to two pendent/4-pyridyl groups. And the central site is used in order to complex a copper(I) center whereas the lateral pyridine groups are coordinated to palladium(II). This new strategy enabled the author to quantitatively obtain a 4-crossing [2]catenane **7** incorporating two different metal centers: 4 Pd(II) and 2 Cu(I) (Scheme 5). The properties based on chirality are also mentioned.



Scheme 5. High efficient synthesis of doubly interlocking catenane **7**

1-4 Molecular lock concept

In contrast to labile Pd(II)-Py bonds, Pt(II)-Py coordination bond is inert in water at room temperature. However, the inert Pt(II)-Py bond turns into labile one at elevated temperature. Due to this behavior, the Pt(II)-Py coordinate bond can be likened to a lock made of molecules. Thus, the author proposed "*a molecular lock*" concept and applied to the synthesis of stable catenanes and square complexes. In **Chapter 4**, the author deal with kinetically stable [2]catenane by using "molecular lock" concept. By the incorporation of this Pt(II)-Py bond or "*molecular lock*" into ring frameworks, the one-way formation of a [2]catenane **8** was achieved (Scheme 6). Application of molecular lock into the synthesis of kinetically stable tetranuclear square complex is also described.



Scheme 6. One-way interconversion into [2]catenane **8**

Furthermore, the molecular lock concept is applied to the synthesis of a kinetically stable nano-sized cage complex. **Chapter 5** describes that an incorporation of Pt(II)-Py bonds into the vicinity of a cage structure allowed to obtain the stable nano-sized cage complex **9** in a high yield (Figure 3). A suitable guest molecule showed remarkable template effect for the generation of the cage compound. In addition, the assembled complex was revealed to have remarkable stability toward acidic or basic conditions.

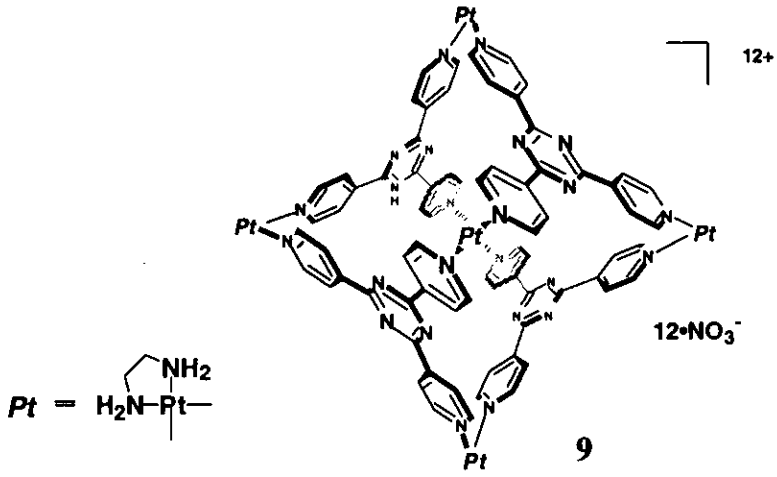


Figure 3. High efficient synthesis of cage-like structure **9**

1-5 References

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Chapter 2

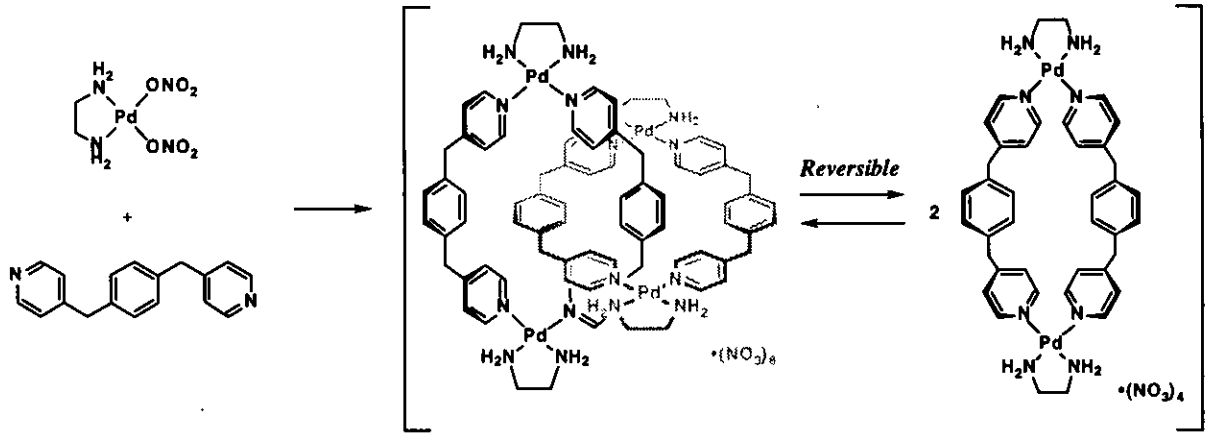
Rational Design of [2]Catenanes Self-assembling from a Cis-protected Palladium(II) Building Block and Pyridine-based Bridging Ligands

Nature **1994**, *367*, 720.

J. Am. Chem. Soc. **1996**, *118*, 899.

J. Am. Chem. Soc. **1998**, *120*, 611.

Abstract: This chapter describes the quantitative self-assembly of [2]catenanes by incorporating metal centers into frameworks of ring structures. These metal-mediated rings show the unique behavior in which two rings spontaneously interlock into catenanes. In addition, [2]catenanes are rationally designed by the consideration of appropriate conformation of monomeric rings and weak interactions. When a monomer ring has ideal van der Waals interplane separation (3.5 Å) in its structures, [2]catenane readily self-assembles. Furthermore, weak interactions, such as hydrophobic interaction, a edge-to-face or CH-π aromatic interaction are crucial factors to stabilize the catenane structure. X-ray studies afforded reliable evidences for the catenane structures, indicating the importance of weak interactions in the stabilization of catenanes. ESI-MS has also made it possible to confirm the formation of [2]catenanes. NMR studies give critical proofs about the structure of [2]catenanes. And more, some thermodynamic parameters are estimated by careful NMR measurement.



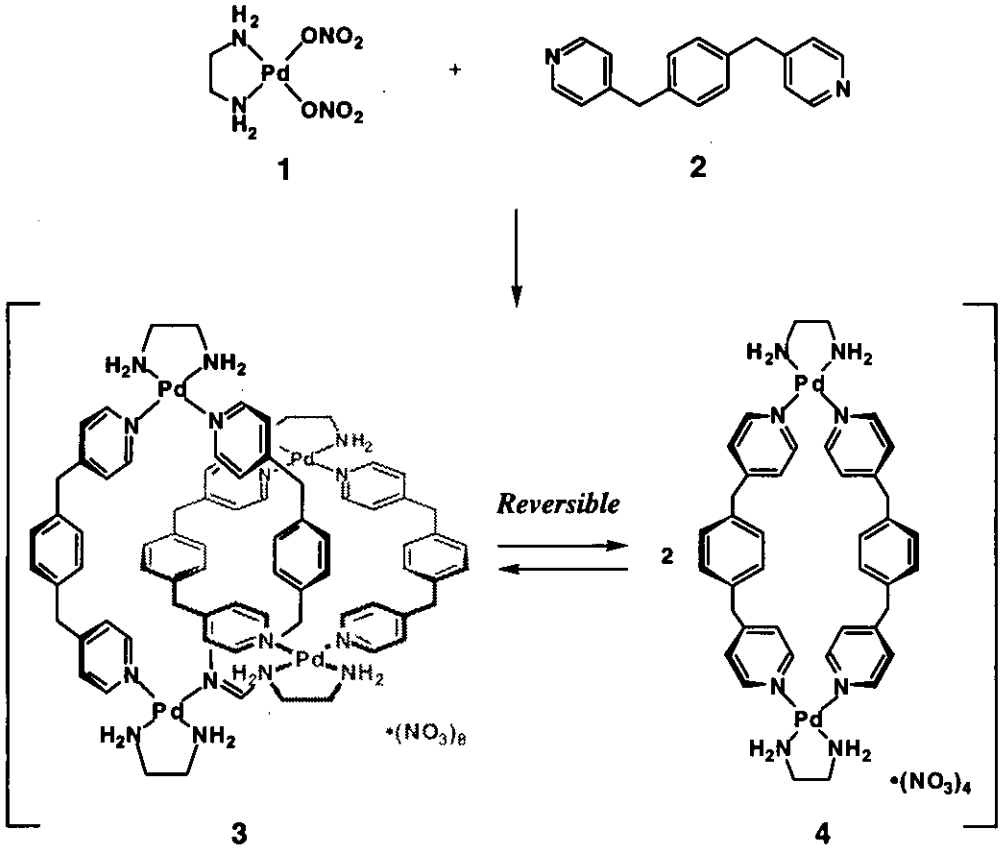
2-1 Introduction

Self-assembly phenomena have provided new concepts and methodologies for constructing highly ordered and functionalized molecules and materials.[1-3] In particular, the use of transition metal centers to direct the self-assembly events has become a rapidly growing discipline and triggered extensive studies on the self-assembly of well-defined structures such as helicates, chains, ladders, grids, macrocycles, and cages.[4] In order to develop this rapidly growing field, it is necessary to understand non-covalent interactions (e.g., aromatic interactions, hydrogen bonding, metal coordination, etc) because cooperation of a variety of non-covalent interactions is essential to design and then to realize the well-organized self-assembling molecular systems.

Interlocking compounds incorporating metals are good target for this purpose because there are many factors to be studied for understanding their self-assembly processes: i.e., cooperation of different bonds (covalent, coordinate, and non-covalent), thermodynamic balance (entropy vs. enthalpy), electronic and steric matching. A metal-containing rotaxane was first prepared through self-assembly in 1981.[5] Molecular assembly around the tetrahedral coordination geometry of copper(I) has been successfully employed in a template synthesis of catenanes and knots since 1983.[6] Recently, an organometallic catenane involving carbon-magnesium bond as well as a gold catenane was reported.[7] A systematic study was reported on the self-assembly of helicates versus catenanes through complexation of benzimidazole-based ligands and transition metals.[8] Preparation of fully organic catenanes via self-assembly process is of course attracting considerable current interest.[9]

In 1994, we found that metal-containing catenane **3** quantitatively self-assembled from small component molecules **1** and **2**.[10] This unique molecule was also shown to be in rapid equilibrium with monomer ring **4** (Scheme 1). Since neither covalent nor coordinate bonds exist between component rings, the assembly of **1** lies on a very delicate thermodynamic balance.

The formation of this interesting catenated structures arose the question whether or not it is possible to rationally design the self-assembly of various interlocked systems. Thus, to elucidate the major factors that control the self-assembly of interlocked molecules, series of pyridine-based bridging ligands were prepared and the examinations were done on the self-assembly of these ligands into catenanes upon treatment with (en)Pd(II) unit. Here important factors for the self-assembly of metal-linked catenanes are discussed and elucidated.



Scheme 1. Formation and equilibrium of catenane **3** and monomeric ring **4**

2-2 Self-assembly of macrocycles and catenanes from (en)Pd(II) unit and various bridging ligands

After obtaining catenane **3**, self-assembly of catenanes were examined from a variety of bridging ligands including fluorinated derivative **5**, mono-methylene homologue **8**, bismethylene homologue **11**, mono-methylene degraded derivative **14**, biphenyl derivatives **17** and **19**, and terphenyl derivative **22**.[11] Complexations of these ligands with (en)Pd(NO_3)$_2$ (**1**) were examined and self-assembled product(s) in the complexation are listed in Table 1. Typically, **1** was treated with an equimolar amount of ligands and experiments were carried out at 10 mM/[Pd] in D_2O. Three-component systems were also examined (**1** + **17** + **23** or **1** + **22** + **26** in a 2:1:1 ratio).

Table 1.

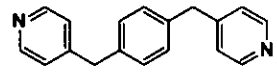
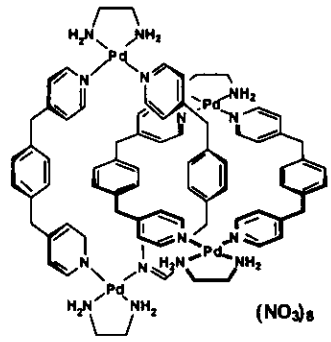
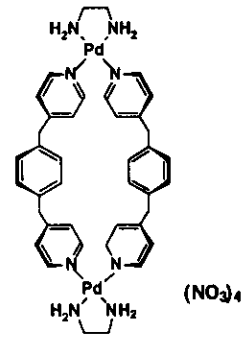
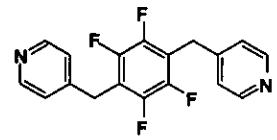
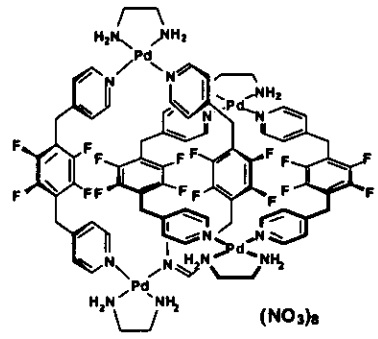
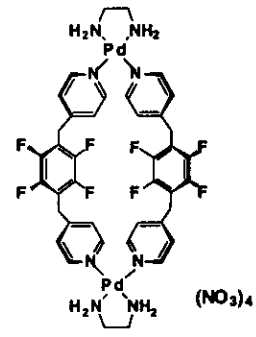
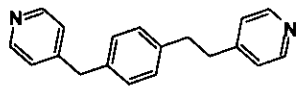
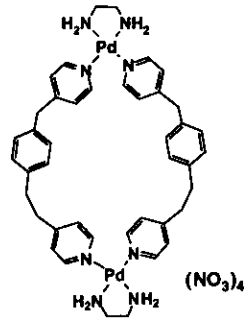
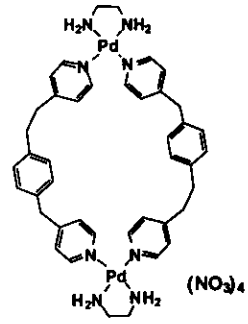
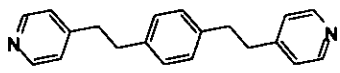
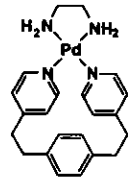
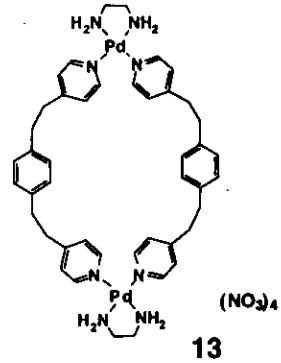
Ligands	Products
 2	 $(NO_3)_8$ 3 +  $(NO_3)_4$ 4
 5	 $(NO_3)_8$ 6 +  $(NO_3)_4$ 7
 8	 $(NO_3)_4$ 9 or  $(NO_3)_4$ 10
 11	 $(NO_3)_2$ 12 +  $(NO_3)_4$ 13

Table 1(continued).

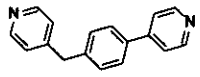
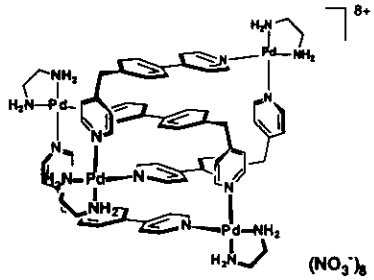
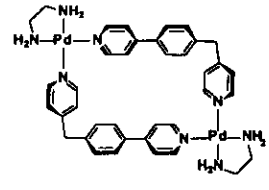
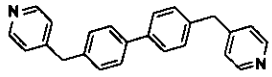
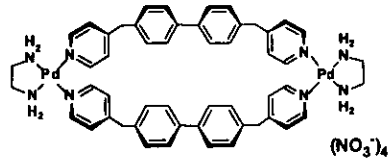
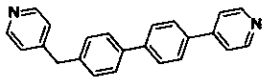
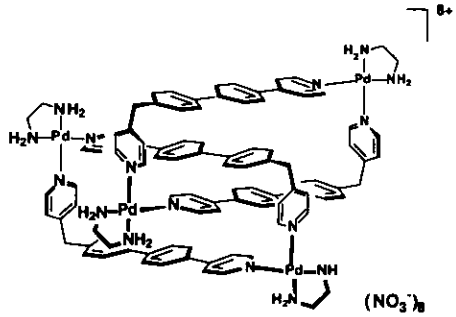
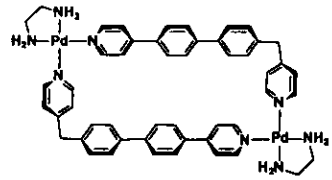
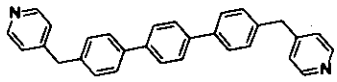
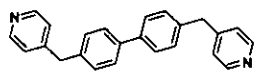
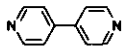
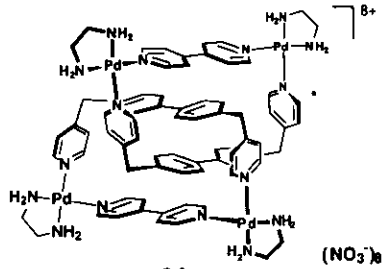
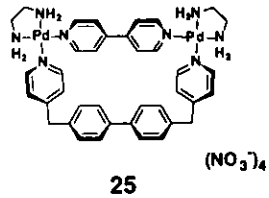
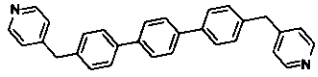
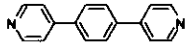
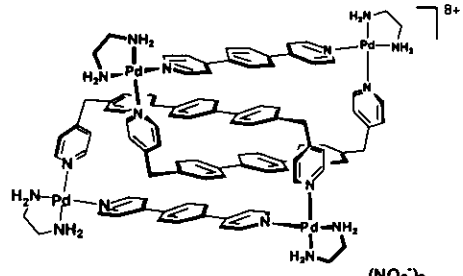
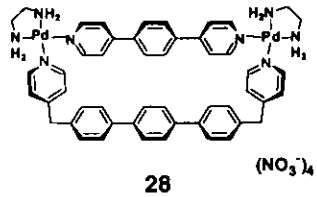
Ligands	Products
 14	 $(NO_3^-)_8$ 15
	 $(NO_3^-)_4$ 16
 17	 $(NO_3^-)_4$ 18 + oligomeric mixture
 19	 $(NO_3^-)_8$ 20
	 $(NO_3^-)_4$ 21
 22	oligomeric mixture

Table 1(continued).

Ligands	Products
 17 +  23	 24
	 25
 22 +  26	 27
	 28

2-2-1 Complexation with ligand 2 or 5

To study electronic interactions between two aromatic rings of **3**, its fluorinated analogue **5** was examined. We have previously reported that the complexation of **1** with **5** gave rise to the self-assembly of macrocycle **7** which showed high ability for molecular recognition to electron rich aromatic compounds.[12] In this previous report, experiments were carried out at low concentrations (< 2 mM), and we could not notice the formation of catenane structure in such conditions. However, when the complexation was examined at higher concentrations, it was found that fluorinated macrocycle **7** is also in equilibrium with [2]catenane **6** though the equilibrium ratio tends to lie toward **7**. Spectroscopic behavior of **6** in NMR is quite similar to that of **3**. Nonequivalent two $PyCH_2C_6F_4CH_2Py$ units, each of which is symmetric, were observed. Furthermore, the popularity of **6** increased as the concentration was raised. Unfortunately, exclusive formation of **6** could not be achieved since the components became insoluble at higher concentrations (>10 mM/Pd). The ratios of **7** to **6** [mM/Pd] are as follows: >95:<5 [1]; 93:7 [2]; 84:16 [5]; 68:32 [10].

2-2-1-1 CH-π interactions to stabilize the catenane structure

The catenane formation from non-fluorinated ligand **2** was apparently more effective than that of the fluorinated ligand **5**. For example, the ratio of catenane to monomer at 10 mM/Pd was 59:41 or 32:68 for **3**:**4** or **6**:**7**, respectively. This difference is most probably due to attractive edge-to-face or CH-π interaction in catenane **3**. To discuss the interaction in more detail, it is helpful to see the crystal structure of catenane **29** (a platinum analogue of catenane **3**) in Figure 1a.[13] This crystal structure must resemble to that of a stable conformation of Pd(II) catenane **3** because the bond length of a Pt(II)-nitrogen (2.1 Å) is the same to that of Pd(II)-nitrogen. Efficient edge-to-face aromatic contacts between two phenylene units or a phenyl and a pyridine ring can be observed. An edge-to-face or CH-π aromatic interaction can be explained by electrostatic attraction between positively charged aromatic hydrogen and negatively charged π-electrons. This interaction effectively works in the catenated structure of **3** whereas not in the structure **6** that has no C-H bonds on the phenylene ring. Synthetic procedures for this catenane **29** are addressed in chapter 4.

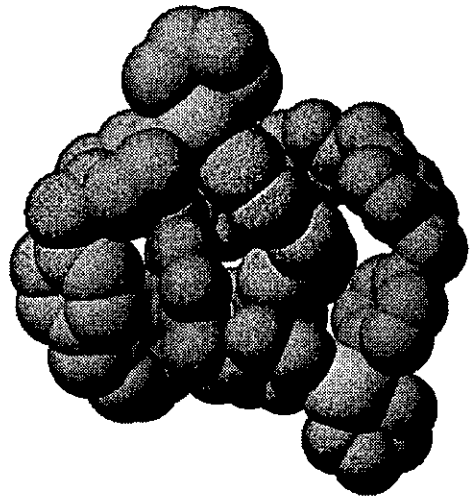


Figure 1a. CPK presentation of X-ray structure of Pt analogue **29**: This crystal structure must resemble to that of a stable conformation of Pd(II) catenane **3**. Efficient edge-to-face aromatic contacts between two phenylene units or a phenyl and a pyridine ring can be observed.

2-2-1-2 Medium effects for hydrophobic interactions

The CPK presentation makes it easy to understand weak aromatic interactions in the catenane structure **29**. In fact, Figure 1a clearly shows efficient aromatic contact between two rings. It suggests that the self-assembly of catenane **3** is directed by "double molecular recognition" by

which two molecules of **4** bind each other in their cavities. The importance of the double molecular recognition by aromatic contact is confirmed by a remarkable medium effect on the equilibrium ratio of **3**:**4** (Table 2). That is, the ratio of **3** was increased up to >99% at 10 mM by the use of a more polar media (D_2O solution of $NaNO_3$) probably due to enhanced hydrophobic interaction in highly polar media. In contrast, the ratio of **3** decreased with less polar media (CD_3OD-D_2O).

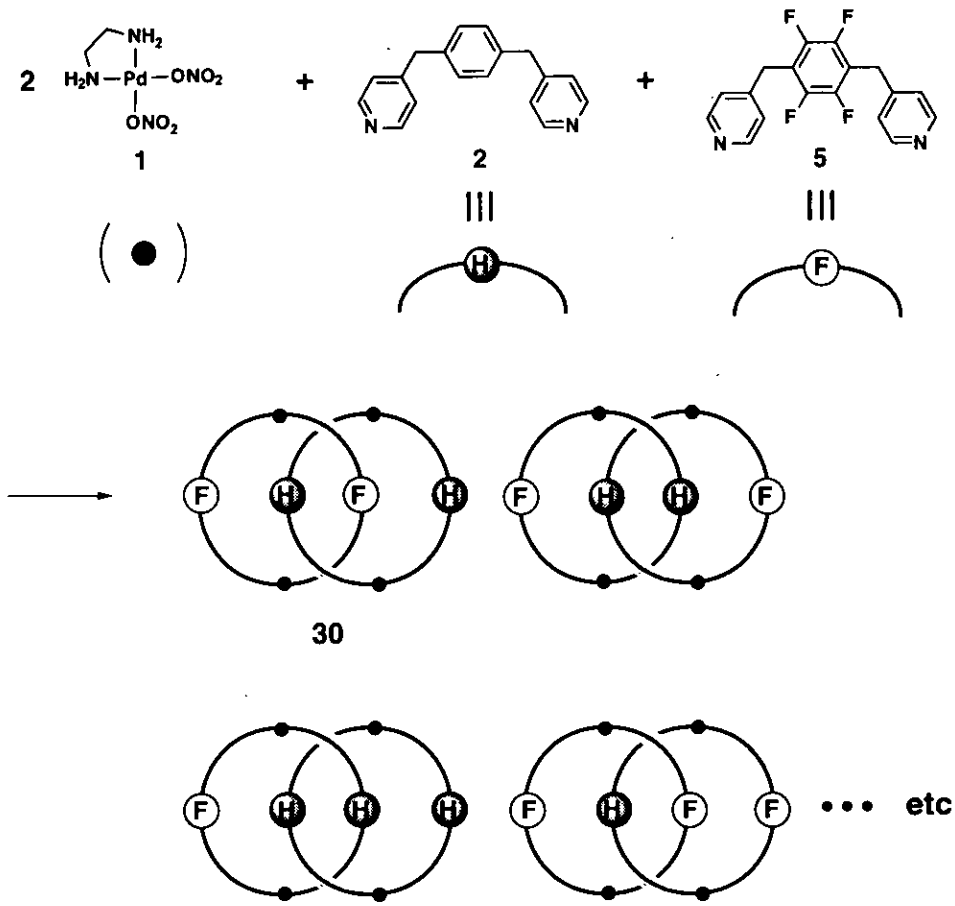
Table 2. Medium effects on the equilibrium ratio of **3** and **4** [a]

medium	guest [b] / mol equiv	**3** : **4**
1.0 M $NaNO_3$ / D_2O		> 99 : < 1
0.2 M $NaNO_3$ / D_2O		95 : 5
0.05 M $NaNO_3$ / D_2O		86 : 14
D_2O		59 : 41
D_2O	0.5	27 : 73
D_2O	2.0	12 : 88
D_2O - CD_3OD (7 : 3)		9 : 91
D_2O - CD_3OD (5 : 5)		< 1 : > 99

[a] Measured at 10 mM, room temperature.
[b] Sodium *p*-methoxyphenylacetate.

2-2-1-3 Electronic interactions between non-fluorinated aromatic rings and fluorinated ones

We expected the selective formation of catenane **30**, in which C_6H_4 and C_6F_4 are arranged alternatively, from three species **1**, **2**, and **5** (Scheme 2) because a stable benzene-perfluoro-benzene 1:1 complex is known.[14] When these three components were combined in a 2:1:1 ratio, several upfield-shifted C_6H_4 signals were observed around δ 5.0-5.5 which were assignable to inside phenylene rings of catenanes. This result indicated that, though catenanes are formed, two ligands **2** and **5** were completely scrambled in the catenane structure. Thus, there seemed no selectivity in the formation of a special combination such as **30** possessing an alternative contact of C_6H_4 and C_6F_4 rings. This complete scrambling is probably due to the high entropy price of the highly ordered structure of **30**. The stabilization by electronic interaction was not large enough to achieve the formation of catenane **30** as the sole product.



Scheme 2. Complexation of palladium centers, phenylene ligands, and fluorinated ones: It seemed that the **30** (in this scheme) would be most stable and the sole product due to the electronic effects. However, quite complicated NMR spectrum implied that complete scrambling products were formed.

2-2-2 Complexation with ligand 8, 11, 14, 17, 19, or 22

Though there are small structural differences in these ligands, dramatic change was observed in the efficiency of catenane formation. Ligands **14** and **19** gave catenane **15** and **20**, respectively, upon treatment with **1**.[15] These catenanes were found to be more stable than catenane **3** or **6** because any dissociation into monomer rings was not observed even at a low concentration (1 mM). In contrast, no catenane formation was observed from ligand **8**, **11**, **17**, or **22**. Ligand **8** and **1** self-assembled into a dinuclear macrocycle as a sole product whose structure was assigned as head-to-head type **9** or head-to-tail type **10**. Upon treatment of **11** with **1**, two products were observed both of which did not show any characteristics of the catenane structure (i.e., the observation of two unequivalent ligands for inside and outside units of the catenane with upfield shifting of the inside unit). Tentatively, these two components were assigned as mono-

and dinuclear macrocycles **12** and **13**, respectively, because molecular modeling did not have significant ring strain in both structures.[16]

Although biphenylene derivative ligand **17** has almost the same conformational freedom to **2**, it did not give a catenane but gave macrocycle **18** and considerable amount of oligomeric products. Terphenylene derivative **22** also gave an oligomer mixture.

2-2-3 Self-assembly of catenanes from three species

The remarkable formations and stability of catenanes **15** and **20** suggest the important factors for catenations. That is, rectangular box structures of the component rings are very much effective for the catenated structures. Therefore, other rectangular frameworks were designed from a set of **1** and two different ligands. Surprisingly, these three-component systems worked very well and highly efficient self-assembly of catenanes **24** and **27** from three-component-eight-species [$(\mathbf{1})_4 + (\mathbf{17})_2 + (\mathbf{23})_2$ or $(\mathbf{1})_4 + (\mathbf{22})_2 + (\mathbf{26})_2$] was successful.[17] The rectangular structures have van der Waals surface-to-surface interplane separation of ca 3.5 Å in the component rings, whose distance could be considered as an ideal distance for encapsulations of aromatic rings. The importance of this interplane distance will be discussed later with X-ray structures.

2-3 X-ray studies

To understand the important factors for catenations in this course of studies, crystal structures is quite helpful. Figure 1b,c show the crystal structures of **15**, and **24**, which have been already communicated.[18] Crystal structure of **15** (Figure 1c) is also shown although the quality of the diffraction data of **15** is still poor (R = 0.266; Rw = 0.331) due to significant disorder of counter ions and solvents in the crystal. It is not appropriate to discuss details about bond lengths or angles with this data. However, such a low quality data still makes a sense to confirm the catenated structure and roughly understand the weak interactions between the two rings.

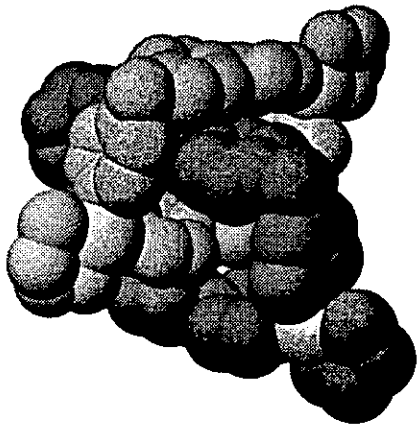


Figure 1b. Crystal structure of catenane **15**

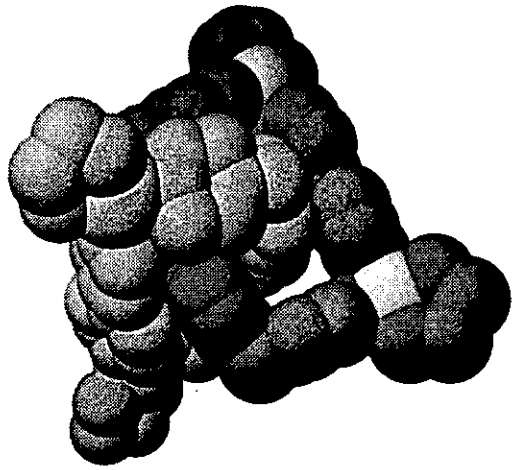


Figure 1c. Crystal structure of catenane **24**

All crystal structures are depicted by CPK presentation because it makes easy to understand weak interactions in the catenane structures. Whereas efficient edge-to-face interactions are observed in the structure of catenane **3**, face-to-face stacks of four aromatic rings are found in these catenanes **15** and **24**. The very efficient aromatic stacking brought great stability to catenanes **15** and **24**, thus the dissociation of the catenanes into component rings was completely suppressed even at a low concentration or in a less polar media (D_2O-CD_3OD 1:1) in contrast to the behavior of catenane **3** which dissociated under these conditions.

2-4 ESI-MS studies

Recently, electrospray ionization mass spectrometry (ESI-MS) has been proven very helpful for analyzing polynuclear transition metal complexes.[19] In the analysis of metal complexes, series of multiply charged ions with a formula of $[\ M\text{-}X_n\ ]^{n+}$ are usually observed, where M and X denote formula of the complex and counter anion, respectively. When these catenanes **3**, **15**, **20**, **24**, and **27** were employed to ESI-MS, the clear peaks of $[\ M\text{-}(NO_3)_n\ ]^{n+}$ (n = 2-4) were observed. As a typical example, ESI-MS spectrum of **15** is shown in Figure 2a. A peak at 653.5 must be provided by a triply charged component because the signal is split by 1/3 mass unit. Thus this fragment is ascribable to $[\ \mathbf{15}\text{-}(NO_3)_3\ ]^{3+}$ (calcd: 653). Around *m/z* 1012.7, peaks of $[\ \mathbf{15}\text{-}(NO_3)_2\ ]^{2+}$ (calcd: 1010) and $[\ \mathbf{15}\text{-}(NO_3)_4\ ]^{4+}$ (calcd: 474) seem to be overlapped since clear splitting was not observed in the expanded spectrum.

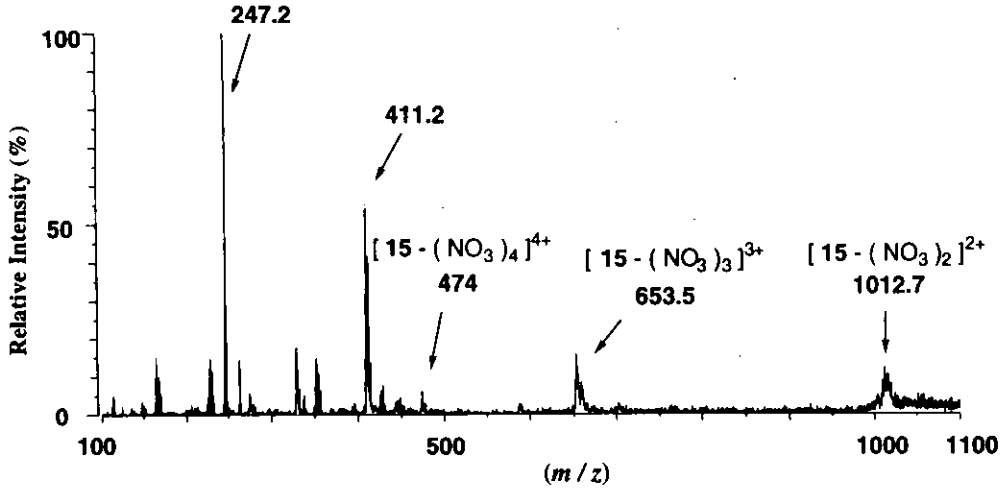


Figure 2a. ESI-MS for catenane **15**

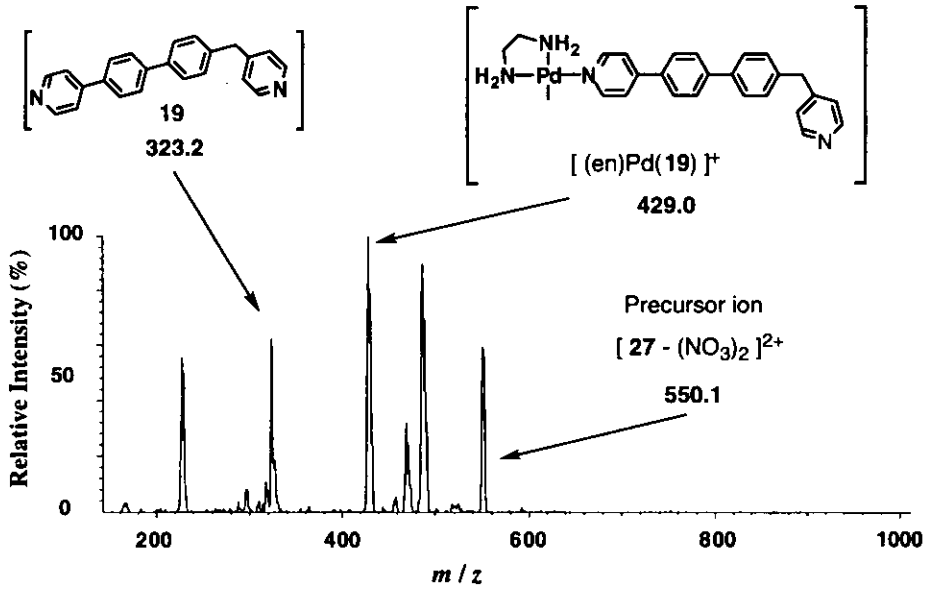


Figure 2b. MS-MS collision experiment for [Catenane **27** - $(NO_3)_n$]$^{n+}$

Furthermore, MS-MS collision experiment supported the assignment for [M-$(NO_3)_n$]$^{n+}$ by employing catenane **27** into this measurement (Figure 2b).[20] A prominent peak at 550.0 was analyzed by the second mass after being decomposed by collision with helium. With this procedure, the assignment of the peak at 550.1 as [**27**-$(NO_3)_3$]$^{3+}$ was confirmed because the fragments which were derived from the ion at *m/z* 550.1 involves partial structure of catenane **20** (e.g. : *m/z* 429.0 [(en)Pd(ligand **19**)]$^{2+}$, 323.2 [ligand **19**]).

Similar ESI-MS fragmentation patterns were observed for other catenanes. Since the structures of **15**, **24**, and **29** (a Pt(II) analogue of **3**) were unambiguously determined by X-ray

analysis, it can conclude that the observation of [M-$(NO_3)_n$]$^{n+}$ peaks is a reliable evidence for the catenane structures.

2-5 Thermodynamics of the equilibration between 3 and 4

In order to calculate some thermodynamic parameters, temperature-dependent equilibrium ratios of catenane **3** to monomeric ring **4** were examined. From the integral ratio of **3**:**4** in NMR, the equilibrium constant *Keq* was easily estimated (Table 3). From a simple Ln*Keq* - (1/T) plot, ΔH and ΔS value of this equilibration was evaluated to be -7.0 kcal • mol^{-1} and -24.1 cal • K^{-1} • mol^{-1}, respectively.[21] The large negative value of ΔH is consistent with the efficient aromatic contact that makes the catenation process exothermic. The large negative ΔS is also in good accordance with the catenation in which two molecular rings slide into one molecule.

Table 3. The ratio[a] of **3** and **4**

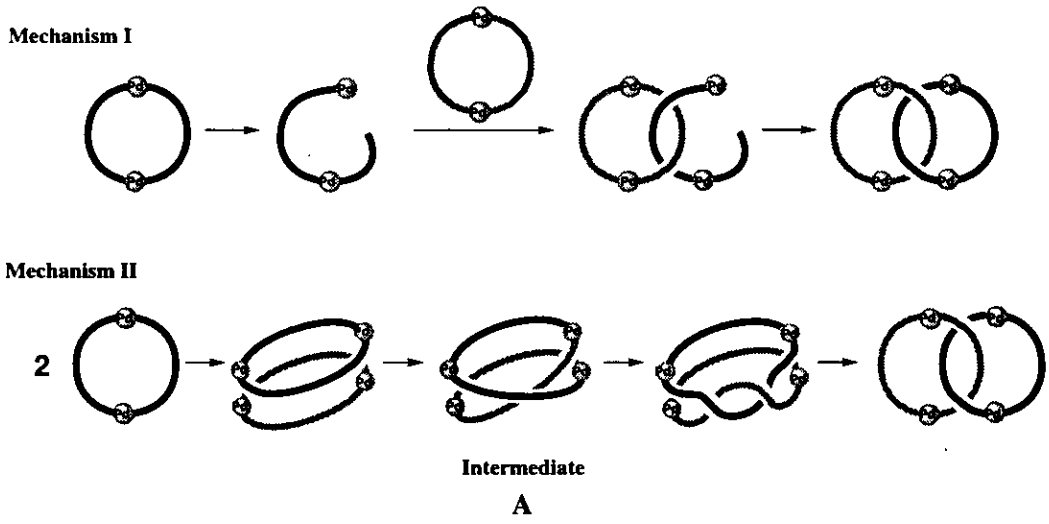
T (K)	**3**	:	**4**	*Keq*[b]
343	15	:	85	0.214
333	22	:	78	0.350
323	27	:	73	0.512
313	34	:	66	0.798
303	31	:	61	1.06
298	42	:	58	1.28
293	45	:	55	1.51
283	49	:	51	1.91

[a]: Calculated by the integral ratio of ^{1}H NMR
[b]: *Keq* value was calculated by following equation: *Keq* = [**3**] / [**4**]^2. [Pd] = 10 mM. Solvent: D_2O

2-6 Mechanism of the rapid interconversion: *Möbius strip mechanism*

It is quite remarkable that the two preformed rings **4** rapidly interconvert into the catenane structure **3** under suitable conditions. The coordination bond of Pd(II)-Py is ascribed to the unique behavior as "*molecular magic ring*". The compounds which consist of only covalent bonds never show such a process except for the recent research report.[9] The might lie under this unique movememnt. Therefore, the mechanism for the catenane formation should be made clear. Conventionally, the simplest mechanism involves the following processes: dissociation of a ring, threading another ring on the thread, and reconnection of the ends of the thread (Mechanism I,

scheme 3). However, the careful consideration of NMR spectra, as well as a few additional experiments, indicated the following two significant insight into the mechanism: (i) An intermediate A must be involved in the interconvertion between catenane **3** and monomeric ring **4**. (ii) Reversible coordinate bonds must be involved in both rings. These NMR observation negated the simple mechanism I and strongly supported an alternative. Here, it is suggested that the rapid interconvertion is explained in terms of ligand exchange between Pd(II)-N bonds. It can be strongly supported the Möbius strip mechanism[23] (Mechanism II, Scheme 3) that involves two sequential ligand exchange between two molecular rings concomitant with a twisting of the rings around each other.



Scheme 3. Schematic presentation of possible catenation mechanism: (Mechanism I) This process is involved by dissociation of a ring, threading another ring on the thread, and reconnection of the ends of the thread. (Mechanism II) Two sequential ligands exchange between two molecular rings concomitant with a twisting of the rings around each other. This figure presents only the topology of the pathways. Thus, the second ligand exchange in mechanism II may happen between any Pd(II)-N bonds.

2-7 Evidence for Möbius strip mechanism by TOE spectroscopies

As mentioned above, the involvement of an intermediate A is suggested by NMR experiments. Rapid chemical exchange between the C_6H_4 signals of **3** and **4** was clearly observed by ^{1}H NMR truncated driven nuclear Overhauser effect (TOE) difference spectroscopies (Figure 3c).[24] For this NMR experiment, an equilibrium mixture of **3** and **4** (59:41) at 10 mM/Pd(II) in D_2O was used and the signal of the inside C_6H_4 of **3** (δ 5.3) was irradiated with initial pulse interval (PI_1) times ranging from 0.5 to 25 sec.

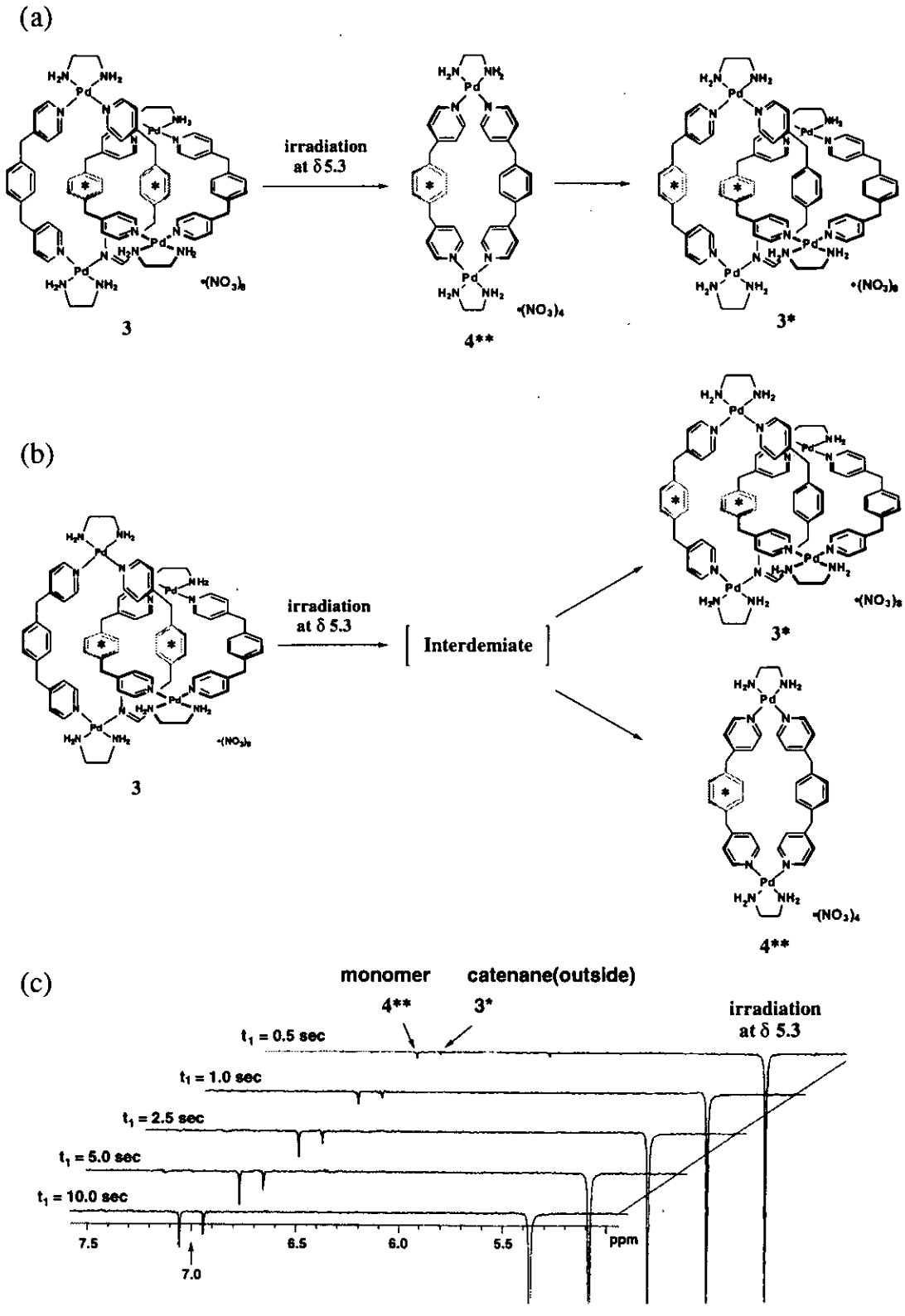
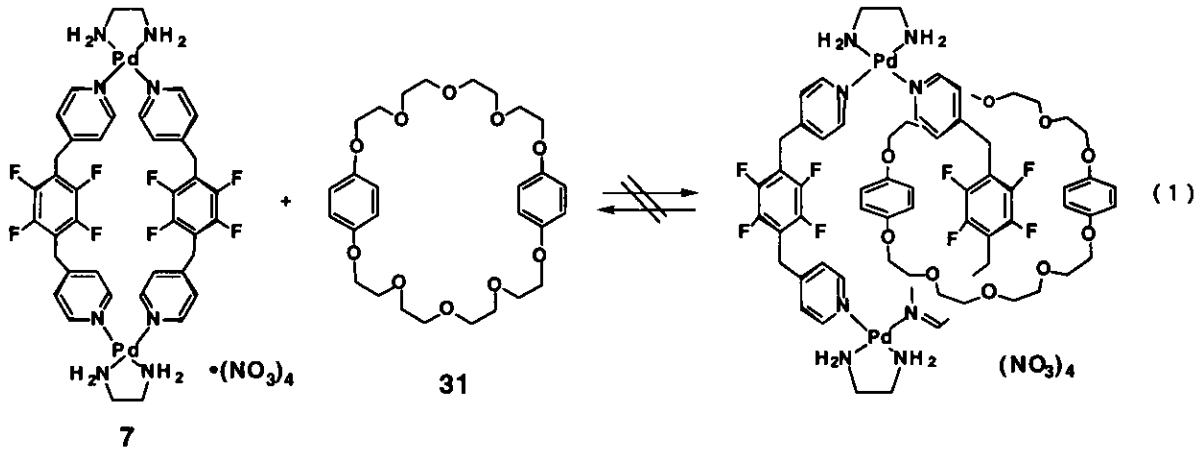


Figure 3. (a) Stepwise mechanism; [2]catenane **3** separates into two rings **4**, then re-combines to [2]catenanes **3**. In this process, the aromatic rings with the saturated protons statistically go outside of frameworks. (b) Intermediate mechanism; In this process, some intermediate must involve. [2]catenane **3** converts into the intermediate, which transform into [2]catenane **3*** and ring structure **4****, simultaneously. (c) NMR spectra of TOE experiment; By irradiation of aromatic protons at 5.3 ppm, differential spectra were observed at 6.95, 7.10 ppm. Interestingly, the ratio of two peaks was almost same.

In this experiment, two negative peaks appeared at δ 7.10, 6.95. The peak at δ 6.95 indicated the existence of a chemical exchange between the inside and outside C_6H_4 groups. A time-resolved technique showed that magnetically saturated aromatic rings converted into **3** and **4**, simultaneously. These spectroscopic observations supported the *Möbius strip mechanism* in which *a certain intermediate must exist and convert* into **3*** and **4**** at the same time (Figure 3b). A straightforward formation of **3*** via internal rotation of one ring in **3** around the inside unit of another ring is inhibited because of the steric bulkiness of the (en)Pd moiety. On the other hand, this NMR observation showed that the internal rotation of the ring was inhibited, otherwise the outer and inner ligands would be equivalent. Surprisingly, the internal rotation was not occurred even at 90 °C. The internal rotation was restricted by the steric demand of (en)Pt moiety, which was readily understood from the crystal structure of the catenane.

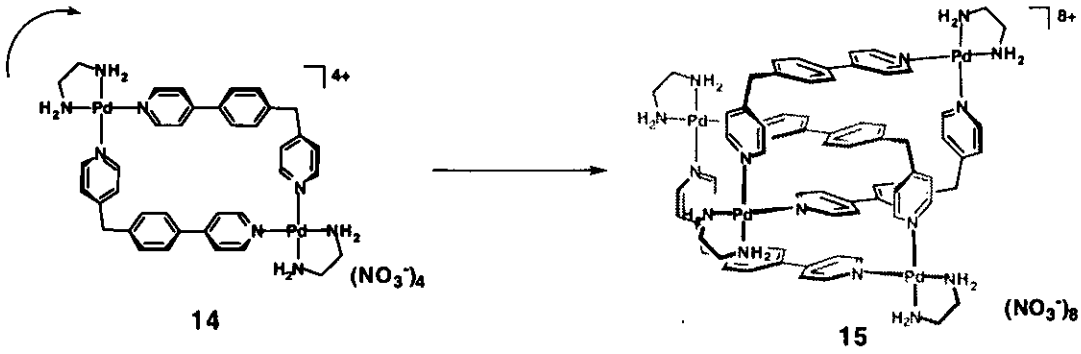
In addition to this mechanism, reversible coordinate bonds must be involved in both rings for catenane formation. It is interesting that, in contrast to the rapid formation of catenanes from **3** and/or **4**, no interaction was observed between ring structure **7** and Stoddart's polyether ring **31** [2e] (eq 1) despite their high ability to recognize electronically complementary aromatic rings: i. e., **7** recognizes *p*-dimethoxybenzene (a partial structure of **31**) with K_a value of 2680 $L \cdot mol^{-1}$ while **31** strongly binds cationic pyridinium systems.[25]



2-8 Topological chirality for Catenane 15

The inside and outside units were also unequivalent in catenane **15**. In this catenane, it is noteworthy that topological chirality exists in the framework of **15**. Because the direction of rotation can be defined along the cyclic framework of compound **14**, catenane **15** produced one

pair of mirror image when second ring interlocks to first one with the clockwise or anti-clockwise direction as schematically illustrated below (Figure 4).



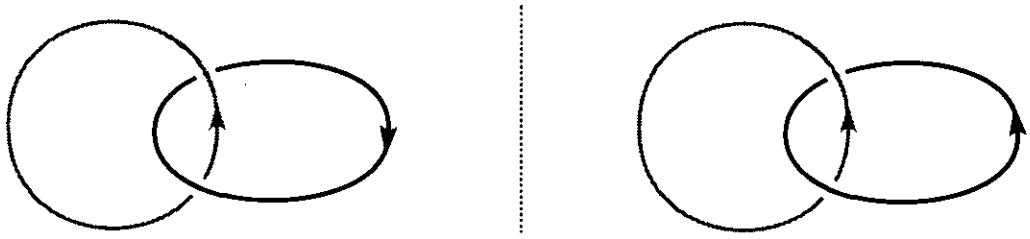


Figure 4. Topological chirality of [2]catenane **15**: Each ring has a directionality in its frameworks. Two possible combinations for two rings imply that this is a mirror image to each other.

The NMR analysis of catenane complex **15** gave not only the structural evidences but also the valuable information about dynamic molecular motion. Due to the topological chirality, aromatic protons can be chiral probes.[26] Namely, equivalent aromatic proton couples become diastereotopic if the free turn of the aromatic ring is restricted. Thus, four couples on inside Py_2 and phenylene became unequivalent ($Py_2H\beta$ and $Py_2H\beta'$, ArH_α and ArH_α', and $ArH\beta$ and $ArH\beta'$) (Figure 5). This observation showed that free rotation of the Py_2 and phenylene rings was inhibited. Interestingly, signals $Py_2H\beta$ and $Py_2H\beta'$ coalesced at approximately 50 °C, showing the inside Py_2 ring turns on the NMR time scale above this temperature. The $\Delta G^{\dagger}$ for the free turn of the inside Py_2 ring is roughly estimated to be 15.8 kcal · mol^{-1}.[27] In contrast, inside Py_1 and outside aromatic rings turned freely at room temperature because the splitting of originally equivalent proton was not observed.

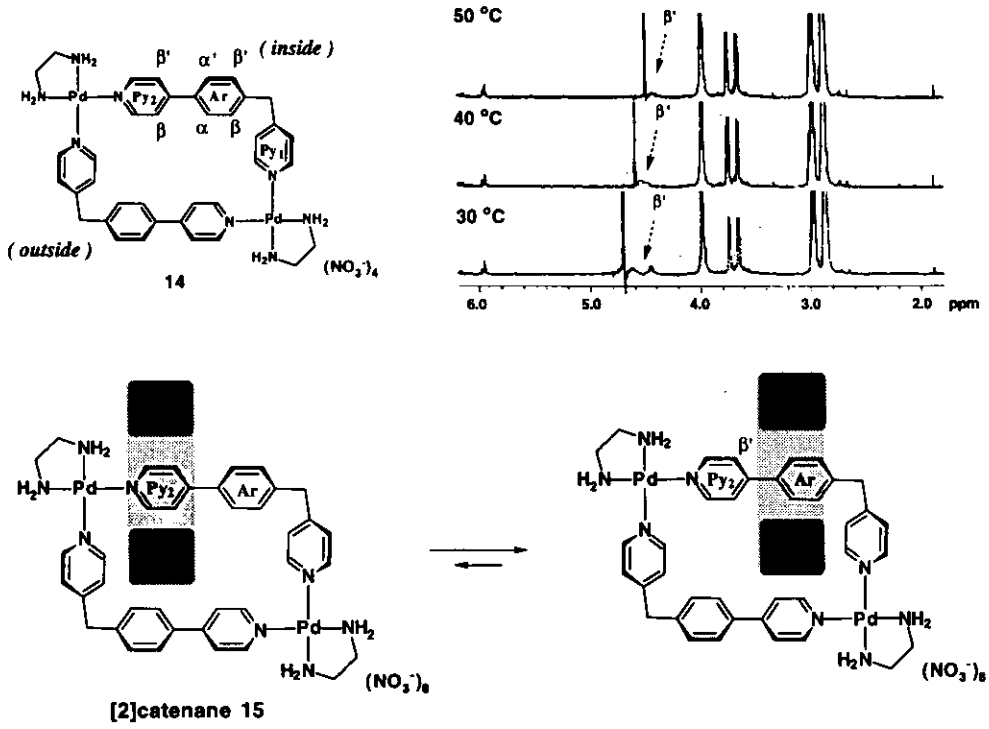


Figure 5. Dynamic molecular motion of [2]catenane **15**: In NMR spectrum, coalesced peak at about 50 °C indicated, by the broken arrow, that Py_2 ring turned on the NMR time scale. The $G^{\dagger}$ for this turning is around 15.8 kcal · mol^{-1}.

Catenane **24** consists of similar rectangular boxes, but its NMR is impressively simple. Again, remarkable upfield shift was observed for inside aromatic protons. Neither other products nor impurities were found in the crude NMR. More surprisingly, NMR spectroscopy showed that the self-assembled catenane **24** consisted of a single conformational isomer with outside bipyridine ligands although there were many possible isomers having, for example, bipyridine ligand(s) inside. The exclusive formation of this isomer is most probably due to minimization of electrostatic repulsion among Pd^{2+} ions and maximization of hydrophobic contact between two molecules of inside **2** which is more hydrophobic than bipyridine.

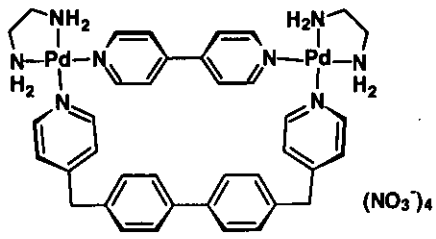
2-9 Dynamic properties of catenanes

As shown above, the dynamic properties of a ring movement in catenane **15** were indicated by the ^1H NMR measurements. There were outstanding high upfield shifts in observation of catenane **15** whose phenylene protons were shown at δ 3.6-3.8 ppm. Whereas centered phenylene rings in catenane **20** were observed at δ 5.6-6.0 ppm. It was considered that this difference was ascribed to the flexibility of the ring structures. The cyclic frameworks of catenane **15** might be fixed at the position where the phenylene rings were always surrounded by the other aromatic rings. In contrast, the free movement of aromatic moiety might be allowed in catenane **20** because the ring size would be large enough to move freely, and the movement might be faster than NMR time scale.

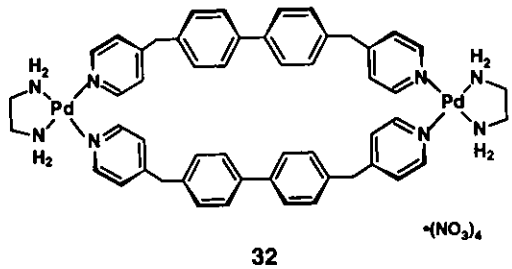
The similar tendency was observed in catenane **24** and **27**. In catenane **27**, phenylene protons were observed at about δ 5.8 indicating that the upfield shift was not so striking compared to that of catenane **15** in which the movement of phenylene rings was restricted. On the other hand, the protons of catenane **24** were highly shifted to appear at δ 3.8 ppm. The restriction of free movement of phenylene rings could cause this upfield shift.

2-10 A combination problem

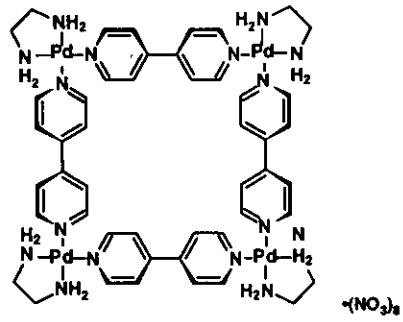
It is noteworthy that the remarkable thermodynamic stability of catenane **24** overcame "*a combination problem*" which should arise in a self-assembly from larger sets of components.[28] This combination problem means the possibility for the formation of at least three component rings **25**, **32**, **33** because of the comparability of their thermodynamic stability (Figure 5). Nevertheless, catenane **24** readily self-assembled as a sole product. This result showed that only rectangular box **25**, *having an ideal van der Waals separation (3.5 Å) in its framework,* can be stabilized by filling its cavity with another copy of itself.



25



32



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2-11 Conclusion

The quantitative self-assembly of [2]catenanes was achieved by incorporating metal centers into frameworks of ring structures. These metal-mediated rings show the unique behavior in which two rings spontaneously interlock into catenanes. The consideration of ring structures and weak interactions makes it possible to rationally design the [2]catenane at will. When a monomer ring has ideal van der Waals interplane separation (3.5 Å) in its structures, a [2]catenane can readily self-assemble. Furthermore, weak interactions, such as hydrophobic interaction, edge-to-face or CH-π aromatic interaction are crucial factors to stabilize the catenane structure.

X-ray studies are, of course, informative to design new catenane structures. The weak interactions can be seen in the crystal structures. The considerable innovations of ESI-MS make it possible to surely detect the formation of [2]catenanes. NMR studies suggest critical proofs about the structure of [2]catenanes. Furthermore, some thermodynamic parameters are estimated by NMR measurements.

2-12 Experimental section

Instrumentation and General procedure The following details apply all experimental parts of this thesis. Melting points were determined with Yamagimoto micro melting point apparatus and were not corrected. ^{1}H, ^{13}C NMR, and other 2D NMR spectra were recorded with JOEL

JNM-GSX 270 (270 MHz), JOEL JNM-EX 270 (270 MHz), JOEL JNM-GSX 400 (400 MHz), JOEL JNM-GSX 500 (500 MHz), JOEL JNM-LA500 (500 MHz). Chemical shifts are reported in parts par million (δ units) relative to tetramethylsilane as standard. Tetramethylsilane served as an internal standard when $CDCl_3$ was used as a solvent. For other solvents, a solution of tetramethylsilane in $CDCl_3$ sealed in capillary was used as an external standard. Spectral splitting are designated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. Infrared (IR) spectra were recorded with JASCO-A-200 spectrometer or SHIMAZU FT-IR 8300. Elemental analysis were carried out using a Perkin-Elemeter 240B or 2400CHN or YANAKO MT-3. Preparative HPLC was performed on a LC-908 (Japan Analytical Industry, Co., Ltd.) with column (AJ2H J49-8F28, AJ1H J45-8F27). Flash chlomatograghy was conducted on Merck silica gel 60 (70-230 mesh). ESI-MS (electrospray ionization mass spectroscopy) was obtained on a TSQ700 spectrometer with electrospray ionization source (Finnigan MAT, San Jose, California). FAB-MS (fast atom bombardment mass spectroscopy) spectra were recorded by JOEL JMS-HX110A spectrometer with an m/z range of 3000 using glycerol as matrix.

Solvents and reagents were purchased from TCI Co., Ltd., WAKO Pure chemical Industries Ltd., Nacarai Tesque Ins., and Aldrich chemical., Ltd. These chemicals were used without purification. And a distillation and other purification procedures were done when it was needed.

Preparation of (en)$Pd(NO_3)_2$ 1 (en)$PdCl_2$ was suspended in an aqueous $AgNO_3$ (2.0 molar equiv). This mixture was heated at 100 °C for 2 h under dark place. The white precipitate was filtered, then the filtrate was employed directly in the next reactions or evaporated to give quantitatively **1** as orange crystals, which were used in the next reaction without purification. ^1H NMR (270 MHz, D_20, TMS/$CDCl_3$ as external standard) δ 2.82 (s).

Synthesis of 1,4-Bis(4-pyridylmethyl)benzene 2 Compound **2** was synthesized by 2 steps as mentioned below: To a THF (100 mL) solution of 1,4-dibromobenzene (2.36 g, 10.0 mmol), *n*-BuLi (*n*-hexane solution, 1.62 M, 15.0 mL, 24.0 mmol) was added at -78 °C, and the mixture was stirred for 30 min at -78 °C. To the reaction mixture, 4-pyridinecarboxaldehyde (2.2 mL, 2.4 mmol) was added at -78 °C. A white precipitate was formed at this time. The mixture was stirred for 15 min at -78 °C, and then for 30 min at room temperature. To the reaction mixture, H_2O (20 mL) was added to quench the reaction. The mixture was filtered to give crude product as white

solid(0.984 g). This crude was used for next reaction without further purification. ^{1}H NMR (270 MHz, $CDCl_3$+CD_3OD, TMS) δ 8.44 (d-like, J = 4.6 Hz, 4 H, Py*H*α), 7.38 (d-like, J = 4.6 Hz, 4 H, Py*H*β), 7.33 (s, 4 H, Ph*H*), 5.75 (s, 2 H, -C*H*(OH)-); IR (KBr, cm^{-1}) 3150, 1600, 1410, 1135, 1000, 780, 635; m.p. 217.0 - 218.5 °C. To this crude product (0.984 g), 6 M HCl (5 mL), ethanol (40 mL) and palladium-charcoal (200 mg) were added. This mixture was vigorously stirred for 12 h at 60 °C under H_2 atmosphere. After the reaction mixture was filtered and basified with saturated Na_2CO_3aq (20 mL), the mixture was extracted with $CHCl_3$ (20 mL x 3). The combined organic layers was dried over $MgSO_4$, filtered and evaporated to give crude product (0.763 g). This crude residue was purified by chromatography (silica gel, ethyl acetate) to give the titled compound as colorless crystal (0.712 g, 2.74 mmol, 27% in two steps). ^{1}H NMR (270 MHz, $CDCl_3$, TMS) δ 8.49 (d-like, J = 4.6 Hz, 2 H, Py*H*α), 7.12 (d-like, J = 4.6 Hz, 2 H, Py*H*β), 7.09 (s, 4 H, Ph*H*), 3.93 (s, 2 H, -C*H*$_2$-); ^{13}C NMR (67.8 MHz, $CDCl_3$, TMS) δ 149.81 (*C*H), 149.61 (*C*q), 137.25 (*C*q), 129.29 (*C*H), 124.08 (*C*H), 40.74 (*C*H$_2$); IR (KBr, cm^{-1}) 1600, 1505, 1415, 1220, 990, 805, 595, 500; m.p. 106.0 - 107.0 °C; Anal. Calcd for $C_{18}H_{16}N_2$: C, 83.04; H, 6.19; N, 10.71. Found: C, 82.90; H, 6.12; N, 10.48.

Preparation of catenane 3 and monomeric compound 4 To a water solution (4 mL) of (en)Pd(NO_3)$_2$ **1** (58 mg, 0.2 mmol), 1,4-Bis(4-pyridylmethyl)benzene (**2**) (52 mg, 0.2 mmol) was added. This mixture was heated at 60 °C for 30. The clear colorless solution obtained here was evaporated, and dried *in vacuo* to give catenane **3**, quantitatively. Catenane **3**: ^{1}H NMR (D_2O, TMS/$CDCl_3$ as external standard) δ 8.55 (d-like, J = 6.6 Hz, 8 H, Py*H*α), 8.30 (d-like, J = 6.6 Hz, 8 H, Py*H*'α), 7.38 (d-like, J = 6.6 Hz, 8 H, Py*H*β), 6.91 (s, 8 H, Ph*H*), 6.59 (d-like, J = 6.6 Hz, 8 H, Py*H*'β), 5.34 (s, 8 H, Ph*H*'), 3.93 (s, 8 H, -C*H*$_2$-), 3.04 (s, 8 H, -C*H*'$_2$-), 2.83 (s, 16 H, -NC*H*$_2$C*H*$_2$N-); ^{13}C NMR (D_2O, TMS/$CDCl_3$ as an external standard) δ 156.24 (*C*q), 154.98 (*C*q), 150.78 (*C*H), 150.67 (*C*H), 136.22 (*C*q), 135.42 (*C*q), 129.72 (*C*H), 128.45 (*C*H), 127.27 (*C*H), 126.56 (*C*H), 46.73 (*C*H$_2$), 46.65 (*C*H$_2$), 39.80 (*C*H$_2$), 39.57 (*C*H$_2$). Monomeric compound **4**: ^{1}H NMR (D_2O, TMS/$CDCl_3$ as an external standard) δ 8.42 (d-like, J = 6.6 Hz, 8 H, Py*H*α), 7.29 (d-like, J = 6.6 Hz, 8 H, Py*H*β), 7.07 (s, 8 H, Ph*H*), 4.03 (s, 8 H, -C*H*$_2$-), 2.84 (s, 8 H, -NC*H*$_2$C*H*$_2$N-); ^{13}C NMR (D_2O, TMS/$CDCl_3$ as an external standard) δ 156.67 (*C*q), 150.91 (*C*H), 136.59 (*C*q), 130.08 (*C*H), 127.22 (*C*H), 127.19 (*C*q), 46.96 (*C*H$_2$), 39.95 (*C*H$_2$). Addition of

$NaClO_4$ to the aqueous solution of **4** precipitated pale yellow powder whose composition agreed with the ClO_4 salt of **4** (48% yield). m.p. 235.0-237.0 °C dec.; Anal. Calcd for $C_{40}H_{48}Cl_4N_8O_{16}Pd_2$: C, 38.59; H, 4.09; N, 9.20. Found: C, 38.39; H, 3.87; N, 8.95.; FAB-MS (based on ^{106}Pd, glycerol): *m/z* 1149 [M-(ClO_4)], 1049 [M-(ClO_4)-($HClO_4$)], 949 [M-(ClO_4)-($HClO_4$)$_2$].

Physical data of catenane 29 (as ClO_4 salt) ^1H NMR (500 MHz, D_2O, TMS/$CDCl_3$ as external standard) δ 8.60 (d-like, *J* = 6.6 Hz, 8 H, Py*H*α), 8.39 (d-like, *J* = 6.6 Hz, 8 H, Py*H'*α), 7.39 (d-like, *J* = 6.6 Hz, 8 H, Py*H*β), 6.97 (s, 8 H, Ph*H*), 6.65 (d-like, *J* = 6.6 Hz, 8 H, Py*H'*β), 5.39 (s, 8 H, Ph*H'*), 3.99 (s, 8 H, -CH_2-), 3.10 (s, 8 H, -C*H'*$_2$-), 2.80 (s, 16 H, -NCH_2CH_2N-); ^{13}C NMR (100 MHz, D_2O, TMS/$CDCl_3$ as an external standard) δ 156.02 (*C*q), 154.66 (*C*q), 151.57 (*C*H), 151.38 (*C*H), 136.07 (*C*q), 135.20 (*C*q), 129.72 (*C*H), 128.51 (*C*H), 127.63 (*C*H), 126.96 (*C*H), 47.53 (*C*H_2), 47.43 (*C*H_2), 39.77 (*C*H_2), 39.52 (*C*H_2); m.p. 250 °C dec; Anal. Calcd for $C_{80}H_{96}Cl_8N_{16}O_{32}Pt_4 \cdot 4H_2O$: C, 32.80; H, 3.58; N, 7.65. Found: C, 32.58; H, 3.77; N, 7.75.; FAB-MS (based on ^{106}Pd, glycerol): *m/z* 2757 [M - (ClO_4)], 2657 [M - (ClO_4) ($HClO_4$)], 2558 [M - (ClO_4) - ($HClO_4$)$_2$], 2458 [M - (ClO_4) - ($HClO_4$)$_3$].

Preparation of 1,4-Bis(4-pyridylmethyl)-2,3,5,6-tetrafluorobenzene 5 To a THF (40 mL) solution of γ-picolin (16.0 mmol), lithium diisopropylamide (1.5 M in cyclohexane, 19.2 mmol) was added at -78 °C. After stirred for 0.5 h at -78 °C and for 2 h at room temperature, this solution was added to a THF (40 mL) solution of hexafluorobenzene (8.0 mmol) at -78 °C, and the resulting mixture was stirred for 0.5 h at -78 °C and for 1.5 h at room temperature. Usual workups and the purification by column chromatography (silica gel, ethyl acetate) gave **5** (46%) as colorless crystals. ^1H NMR (270 MHz, $CDCl_3$, TMS) δ 8.67 (d-like, *J* = 5.9 Hz, 4 H, Py*H*α), 7.16 (d-like, *J* = 5.9 Hz, 4 H, Py*H*β), 4.04 (s, 4 H, -CH_2-); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 150.22 (*C*H), 146.32 (*C*q), 144.75 (d of m, J_{C-F} = 232.7 Hz, *C*q), 123.62 (*C*H), 116.57 (m, *C*q), 28.02 (*C*H_2); ^{19}F NMR (188 MHz, $CDCl_3$, $CFCl_3$ as standard) δ -143.60 (s); IR (KBr, cm^{-1}) 1592, 1475, 991, 786, 601, 474; MS (EI) *m/z* (rel intensity) 333 ($[M + H]^+$, 42), 332 ($[M]^+$, 100), 331 (13), 313 (22), 312 (35), 255 (20), 254 (14), 234 (11), 93 (25). m.p. 131.0 - 132.0 °C; Anal. Calcd for $C_{18}H_{12}F_4N_2$: C, 65.06; H, 3.64; N, 8.43. Found: C, 64.83; H, 3.40; N, 8.14.

Synthesis of monocyclic fluorinated compound 7 To a water solution (5 mL) of (en)Pd(NO_3)$_2$ **1** (2.9 mg, 0.01 mmol), 1,4-Bis(4-pyridylmethyl)-2,3,5,6-tetrafluorobenzene **5** (3.4

mg, 0.01 mmol) was suspended. This mixture was heated for 30 min at 60 °C to give a clear colorless solution. ^{1}H NMR (500 MHz, D_2O-CD_3OD, TMS in $CDCl_3$ as an external standard) δ 8.53 (d, J = 6.6 Hz, 8 H, Py$H\alpha$), 7.36 (d, J = 6.6 Hz, 8 H, Py$H\beta$), 4.23 (s, 8 H, -CH_2-), 2.87 (s, 8 H, -NCH_2CH_2N-); ^{13}C NMR (126 MHz, D_2O, TMS/$CDCl_3$ as an external standard) δ 155.11 (C(Py)$_g$), 154.07 (C(Py)$_a$), 149 (d of m, J = 59 Hz, C(Ar)-F), 49.64 (NH_2CH_2), 129.84 (C(Py)$_b$), 118 (m, PyCH_2CAr), 30.23 (ArCH_2); ^{19}F NMR (187 MHz, D_2O, CF_3COOH in $CDCl_3$ as an external standard) δ -67.38; The perchlorate salt was isolated as pale yellow powder (yield 57%). m.p. 240 °C (dec); Anal. Calcd for $C_{40}H_{40}Cl_4F_8N_8O_{16}Pd_2$: C, 34.43; H, 2.89; N, 8.03. Found: C, 34.22; H, 2.69; N, 7.91. The tetrafluoroborate salt was isolated as pale-yellow powder (yield 59%). FAB -MS (glycerol) *m/z* 1256 (M-HBF_4), 1168 (M-$(HBF_4)_2$); m.p. 240 °C (dec); Anal. Calcd for $C_{40}H_{40}B_4F_{24}N_8Pd_2$: C, 35.72; H, 3.00; N, 8.33. Found: C, 35.95; H, 3.29; N, 8.52.

Preparation of 1-(4-pyridylmethyl)-4-[2-(4-pyridyl)ethyl]benzene 8 The compound **8** was synthesized by 3 steps as mentioned below: In a sealed test tube, 1,4-dibromobenzene (11.8 g, 50 mmol), palladium acetate (168 mg, 0.75 mmol), triphenyphosphine (393 mg, 1.5 mmol), 4-vinylpyridine (2.7 mL, 25 mmol), triethylamine (3.5 mL, 25 mmol) was mixed. The sealed mixture was heated at 100 °C for 4 days. To the reaction mixture, H_2O (200 mL) was added, and then the mixture was extracted with $CHCl_3$ (200 mL x 2). The combined organic layers was dried over $MgSO_4$, filtered, and evaporated. The crude product was purified by chromatography (silica gel, ethyl acetate) to give 1-Bromo-4-(4-pyridyl-2-ethenyl)benzene as pale yellow crystal (3.68 g, yield 57%). ^{1}H NMR (270 MHz, $CDCl_3$, TMS) δ 8.58 (d-like, J =6.2 Hz, 2 H, Py$H\alpha$), 7.52 (d, J = 8.6 Hz, 2 H, PhH), 7.40 (d, J = 8.6 Hz, 2 H, PhH), 7.35 (d-like, J = 6.2 Hz, 2 H, Py$H\beta$), 7.23 (d, J = 16.5 Hz, 1 H, -CH=CH-), 7.00 (d, J = 16.5 Hz, 1 H, -CH=CH-); ^{13}C NMR (67.8 MHz, $CDCl_3$, TMS) δ 150.28 (CH), 144.20 (Cq), 135.09 (Cq), 132.00 (CH), 131.86 (CH), 128.44 (CH), 126.72 (CH), 122.68 (Cq), 120.84 (CH); IR (KBr, cm^{-1}) 3040, 2940, 1595, 1585, 1497, 1483, 1418, 1073, 1009, 975, 828, 545; m.p. 160.5 - 161.5 °C; Anal. Calcd for $C_{13}H_{10}BrN$: C, 60.03; H, 3.87; N, 5.38. Found: C, 59.93; H, 3.78; N, 5.31. To a THF (50 mL) solution of 1-Bromo-4-[2-(4-pyridyl)ethenyl]benzene (2.60 g, 10 mmol), *n*-BuLi (*n*-hexane solution, 1.7 M, 8.8 mL, 15 mmol) was added at -78 °C over 5 min. After stirring for 30 min at -78 °C, 4-pyridine-carboxaldehyde (1.4 mL, 15 mmol) was added. A white precipitate was formed at this time. The

mixture was stirred for 30 min at -78 °C, and then for 5 h at room temperature. To the reaction mixture, H_2O (50 mL) was added to quench the reaction. At this time, the white precipitate was completely solved. The clear solution was extracted with $CHCl_3$ (50 mL x 3). The combined organic layers was dried over $MgSO_4$, filtered, and evaporated to give crude product as pale yellow solid (4.66 g). This crude was used for next reaction without further purification.; ^1H NMR (270 MHz, $CDCl_3$-CD_3OD, TMS) δ 8.47 (d-like, *J* = 5.9 Hz, 4 H, Py*H*α), 7.51 (d, *J* = 8.3 Hz, 2 H, Ph*H*), 7.38 (d, *J* = 8.3 Hz, 2 H, Ph*H'*), 7.36 (d-like, *J* = 5.9 Hz, 2 H, Py*H*β), 7.28 (d, *J* = 16.5 Hz, 1 H, -C*H*=CH-), 6.99 (d, *J* = 16.5 Hz, 1 H, -CH=C*H*-), 5.79 (s, 1 H, -C*H*(OH)-); IR (KBr, cm^{-1}) 3150, 2870, 2724, 1591, 1413, 1053, 1002, 968, 838, 785, 620, 575; m.p. 205.0 - 206.0 °C. To this crude product, 5 M HCl (30 mL) and palladium-charcoal (420 mg) were added. This mixture was vigorously stirred for 48 h at 50 °C under H_2 atmosphere. The reaction mixture was filtered and basified with K_2CO_3, and then the mixture was extracted with $CHCl_3$ (60 mL x 3). The combined organic layers was dried over $MgSO_4$, filtered and evaporated to give crude product (3.417 g). This crude was purified by chromatography (silica gel, ethyl acetate) to give the titled compound as pale yellow crystal (1.04 g, 3.81 mmol, 38% in two steps). ^1H NMR (270 MHz, $CDCl_3$, TMS) δ 8.49 (d-like, *J* = 5.9 Hz, 2 H, $Py_1H\alpha$), 8.48 (d-like, *J* = 5.9 Hz, 2 H, $Py_2H\alpha$), 7.10 (d-like, *J* = 5.9 Hz, 2 H, $Py_1H\beta$), 7.09 (s, 4 H, Ph*H*), 7.08 (d-like, *J* = 5.9 Hz, 2 H, $Py_2H\beta$), 3.93 (s, 2 H, $PhCH_2Py$), 2.91 (s, 4 H, -NCH_2CH_2N-); ^{13}C NMR (67.8 MHz, $CDCl_3$, TMS) δ 150.42 (*C*q), 150.11 (*C*q), 149.81 (*C*H), 149.68 (*C*H), 139.10 (*C*q), 136.80 (*C*q), 129.13 (*C*H), 128.77 (*C*H), 124.15 (*C*H), 123.92 (*C*H), 40.83 (CH_2), 36.98 (CH_2), 36.1 (CH_2); IR (KBr, cm^{-1}) 3305, 3030, 2935, 1601, 1559, 1511, 1418, 1220, 992, 813, 610, 582; m.p. 39.7 - 40.7 °C; Anal. Calcd for $C_{19}H_{18}N_2$: C, 83.18; H, 6.61; N, 10.21. Found: C, 82.97; H, 6.30; N, 10.10.

Preparation of ring structure 9 or 10 In an aqueous solution (2.0 mL) of Pd(II) complex **1** (14.5 mg, 0.05 mmol), ligand **8** (13.7 mg, 0.05 mmol) was suspended and the mixture was stirred at 60 °C for 1 h to give a clear solution. Addition of KPF_6 aqueous solution (0.25 M, 2.0 mL) to the solution precipitated the mixture of **9** or **10** (PF_6 salt, 31.9 mg, 87% yield) as a pure white powder. We have not assigned the exact structure of this compound. But we are sure that the stricture is assignable to **9** or **10**; ^1H NMR (500 MHz, acetone-d_6, 25 °C, TMS as an external standard) δ 8.80 (d-like, *J* = 6.6 Hz, 2 H, Py*H*α), 8.77 (d-like, *J* = 6.6 Hz, 2 H, Py*H'*α), 7.35 (d-

like, J = 6.6 Hz, 2 H, Py$H\beta$), 7.27 (d-like, J = 6.6 Hz, 2 H, Py$H'\beta$), 6.90 (d, J = 8.1 Hz, 2 H, PhH), 6.78 (d, J = 8.1 Hz, 2 H, PhH'), 4.07 (s, 4 H, -CH_2-), 3.12 (s, 2 H, -CH_2CH_2-), 2.86 (s, 8 H, -NCH_2CH_2N-); ^{13}C NMR (125 MHz, D_2O, 25 °C, TMS as an external standard) δ 157.35 (*C*q), 157.11 (*C*q), 152.19 (*C*H), 151.75 (*C*H), 139.64 (*C*q), 136.62 (*C*q), 130.13 (*C*H), 129.86 (*C*H), 128.20 (*C*H), 127.41 (*C*H), 47.99 (CH_2), 40.74 (CH_2), 37.55 (CH_2), 36.48 (CH_2); IR(KBr, cm^{-1}) 3335, 3287, 3075, 1620, 1591, 1437, 1070, 1059, 838, 558; m.p. 235 °C dec; Anal. Calcd for $C_{42}H_{52}F_{24}N_8P_4Pd_2 \cdot 2H_2O$: C, 33.68; H, 3.77 N, 7.48. Found: C, 33.86; H, 3.67 ; N, 7.44.

Synthesis of 1,4-bis[2-(4-pyridyl)ethyl]benzene 11 Tripheylphosphine (79.8 mg, 3.04 mmol) and palladium acetate (33.9 mg, 1.53 mmol) was added to a pyridine (2 mL) solution of 1,4-dibromobenzene (1.182 g, 5.00 mmol) and 4-vinylpyridine (1.2 mL, 12.0 mmol). The mixture was stirred at 100 °C for 3 days. To the reaction mixture, H_20 (50 mL) was added, and extracted with $CHCl_3$ (80 mL x 5). The combined organic layers was dried over $MgSO_4$, filtered and evaporated to give crude product as yellow solid (4.04 g). This crude product was used to next reaction without further purification. ^{1}H NMR (270 MHz, $CDCl_3$, TMS) δ 8.59 (d-like, J = 6.3 Hz, 4 H, Py$H\alpha$), 7.57 (s, 4 H, -PhH-), 7.38 (d-like, J = 6.3 Hz, 4 H, Py$H\beta$), 7.31(d, J = 16.5 Hz, 1 H, -CH=CH-), 7.06 (d, J = 16.5 Hz, 1 H, -CH=CH-); IR (KBr, cm^{-1}) 3045, 2940, 1595, 1592, 1418, 1192, 1078, 1010, 978, 828, 724, 543; m.p. 272.0 - 273.0 °C. To the crude 1,4-bis[2-(4-pyridyl)ethynyl]-benzene (4.00 g), palladium-charcoal (0.801 g), 5M HCl (30 mL) and EtOH (30 mL) was added. The mixture was vigorously stirred for 24 h at 50 °C under H_2 atmosphere. After the reaction mixture was filtered, the filtrate was evaporated to remove almost all EtOH. The mixture was basified with KOHaq (pH > 11), and then extracted with $CHCl_3$ (40 mL x 3). The combined organic layers was dried over $MgSO_4$, filtered and evaporated to give crude product as yellow solid (1.68 g). The crude product was purified by chromatography (silica gel, ethyl acetate) to give titled product as pale yellow crystal (1.135 g, 3.94 mmol, 78.8% in two steps). ^{1}H NMR (270 MHz, $CDCl_3$, TMS) δ 8.48 (d-like, J = 5.9 Hz, 4 H, Py$H\alpha$), 7.07 (d-like, J = 5.9 Hz, 4 H, Py$H\beta$), 7.05 (s, 4 H, PhH), 2.90 (s, 8 H, -CH_2CH_2-); ^{13}C NMR (67.9 MHz, $CDCl_3$, TMS) δ 150.46 (*C*q), 149.83 (*C*H), 138.56 (*C*q), 128.50 (*C*H), 123.93 (*C*H), 37.02 (CH_2), 36.10 (CH_2); IR (KBr, cm^{-1}) 3460, 3240, 2925, 2855, 1675, 1608, 1560, 1518, 1420, 835, 553; m.p.

124.0 - 125.0 °C; Anal. Calcd for $C_{20}H_{20}N_2$: C, 83.30; H, 6.99; N, 9.71. Found: C, 83.18, H, 6.88; N, 9.64.

Synthesis of ring compounds 12 and 13 In an aqueous solution (2.0 mL) of Pd(II) complex **1** (29.0 mg, 0.10 mmol), ligand **11** (28.8 mg, 0.10 mmol) was suspended and the mixture was stirred at 60 °C for 30 min to give a clear solution. Addition of KPF_6 aqueous solution (1 M, 1.0 mL) to the solution precipitated the mixture of **12** and **13** (PF_6 salt, 54.4 mg, 73% yield) as a pure white powder. The approximate ratio of **12** and **13** is 1:2 by measuring NMR integration curve. ^1H NMR (500 MHz, D_2O, 25 °C, TMS as an external standard) δ 8.72 (d-like, J = 6.6 Hz, 2x(1/3) Py*H*α), 8.64 (d-like, J = 6.3 Hz, 2x(2/3) Py*H'*α), 7.48 (d-like, J = 6.6 Hz, 2x(1/3) Py*H*β), 7.33 (d-like, J = 6.3 Hz, 2x(2/3) Py*H'*β), 6.83 (s, 2x(1/3) Ph*H*), 6.79 (s, 2x(2/3) Ph*H'*), 3.22 (dd, J = 6.8 Hz, J = 7.1 Hz, 2x(2/3) -C*H'*$_2$CH$_2$-), 3.07 (dd, J = 7.1 Hz, J = 8.6 Hz, 2x(1/3) -C*H*$_2$CH$_2$-), 3.02 (dd, J = 6.8 Hz, J = 7.1 Hz, 2x(2/3) -CH$_2$C*H'*$_2$-), 2.90 (dd, J = 7.1 Hz, J = 8.6 Hz, 2x(1/3) -CH$_2$C*H*$_2$-), 2.80 (s, 8 H, -NC*H*$_2$C*H*$_2$N-); ^{13}C NMR (125 MHz, D_2O, 25 °C, TMS as an external standard) δ 157.25 (*C*q), 156.69 (*C*q), 151.89 (*C*H), 151.11 (*C*H), 138.68 (*C*q), 136.80 (*C*q), 129.51 (*C*H), 129.22 (*C*H), 128.43 (*C*H), 127.98 (*C*H), 48.14 (*C*H$_2$), 48.03 (*C*H$_2$), 36.94 (*C*H$_2$), 35.74 (*C*H$_2$), 33.68 (*C*H$_2$), 32.98 (*C*H$_2$); IR(KBr, cm^{-1}) 3339, 3287, 1621, 1591, 1437, 1137, 1071, 1059, 832, 558; m.p. 235 °C dec; Anal. Calcd for $C_{44}H_{56}F_{24}N_8P_4Pd_2 \cdot H_2O$: C, 34.64; H, 3.96; N, 7.34. Found: C, 34.52; H, 3.81; N, 7.43.

Preparation of 1-(4-pyridyl)-4-(4-pyridylmethyl)benzene 14 To a toluene solution (80 mL) of 4-trimethylstannylpyridine (2.02 g, 8.36 mmol), were added *p*-dibromobenzene (3.78 g, 16.0 mmol), lithium chloride (3.40 g, 80.3 mmol), and $PdCl_2(PPh_3)_2$ (0.561 g, 0.799 mmol). The mixture was stirred for 16 h at reflux temperature. After the solvent was removed under reduced pressure, H_2O (50 mL) was poured into the residue. Then, the aqueous layer was extracted with $CHCl_3$ (100 mL x 3). The combined organic layers were dried over K_2CO_3 and evaporated to give a crude product. The crude product was purified by chromatography (silica gel, $CHCl_3$: MeOH = 60:1 - 30:1) to give pale yellow crystals (4.0 mmol, 48%). ^1H NMR (500 MHz, $CDCl_3$, TMS) δ 8.67 (d-like, 2 H, J = 6.2 Hz, Py*H*α), 7.50 (d, 2 H, J = 8.6 Hz, Ph*H*a), 7.50 (d, 2 H, J = 8.6 Hz, Ph*H*b), 7.46 (d-like, 2 H, J = 6.2 Hz, Py*H*β); ^{13}C NMR (67.8 MHz, $CDCl_3$, TMS) δ 150.4 (*C*H), 147.1 (*C*q), 137.1 (*C*q), 132.3 (*C*H), 128.6 (*C*H), 123.6 (*C*q), 121.4 (*C*H);

MS (EI) m/z 233 [M^+]; IR (KBr, cm^{-1}) 1590, 1533, 1470, 1413, 1388, 1075, 1005, 993, 815, 809, 778, 500; m.p. 129.0 - 131.0 °C; Anal. Calcd for $C_{11}H_6BrN$: C, 56.44; H, 3.44; N, 5.98. Found: C, 56.36; H, 3.06; N, 5.87. To a THF (5 mL) solution of diisopropylamine (0.85 mL, 6.0 mmol, 3 equiv), *n*-BuLi (1.6 M hexane solution, 3.8 mL, 6.0 mmol) was added at 0 °C. After stirred for 5 min, 4-methylpyridine (0.6 mL, 6.0 mmol) was added at 0 °C over 5 min, and the mixture was stirred for more 5 min. A THF solution of $ZnCl_2$ (0.5 M, 12 mL, 6.0 mmol) was added at 0 °C over 10 min. An insoluble orange precipitate was formed. Then the mixture was stirred for 1 h at room temperature. After an addition of $PdCl_2(PPh_3)_2$ (140 mg, 0.2 mmol) and 4-(4-bromophenyl)pyridine (268 mg, 1.2 mmol), this mixture was stirred at reflux temperature for 2 days. Ethylenediamine (1.5 mL) and H_2O (20 mL) was added to the reaction mixture, and the mixture was stirred for 30 min. After the two layers were separated, the aqueous layer was extracted with $CHCl_3$ (50 mL x 3). The combined organic layer was dried over $MgSO_4$ and evaporated to give a crude product. The crude product (873 mg) was purified by chromatography (silica gel, ethyl acetate) to give the titled compound as pale yellow crystal (72 mg, 0.29 mmol, 25%). ^1H NMR (500 MHz, $CDCl_3$, TMS) δ 8.65 (d-like, 2 H, J = 6.3 Hz, $Py_1H\alpha$), 8.53 (d-like, 2 H, J = 6.3 Hz, $Py_2H\alpha$), 7.60 (d, 2 H, J = 8.2 Hz, Ph*H*), 7.49 (d-like, 2 H, J = 6.3 Hz, $Py_1H\beta$), 7.30 (d, 2 H, J = 8.2 Hz, Ph*H*), 7.13 (d-like, 2 H, J = 6.3 Hz, $Py_2H\beta$), 4.03 (s, 2 H, -CH_2-); ^{13}C NMR (67.8 MHz, $CDCl_3$, TMS) δ 150.3 (*C*H), 150.0 (*C*H), 149.4 (*C*q), 147.8 (*C*q), 140.0 (*C*q), 136.6 (*C*q), 129.8 (*C*H), 127.3 (*C*H), 124.1 (*C*H), 121.5 (*C*H), 40.9 (CH_2); IR(KBr, cm^{-1}) 1594, 1486, 1414, 1403, 830, 804, 788, 709, 612, 555, 483, 402.; MS (EI) *m/z* (rel intensity) 247 [(M+H), 45], 246 [(M), 100], 245 [(M-H), 57], 168 [(M-Py), 72]; m.p. 84.0 - 85.0 °C; HR-MS (EI) Cacld for $C_{17}H_{14}N_2$: 246.1157. Found: 246.1148.

Preparation and physical properties of catenane 15 In an aqueous solution (1.2 mL) of Pd(II) complex **1** (0.06 mmol), ligand **14** (0.06 mmol) was suspended and the mixture was stirred at 60 °C for 0.5 h to give a clear solution. An addition of aqueous $NaClO_4$ (1 M, 1.5 mL) to the solution precipitated **15** (ClO_4 salt, 87% yield) as a pure cream yellow powder. ^1H NMR (400 MHz, D_2O, 25 °C, TMS as an external standard, The letters o and i indicate an aromatic ring located outside and inside of the catenane structure.) δ 8.95-9.00 (m, 8 H, $Py_1H\alpha$(o) and $Py_2H\alpha$(o)), 8.58 (d, J = 6 Hz, 4 H, $Py_1H\alpha$(i)), 8.50 (d, J = 6 Hz, 4 H, $Py_2H\alpha$(i)), 7.85 (d, J = 6.0

Hz, 4 H, $Py_1H\beta(o)$), 7.81 (d, J = 6 Hz, 4 H, $Py_2H\beta(o)$), 7.10 (d, J = 7 Hz, 4 H, Ph*H*a(o)), 6.85 (d, J = 6 Hz, 4 H, $Py_1H\beta(i)$), 6.67 (d, J = 7 Hz, 4 H, Ph*H*b(o)), 6.53 (d, J = 7 Hz, 2 H, Ph*H*b(i)), 6.32 (d, J = 6 Hz, 2 H, $PhH_b'(i)$), 4.61 (m, 2 H, $Py_2H\beta(i)$, 4.46 (m, 2 H, $Py_2H\beta'(i)$, 4.02 (s, 8 H, CH_2(i and o)), 3.75 (d, J = 6 Hz, 2 H, Ph*H*a(i)), 3.68 (d, J = 6 Hz, 2 H, Ph*H*a'(i)), 3.00 (s, 8 H; $NCH_2CH_2N(o)$, 2.90 (s, 8 H, $NCH_2CH_2N(i)$); ^{13}C NMR (125 MHz, D_2O, 25 °C, TMS as an external standard): δ 156.89 (*C*q), 156.44 (*C*q), 151.48 (*C*H), 151.23 (*C*H), 150.6 (*C*H), 150.6 (*C*H), 149.44 (*C*q), 148.04 (*C*q), 142.74 (*C*q), 142.26 (*C*q), 131.77 (*C*q), 129.85 (*C*q), 128.83 (*C*H), 128.44 (*C*H), 128.21 (*C*H), 127.32 (*C*H), 127.02 (*C*H), 126.63 (*C*H), 125.55 (*C*H), 125.38 (*C*H), 122.68 (*C*H), 121.53 (*C*H), 121.00 (*C*H), 46.94 (CH_2), 46.84 (CH_2), 46.63 (CH_2), 45.76 (CH_2), 40.76 (CH_2), 40.55 (CH_2); ESI-MS (based on ^{106}Pd) *m/z* 1010 [$(M-(NO_3)_2)]^{2+}$, 653 [$(M-(NO_3)_3)]^{3+}$, 474 [$(M-(NO_3)_4)]^{4+}$; m.p. 290 °C dec; Anal. Calcd for $C_{76}H_{88}Cl_8N_{16}O_{32}Pd_4 \cdot 4H_2O$: C, 36.24; H, 3.84; N, 8.90. Found: C, 36.16; H, 3.79; N, 8.65.

Preparation of 4,4'-bis(4-pyridylmethyl)biphenyl 17 To a THF (10 mL) solution of 4,4'-dibromobiphenyl (0.312 g, 10 mmol), a hexane solution of *n*-BuLi (1.73 M, 6.36 mL, 11.0 mmol) was added at -78 °C. After stirred for 1.5 h, 4-pyridinecarboxaldehyde (1.1 mL, 11.0 mmol) was added. The solution was stirred for 1.5 h at -78 °C and for 1 h at 0 °C. The resulting mixture was quenched with water, extracted with 1 M HCl (20 mL x 2) and H_2O (20 mL). An addition of NaOHaq (10 mL) precipitated solid materials which were filtered and dried under reduced pressure to give 4,4'-di(hydroxy-4-pyridylmethyl)biphenyl (1.58 g, yield 86%). The product was used in a subsequent reaction without further purification. ^1H NMR (270 MHz, CD_3OD, TMS) δ 8.45 (d, J = 5.9 Hz, 4 H, Py*H*α), 7.58 (d, J = 8.2 Hz, 4 H, Ph*H*), 7.48 (d, J = 5.9 Hz, 4 H, Py*H*β), 7.43 (d, J = 8.2 Hz, 4 H, Ph*H*), 5.82 (s, 2 H, C(OH)*H*); IR (KBr, cm^{-1}) 3100, 1594, 1492, 1404, 1188, 1042, 998, 786, 602, 560; m.p. 200 - 201 °C. 4,4'-di(hydroxy-4-pyridylmethyl)biphenyl (1.58 g, 4.28 mmol) was dissolved in ethanol - 2 M HCl (5:1, 60 mL) and stirred with 5% palladium charcoal (0.31 g) under the atmospheric pressure of H_2 gas at 60 °C for 6 days. The catalyst was removed by filtration and the filtrate was basified with NaOHaq (20 mL). The resulting mixture was extracted with $CHCl_3$ (50 mL x 4). The combined organic layers was dried over Na_2SO_4, filtered, and evaporated. The residue was purified by column chromatography (silica gel, $CHCl_3$:MeOH:AcOEt = 10:1:10) to give titled compound as colorless

crystals (0.631 g, 44%). ^{1}H NMR (270 MHz, $CDCl_3$, TMS) δ 8.50 (d, 4 H, *J* = 5.9 Hz, Py*H*α), 7.52 (d, 4 H, *J* = 8.2 Hz, Ph*H*), 7.23 (d, 4 H, *J* = 8.2 Hz, Ph*H*), 7.14 (d, 4 H, *J* = 5.9 Hz, Py*H*β), 5.82 (s, 4H, -C*H*$_2$-); ^{13}C NMR (67.8 MHz, $CDCl_3$, TMS) δ 149.90 (*C*H), 149.84 (*Cq*), 139.14 (*Cq*), 137.97 (*Cq*), 129.47 (*C*H), 127.29 (*C*H), 124.19 (*C*H), 40.84 (*C*H$_2$); IR (KBr, cm^{-1}) 3015, 1594, 1488, 1408, 1060, 922, 862, 780, 608, 474; MS (EI) *m/z* 336 (M^+); m.p. 126.3 - 127.0 °C; Anal. Calcd for $C_{24}H_{16}N_2$: C, 85.68; H, 5.99; N 8.33. Found: C, 85.88; H, 5.70; N 8.23.

Preparation of 4-pyridyl-4'-(4-pyridylmethyl)biphenyl 19 To an anhydrous toluene (100 mL) mixture of LiCl (2.12 g, 50.0 mmol), $PdCl_2(PPh_3)_2$ (0.351 g, 0.50 mmol), and 4,4'-dibromobiphenyl (7.80 g, 25.0 mmol), 4-trimethylstannylpyridine (2.42 g, 10.0 mmol) was added under N_2 atmosphere. The mixture was stirred for 30 h at reflux temperature. After an addition of H_2O (2 mL) to quench the reaction, the mixture was concentrated to give a residue. The residue was solved into $CHCl_3$ (200 mL). The solution was washed with H_2O (200 mL x 3). The resulting organic layers was dried over K_2CO_3, filtered, and evaporated to give a crude product. The crude was purified by chromatography (silica gel, hexane : ethyl acetate = 1 : 4) to give 4-bromo-4'-(4-pyridyl)biphenyl (63 mg, 0.214 mmol, 48%). ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 8.69 (d-like, *J* = 6.2 Hz, 2 H, Py*H*α), 7.73 (d, *J* = 8.8 Hz, 2 H, Ph*H*), 7.68 (d, *J* = 8.8 Hz, 2 H, Ph*H*), 7.60 (d, *J* = 8.8 Hz, 2 H, Ph*H*), 7.55 (d-like, *J* = 6.2 Hz, 2 H, Py*H*β), 7.51 (d, *J* = 8.8 Hz, 2 H, Ph*H*); ^{13}C NMR (125.65 MHz, $CDCl_3$, TMS) δ 150.29 (*C*H), 147.63 (*C*q), 140.69 (*C*q), 139.07 (*C*q), 137.28 (*C*q), 132.01 (*C*H), 128.61 (*C*H), 127.58 (*C*H), 127.49 (*C*H), 122.05 (*C*q), 121.44 (*C*H); IR (KBr, cm^{-1}) 3854, 3752, 3650, 2963, 2345, 1560, 1542, 1261, 1093, 803; m.p. 236 - 237 °C; Anal. Calcd for $C_{17}H_{12}NBr \cdot 0.2\ H_2O$: C, 65.07; H, 3.85; N, 4.46. Found: C, 64.93; H,3.69; N, 4.41.; HR-MS (FAB) Calcd for $C_{17}H_{13}NBr$: 310.0231. Found: 310.0211[M^+]. To a THF (15 mL) solution of diisopropylamine (0.84 mL, 6.0 mL), *n*-BuLi (1.60 M hexane solution, 3.75 mL, 6.0 mL) was added at 0 °C under N_2 atmosphere. This reaction solution was stirred for 30 min. To the solution, 4-methylpyridine (0.588 mL, 6.0 mmol) was added. After stirred for 50 min at 0 °C, $ZnCl_2$ (0.5 M THF solution, 12.0 mL, 6.0 mmol) was added to the mixture. The mixture was stirred for 1 h at room temperature. A THF (20 mL) solution of 4-bromo-4'-pyridylbiphenyl (0.620 g, 2.0 mmol) and a THF (60.0 mL) solution of $PdCl_2(PPh_3)_2$ (0.14 g, 0.01 mmol) was added to this mixture. The mixture was stirred for 70 h at that

temperature. After an addition of ethylenediamine (0.4 mL, 6.0 mmol), the mixture was evaporated to give a residue. The residue was solved into $CHCl_3$ (150 mL). The solution was washed with H_2O (200 mL x 3). The resulting organic layer was dried over K_2CO_3, filtered, and evaporated to give a crude product The crude was purified by chromatography (silica gel, chloroform : methanol = 20 : 1) and by HPLC ($CHCl_3$) to give titled compound as colorless crystal (0.45 g, 1.38 mmol, 30%). ^1H NMR (500 MHz, $CDCl_3$, TMS) δ 8.68 (d-like, J = 5.6 Hz, 2 H, $Py_2H\alpha$), 8.57 (d, J = 5.9 Hz, 2 H, $Py_1H\alpha$), 7.73 (d, J = 9.1 Hz, 2 H, Ph*H*a), 7.70 (d, J = 9.1 Hz, 2 H, Ph*H*b), 7.61 (d, J = 8.4 Hz, 2 H, Ph*H*'a), 7.56 (d, J = 5.6 Hz, 2 H, $Py_2H\beta$), 7.28 (d, J = 8.4 Hz, 2 H, Ph*H*'b), 7.16 (d, J = 5.9 Hz, 2 H, $Py_1H\beta$), 4.00 (s, 2 H, -CH_2-); ^{13}C NMR (125.65 MHz, $CDCl_3$, TMS) δ 150.36 (*C*H), 149.97 (*C*H), 149.82 (*C*q), 147.75 (*C*q), 141.44 (*C*q), 138.62 (*C*q), 138.52 (*C*q), 136.87 (*C*q), 129.60 (*C*H), 127.66 (*C*H), 127.40 (*C*H), 127.38 (*C*H), 124.21 (*C*H), 121.43 (*C*H), 40.87 (CH_2); IR (KBr, cm^{-1}) 3020, 2300, 1550 - 1570, 1520, 1380, 850, 810, 730, 630, 580; m.p. 193 - 194 °C; Anal. Calcd for $C_{23}H_{18}N_2 \cdot 0.2\ H_2O$: C, 84.73; H, 5.57; N, 8.60. Found: C, 84.77; H, 5.43; N, 8.54.; HR-MS (FAB) Calcd for $C_{23}H_{18}N_2$: 323.1548. Found: 323.1528[M^+].

Synthesis and physical data of [2]catenane 20 To a D_2O solution (2 mL) of palladium complex **1** (2.9 mg, 0.01 mmol), pyridine-based ligand **19** (3.2 mg, 0.01 mmol) was added. This reaction mixture was stirred for 5 min at 60 °C to give a clear solution. ^1H NMR (500 MHz, D_2O, TMS as external standard) δ 8.81 (d, J = 6.3 Hz, 4 H, $Py_1H\alpha$), 8.76 (d, J = 6.3 Hz, 4 H, Py_1H'a), 8.57 (d, J = 6.3 Hz, 8 H, $Py_2H\alpha$), 7.78 (d, J = 6.3 Hz, 8 H, $Py_2H\beta$), 7.27 (d, J = 6.3 Hz, 4 H, $Py_1H\beta$), 7.24 (d, J = 7.7 Hz, 4 H, Ph*H*a), 7.19 (d, J = 7.42 Hz, 4 H, Ph*H*b), 7.03 (s, 8 H, Ph*H*a), 6.89 (d, J = 6.3 Hz, 4 H, $Py_1H'\beta$), 6.69 (d, J = 7.7 Hz, 4 H, Ph_2H), 6.14 (d, J = 8.2 Hz, 4 H, Ph_1H), 5.85 (d, J = 7.7 Hz, 4 H, Ph_2H'), 5.58 (d, J = 8.2 Hz, 8 H, Ph_1H'), 4.04 (s, 4 H,-CH_2-), 4.00 (s, 4 H, -CH_2-), 2.97 (s, 8 H, -NCH_2CH_2N-), 2.89 (s, 8 H, -NCH_2CH_2N-).

Preparation of 4, 4"-bis[(4-pyridyl)methyl]terphenyl 22 To a THF (40 mL) solution of diisopropylamine (3.36 mL, 24 mmol), *n*-BuLi (1.6 M hexane solution, 15 mL, 24 mmol) was added at -78 °C under N_2 atmosphere. After the mixture was stirred for 30 min at -78 °C, 4-methylpyridine (1.96 mL, 20.0 mmol) was added dropwise over 10 min. This reaction mixture

was stirred for 1 h, and then $ZnCl_2$ (0.5 M THF solution, 48 mL, 24 mmol) was added dropwise over 45 min. The mixture was stirred for 80 h at -78 °C, then stirred for 30 min at room temperature. To the reaction were added a 1,4-dioxane (50 mL) solution of 4,4'-dibromo-terphenyl (776 mg, 2.0 mmol) and a 1,4-dioxane (50 mL) solution of $PdCl_2(PPh_3)_2$ (140 mg, 0.2 mmol), respectively. This mixture was gradually heated to 90 °C and stirred at reflux temperature for 45 h. The resulting mixture was concentrated to give a residue. The residue was solved into $CHCl_3$ (150 mL). The solution was washed with H_2O (200 mL x 3). The resulting organic layer was dried over K_2CO_3, filtered, and evaporated to give a crude product. The crude was purified by chromatography (silica gel, $CHCl_3$: MeOH = 15 : 1), and by preparative HPLC (eluent: $CHCl_3$) to titled compound (17.0 mg, 0.04 mmol, yield 2%). ^1H NMR (300 MHz, $CDCl_3$, TMS) δ 8.52 (d-like, *J* = 6.0 Hz, 2 H, Py*H*α), 7.66 (s, 4 H, -PhPh*HP*h-), 7.59 (d, *J* = 8.3 Hz, 4 H, Py-Ph*H*-), 7.27 (d, *J* = 8.38 Hz, 4 H, Py-Ph*H*-), 7.16 (d, *J* = 6.0 Hz, 2 H, Py*H*β), 4.02 (s, 4 H, -C*H*$_2$-); ^{13}C NMR (125.65 MHz, $CDCl_3$, TMS) δ 149.79 (*C*H), 149.73 (*C*q), 139.49 (*C*q), 138.96 (*C*q), 137.98 (*C*q), 129.43 (*C*H), 127.28 (*C*H), 127.21 (*C*H), 124.13 (*C*H), 40.78 (*C*H$_2$); IR (KBr, cm^{-1}) 3448, 1601, 1492, 1385, 1069, 805, 592, 496; m.p. 189 - 190 °C; Anal. Calcd for $C_{30}H_{24}N_2 \cdot 0.2\ H_2O$: C, 86.71; H, 5.90; N, 6.74. Found: C, 86.67; H, 5.89; N, 6.76.; HR-MS(FAB) Calcd for $C_{30}H_{25}N_2$ [M+H]: 413.2018. Found: 413.1967 [M+H].

Preparation and physical properties of catenane 24 In an aqueous solution (1.0 mL) of Pd(II) complex **1** (0.10 mmol), ligand **17** (0.05 mmol) and ligand **23** (0.05 mmol) were suspended and the mixture was stirred at 70 °C for 2 h to give a clear solution. Addition of aqueous $NaClO_4$ (1 M, 1.0 mL) to the reaction solution precipitated **24** (ClO_4 salt, 94% yield) as a pure cream yellow powder. ^1H NMR (500 MHz, D_2O, 25 °C, TMS as an external standard) δ 8.84 (d, *J* = 5.5 Hz, 8 H, Py$_1$*H*α), 8.62 (d, *J* = 5.2 Hz, 8 H, Py$_2$*H*α), 7.76 (d, *J* = 5.5 Hz, 8 H, Py$_1$*H*β), 6.83 (d, *J* = 5.2 Hz, 8 H, Py$_2$*H*β), 6.63 (d, *J* = 7.4 Hz, 8 H, Ph*H*β), 4.01 (s, 8 H; PyC*H*$_2$Ph), 3.80 (d, *J* = 7.4 Hz, 8 H; Ph*H*α), 2.85 (br, 16 H; -N*H*$_2$C*H*$_2$N-); ^{13}C NMR (125 MHz, D_2O, 25 °C, TMS as an external standard) δ 156.89 (*C*q), 156.44 (*C*q), 151.48 (*C*H), 151.23 (*C*H), 150.60 (*C*H), 150.60 (*C*H), 149.44 (*C*q), 148.04 (*C*q), 142.74 (*C*q), 142.26 (*C*q), 131.77 (*C*q), 129.85 (*C*q), 128.83 (*C*H), 128.44 (*C*H), 128.21 (*C*H), 127.32 (*C*H), 127.02 (*C*H), 126.63 (*C*H), 125.55 (*C*H), 125.38 (*C*H), 122.68 (*C*H), 121.53 (*C*H), 121.00 (*C*H), 46.94 (*C*H$_2$), 46.84 (*C*H$_2$), 46.63 (*C*H$_2$),

45.76 (CH_2), 40.76 (CH_2), 40.55 (CH_2); Catenane **24** was also isolated as a nitrate salt by the addition of $NaNO_3$ aqueous solution (8 M, 2.0 mL) in place of $NaClO_4$ in the above procedure.; ESI-MS (based on ^{106}Pd) *m/z* 1010 $[(M-(NO_3)_2)]^{2+}$, 653 $[(M-(NO_3)_3)]^{3+}$, 474 $[(M-(NO_3)_4)]^{4+}$; m.p. 175 - 176.5 ℃; Anal. Calcd for $C_{76}H_{88}N_{24}O_{24}Pd_4 \cdot 5H_2O$: C, 36.24; H, 3.84; N, 8.90. Found: C, 36.16; H, 3.79; N, 8.65.

Synthesis of 1,4-bis(4-pyridyl)benzene 26 To a suspension of 1,4-dibromobenzene (71 mg, 0.30 mmol), $PdCl_2(PPh_3)_2$ (21 mg, 0.030 mmol, 10 mol%) and lithium chloride (127 mg, 3.0 mmol) in toluene (10 mL), was added 4-trimethylstannylpyridine (216 mg, 0.89 mmol) and refluxed for 39 h. The reaction mixture was evaporated and extracted with chloroform (50 mL x 3). The combined organic layers was dried over anhydrous K_2CO_3 and evaporated. The residue was purified by column chromatography (silica gel, eluent: ethyl acetate) and preparative HPLC to give the desired 1,4-bis(4-pyridyl)benzene as colorless crystals (35 mg, 0.15 mmol, yield 50%). ^1H NMR (270 MHz, $CDCl_3$, TMS) δ 8.70 (d-like, *J* = 6.3 Hz, 4 H, Py*H*α), 7.77 (s, 4 H, Ph*H*), 7.55 (d-like, *J* = 6.3 Hz, 4 H, Py*H*β); ^{13}C NMR(126 MHz, $CDCl_3$, TMS) δ 150.47 (*C*H), 147.39 (*C*H), 138.85 (*C*q), 127.77 (*C*H), 121.53 (*C*H); IR (KBr, cm^{-1}) 2940, 1595, 1550, 1480, 1230, 800, 705; m.p. 187.0 - 187.5 ℃; Anal. Calcd for $C_{16}H_{12}N_2 \cdot 0.3\ H_2O$: C, 80.85; H, 5.34; N, 11.79. Found: C, 81.01; H, 5.07; N, 11.57.

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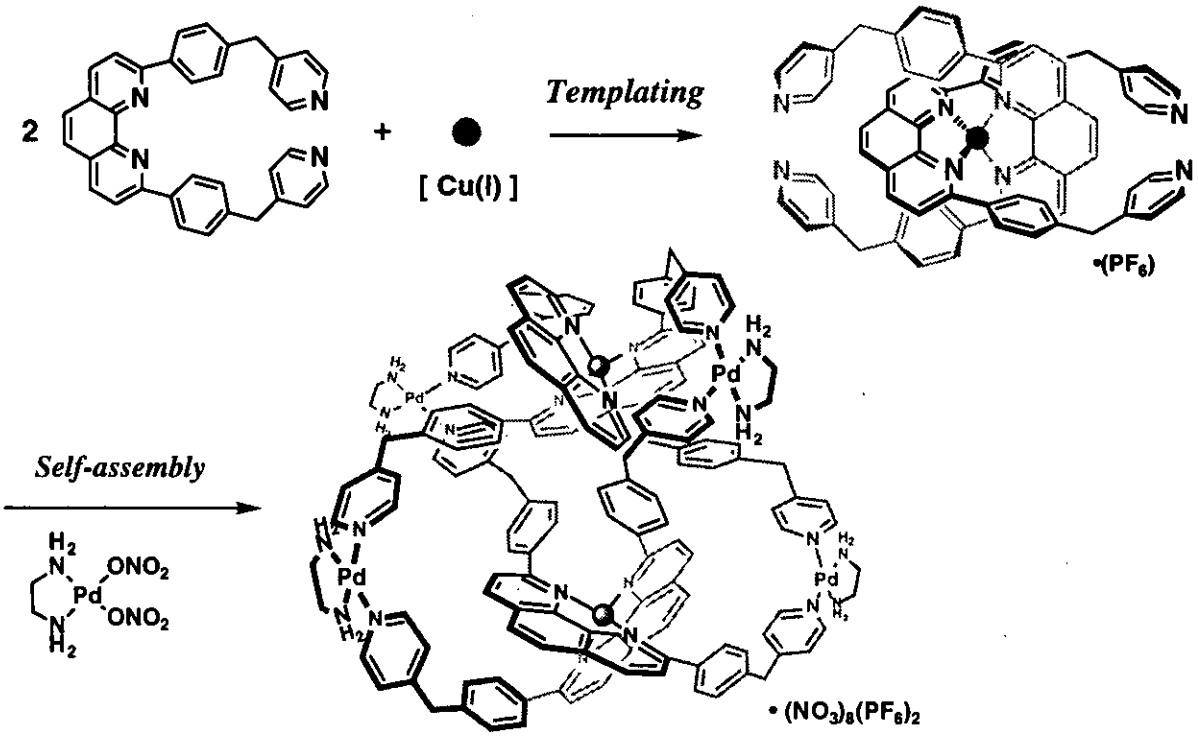
Chapter 3

Quantitative and Spontaneous Formation of a Doubly Interlocking [2]Catenane Using Copper(I) and Palladium(II) as Templating and Assembling Centers

J. Am. Chem. Soc. **1999**, *121*, 11014.

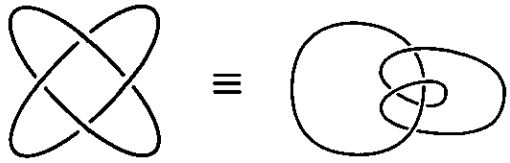
Abstract: A new strategy based on pure coordination chemistry has been used to construct a 4-crossing [2]catenane. The ligand used here contains a central 1,10-phenanthroline site attached to two pendent / 4-pyridyl groups. The central site is used to complex a copper(I) center whereas the lateral pyridine groups are coordinated to palladium(II).

The stepwise complexation procedure is virtually quantitative. It can be carried out both ways (copper(I) followed by palladium(II) or reverse one). The final product is chiral species incorporating 4 ligands, 2 copper(I) and 4 palladium(II) centers. It has been characterized in solution and its structure has been evidenced mainly by ESI-MS.



3-1 Introduction

Template strategies and self-assembly have recently undergone on explosive development, making possible the synthesis of many fascinating and complex structures using only relatively simple procedures.[1] By combining building blocks coming from various families of molecules, the structure of the resulting multicomponent systems can in principle be varied infinitely at will. This chapter describes a new strategy for catenane synthesis,[2] which enabled us to quantitatively obtain a 4-crossing [2]catenane incorporating two different metal centers: 4 Pd(II) and 2 Cu(I).



3-2 Doubly interlocking catenane

Doubly interlocking catenanes are chiral and have complex topologies which have only been described recently.[3] Our approach is to combine the two methods, based on coordination chemistry, which are termed as "template" and "self-assembly" strategies. In the template strategy which has been developed in the course of the last 15 years, copper(I) complexes have been used as precursors, affording simple to topologically very complex catenanes.[2c] On the other hand, the self-assembly process furnishes, in one chemical step, sophisticated structures that include interlocking rings from very simple molecular fragments and under mild conditions.[2j] The two prototypical molecules which were made by using these approaches are the copper(I) catenane[4] and the four-palladium interlocking ring system[5] of Figure 1. Several previous reports are dealing with catenane formation for which the ring-forming reaction is based on transition metal coordination.[6-11]

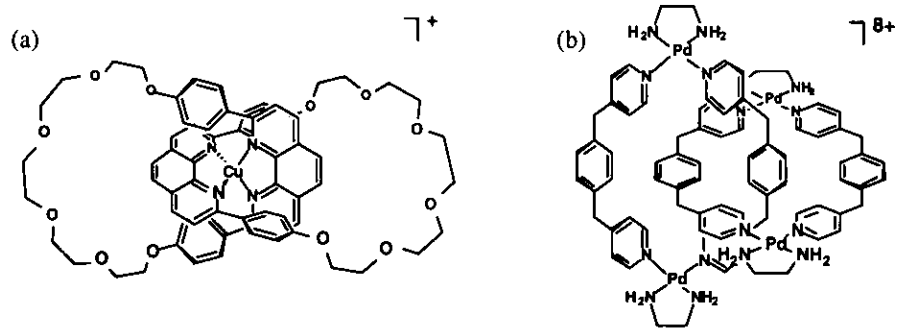
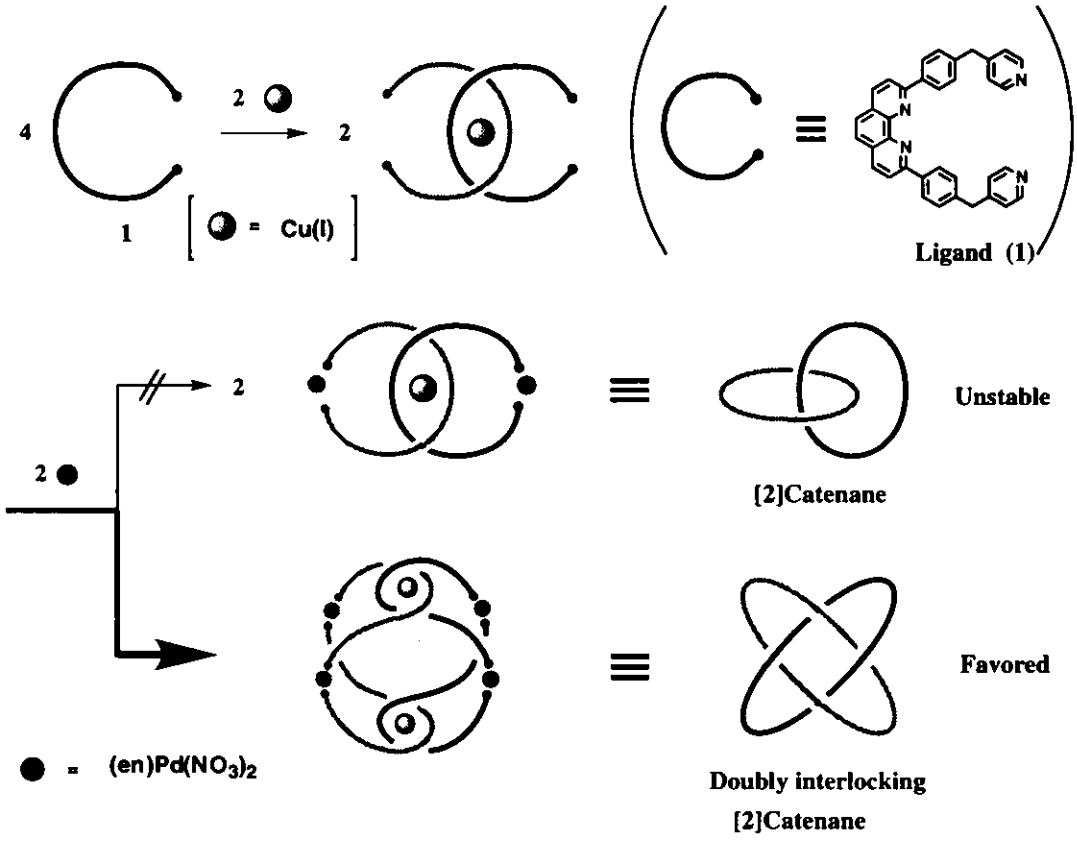


Figure 1. Prototypical interlocking molecules prepared by (a) template[4] and (b) self-assembly[5] strategies

3-3 Combination of template strategy and self-assembly

The first strategy is summarized in Scheme 1. Ligand (**1**) contains both phenanthroline and pyridine units in its structure. It was expected that phenanthroline units would coordinate to Cu(I) and pyridine rings would interact with Pd(II), leading to the sequence of reactions indicated in Scheme 1. In fact, the hypothetical simple [2]catenane built around one Cu(I) center only would be highly strained and thus very unstable. It was anticipated that the doubly interlocking dimer-like structure of Scheme 1 would be favored.

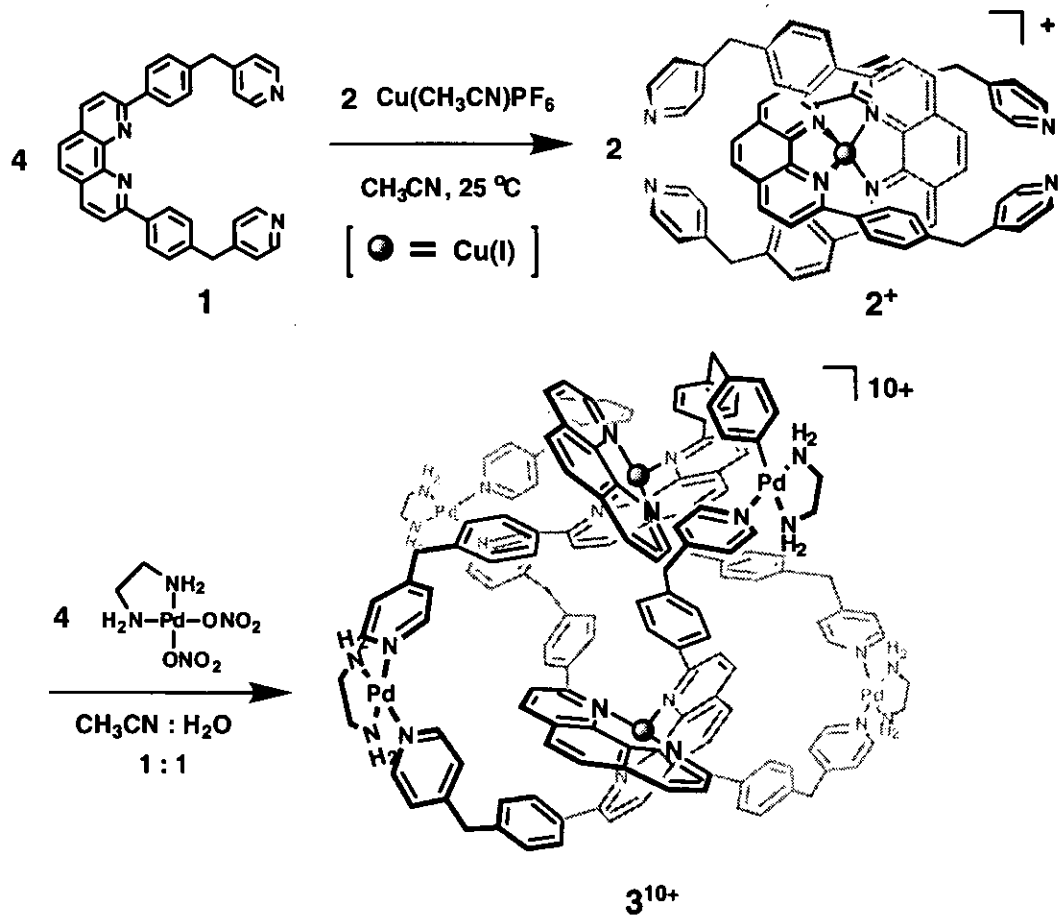


Scheme 1. General strategy for the preparation of doubly interlocking [2]catenanes

3-4 Synthesis of doubly interlocking catenane 3^{10+}

Indeed, following this route, the target catenane 3^{10+} was quantitatively obtained, first as nitrate salt and, after anion exchange, as its hexafluorophosphate one (Scheme 2). The reaction of the pyridine-based ligand (**1**) (0.03 mmol) and $Cu(CH_3CN)_4PF_6$ (0.015 mmol) in acetonitrile (1 mL) immediately gave the catenane precursor (2^+). To this solution, aqueous solution (1 mL) of $(en)Pd(NO_3)_2$ (en = 1,2-diaminoethane, 0.03 mmol) was added, and the reaction mixture was stirred for 1 h at room temperature to give the doubly interlocking catenane compound (3^{10+}).

This quantitative catenane formation was monitored by NMR experiment when the reaction was carried out in a deuterated solvent. The reaction solution was poured into aqueous KPF_6 (0.6 mmol, 5 mL) to give a red brown precipitate, which was filtered and dried. With this simple method, catenane 3^{10+} was isolated in almost quantitative yield as PF_6 salt (92%). It was fully characterized by elemental analysis and various spectroscopic methods (1D- and 2D-NMR, and ESI-MS) as discussed later.



Scheme 2. Preparation of 3^{10+}: i, $Cu(CH_3CN)_4PF_6$ (0.5 equiv. to **1**); ii, $(en)Pd(NO_3)_2$ (2.0 equiv. to **2**)

3-5 Consideration of doubly interlocking catenane 3^{10+}

As shown above, compound 3^{10+} may have doubly interlocking structure. But the uncertainty still remained. In order to unambiguously determine the structure, careful discussion must be done with more informative evidence.

In the first step, the component and molecular weight for the compound 3^{10+} were certificated by elemental analysis and electron spray ionization mass spectrometry (ESI-MS), respectively. According to the elemental analysis, the component of 3^{10+} was indicated as

$Cu(I)_2Pd(II)_4$(ligand **1**)$_4$. ESI-MS showed prominent peaks corresponding to $[3^{10+} \cdot nPF_6^-]^{(10-n)+}$ with n = 3, 4, and 5 (Figure 2).[12] These data clearly evidences that the complex formed here contains four Pd(II), two Cu(I), and four molecules of **1**. Thus, it can not be a simple [2]catenane in Scheme 1.

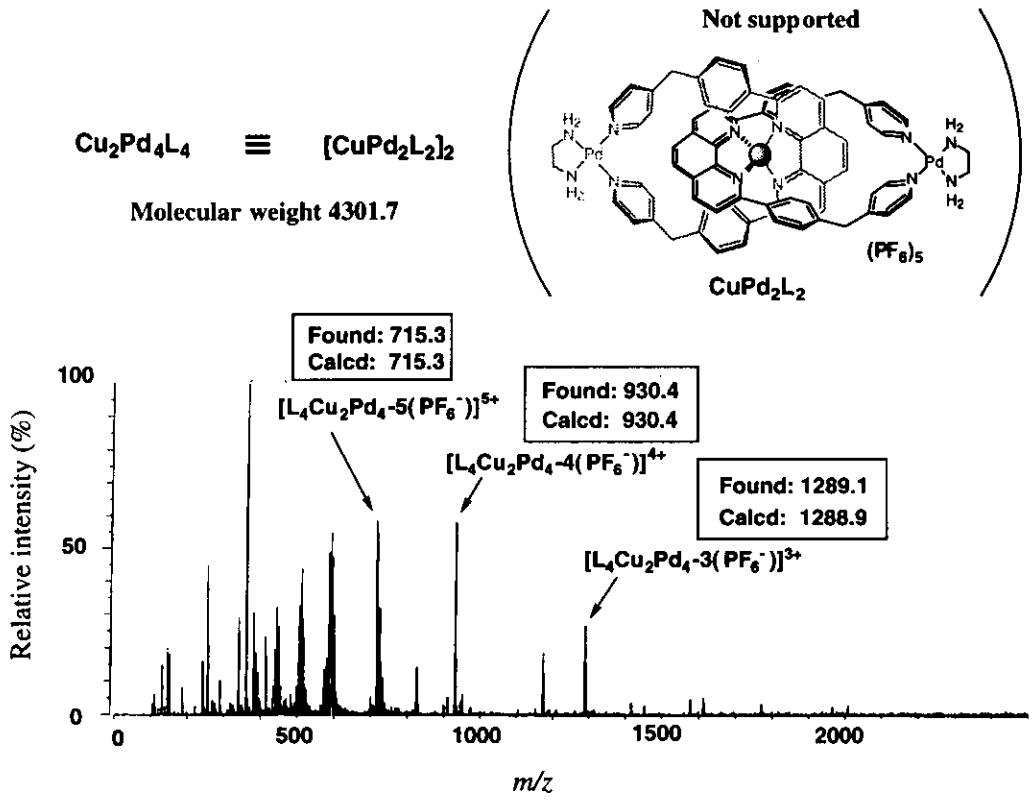


Figure 2. ESI-MS spectrum for compound 3^{10+}: The *m/z* value (relative intensity): 1289.1 {[3^{10+}-$(PF_6^-)_3$]$^{3+}$, 47%}, 930.4 {[3^{10+}-$(PF_6^-)_4$]$^{4+}$, 98%}, 715.3 {[3^{10+}-$(PF_6^-)_5$]$^{5+}$, 100%. Solvent: CH_3CN This ESI-MS method was developed by Dr. Yamaguchi (Chiba Univ.).

3-6 Structural information for doubly interlocking [2]catenane 3^{10+} gained by ^{1}H NMR

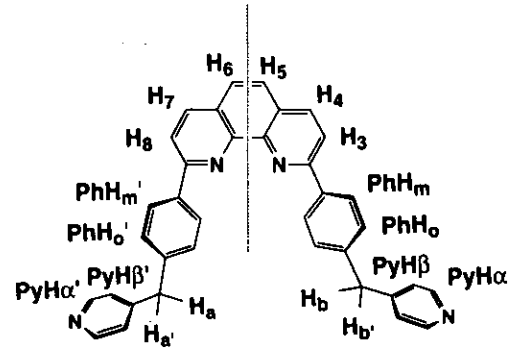
Observations of ^{1}H NMR suggested three important features: (i) the four ligands involved in 3^{10+} are all equivalent; (ii) each ligand is disymmetric as evidenced by the presence of the 14 individual signals in the aromatic region; and (iii) the all protons of the PyCH_2 groups (see Figure 3) are unequivalent. Furthermore, 2D ^{1}H NMR afforded the expected linkage connectivity of the ligand.

^{1}H NMR observation of comound 3^{10+} ($Cu_2Pd_4L_4$)

(i) All four ligands are equivalent.

(ii) Each ligand is disymmetry.

(iii) Methylene protons are unequivalent.



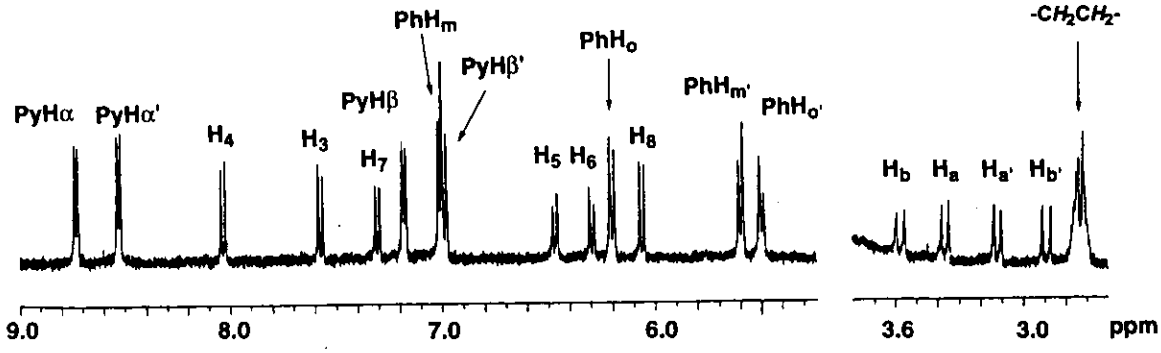


Figure 3. ^{1}H NMR (500 MHz, D_2O) spectra of compound 3^{10+}

3-7 Synthesis of analogous doubly interlocking [2]catenane

In order to obtain the more information to the doubly interlocking structure, an analogue bpy-blocked palladium complex (Pd') was employed. By the same experimental procedure mentioned above, the only one component that has similar structure to **3** quantitatively self-assembled, which was isolated in 85% yield as PF_6 salt. This compound **4** was confirmed by ^{1}H NMR, ^{13}C NMR, 2D NMR, elemental analysis, and ESI-MS.

This ^{1}H NMR observation showed fourth important clue to the doubly interlocking structure. Because of asymmetric environments around bpy units, all protons (eight signals) on a bpy ring were observed separately (Figure 4). And, 2D NMR experiments showed that all protons in the spectra were connected to the same bpy moiety. This means that four bpy units were equivalent in the frameworks in **3**. As the results, four palladium metal centers are equivalent in this structure.

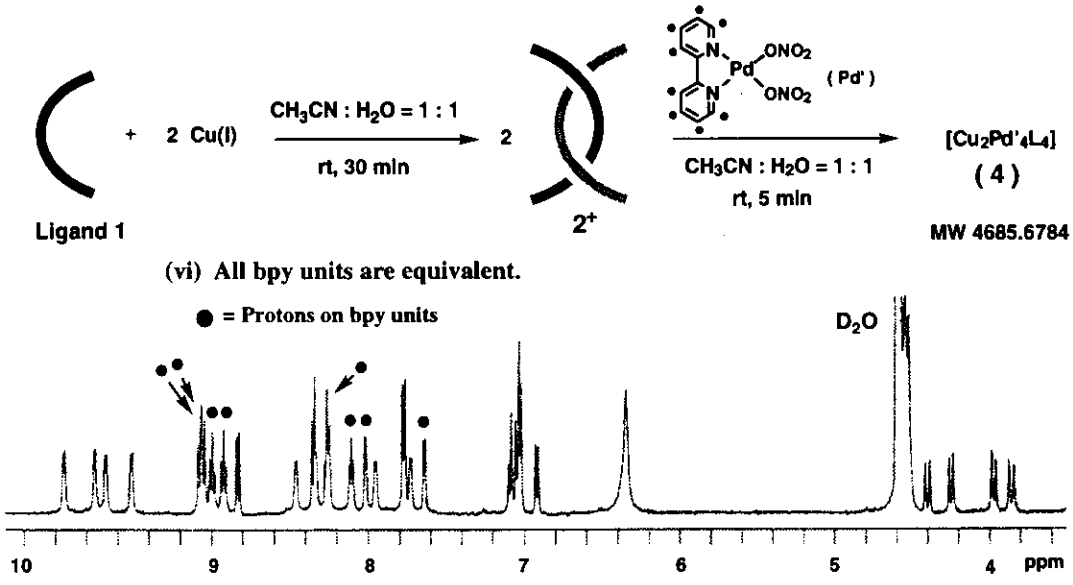


Figure 4. ^{1}H NMR (500 MHz, D_2O:CD_3CN = 1:1): The signals (solid circle) are assigned to protons of bpy units. Other signals have the similarity to the structure of compound $\mathbf{3}^{10+}$.

3-8 High resolution ESI mass spectroscopy for $[Cu_2Pd'_4L_4]$

The molecular weight of bpy analogous compound **4** was confirmed by high resolution ESI mass spectroscopy which have been developed recently.[12] The measurement suggested the molecular weight of the $Cu_2Pd'_4L_4$ (Figure 5). Therefore, ^{1}H NMR and mass spectrometry indicated that the complex assembled here must have the same structure to that of $\mathbf{3}^{10+}$.

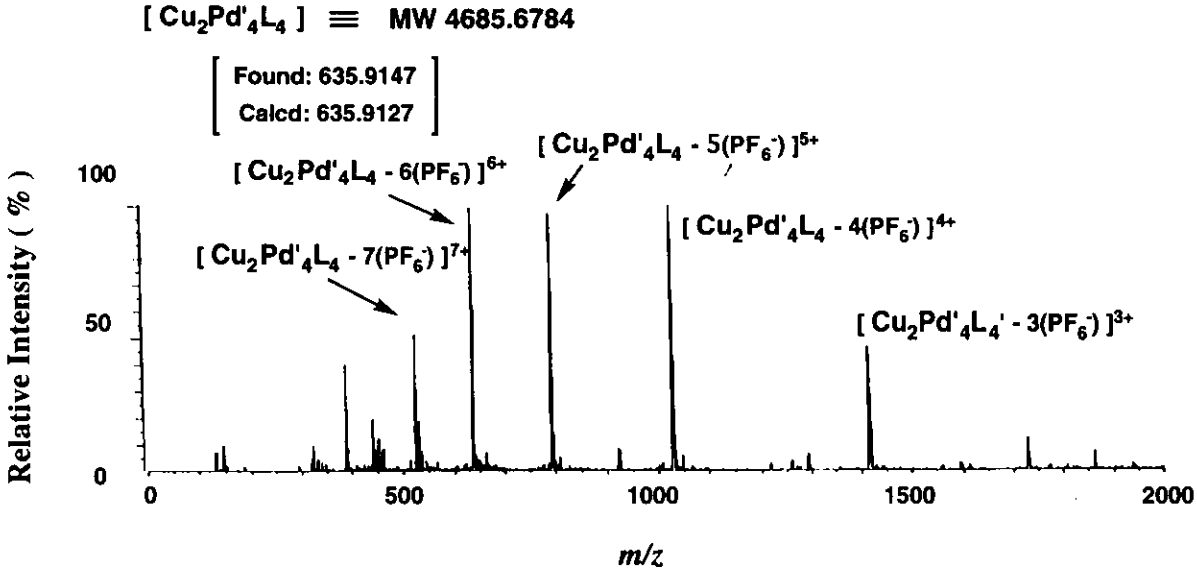
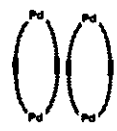
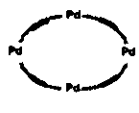
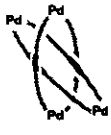
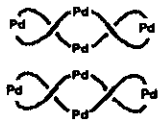


Figure 5. High resolution ESI MS spectrum for component, $[Cu_2Pd'_4L_4]$: Calcld for [$(Cu_2Pd'_4L_4)^{6+}$-6 PF_6]: 635.9127, Found: 635.9147. +2.0mmu, 3.1 ppm; This ESI-MS measurement was done by Dr. Yamaguchi (Chiba Univ.).

3-9 Structural elucidation for $Cu(I)_2Pd(II)_4(ligand)_4$ molecule

Although doubly interlocking structure 3^{10+} is the most plausible for the $Cu_2Pd_4L_4$ species, we should consider and carefully exclude other possible molecular topologies: i. e., two separate rings, a twisted large ring, a two crossing catenane, a trefoil knot, and so on. To elucidate the $Cu_2Pd_4L_4$ structure, we first figured out possible molecular topologies for hypothetical precursor Pd_4L_4 (Table 1, A -F). Among these structure, topologies with more than four crossing points (f or more complex one) can not be formed from only 4 Pd and 4 L because of too short length of the thread. Therefore, the Pd_4L_4 topologies we obtained here must be involved in a to e. It is impossible to construct more complicated topologies such as structure F.

Table 1. Consideration of suitable structure for $Cu(I)_2Pd(II)_4$(Ligand **1**)$_4$

Entry	(A)	(B)	(C)	(D)	(E)	(F)	(G)
Topology for "L_4Pd_4"	 a	 b	 c	 d	 e	 f	more complex topology g
	+ 2 Cu	+ 2 Cu	+ 2 Cu	+ 2 Cu	+ 2 Cu	Impossible	Impossible
Structure	 A	 B	Impossible	 D	 E		
Equivalency							
Ligand	no	yes		no	yes		
Pd	no	no		no	yes		

The incorporation of two Cu(I) metal centers into these hypothetical precursors gave conformationally more restricted species, some of which do not agree with the spectroscopic data. At first, the catenated topology c can be excluded because two sets of phenanthroline can not be combined by Cu(I) centers at the same time due to the steric reason.

^1H NMR experiments showed the equivalency of all four ligands. Thus, structures A and D, which involved inequivalent ligands, should be eliminated. Since NMR also indicated the equivalency of Pd(II) centers, the topology B is ruled out, which has inequivalent Pd(II). Therefore, we can conclude that the structure for $Cu(I)_2Pd(II)_4(ligand)_4$ is the doubly interlocking [2]catenane E.

3-10 Calculated structure of doubly interlocking catenane 3^{10+}

The optimized structure for 3^{10+} is depicted in Figure 6, which shows the absence of any distortion in the framework. This remarkable assembly process leads in a surprisingly efficient fashion to a 10-component architecture (6 metals and 4 ligands). Catenane 3^{10+} consists of two doubly interlocked 50-membered rings.

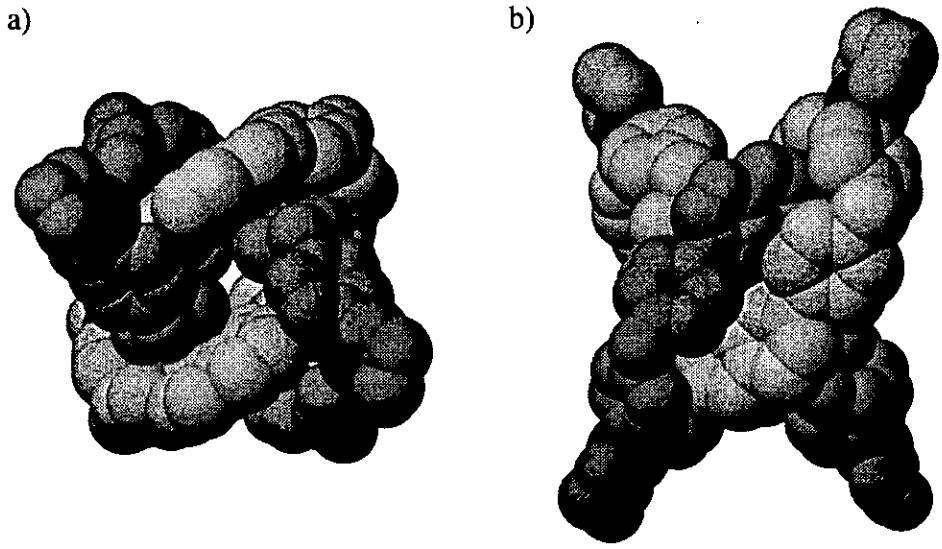
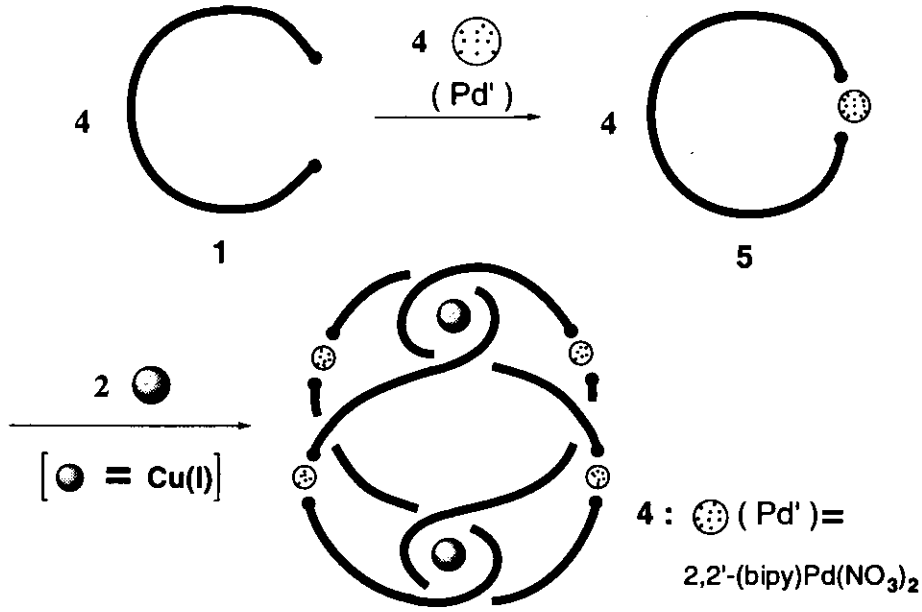


Figure 6. A molecular modeling of 3^{10+} optimized by Cerius^2 3.5 package program: For simplicity, only one enantiomer is represented throughout the paper. a) CPK presentation of optimized structure b) The view from another direction

3-11 Another approach to doubly interlocking catenane

Due to the labile bond of Pd-py, the self-assembly of doubly interlocking catenane was achieved by the different path way. This second approach is based on the catenation reaction from preformed Pd(II)-linked (Scheme 3). Bpy was selected as an ancillary palladium(II) ligand instead of ethylenediamine moiety so as to avoid coordination of the Pd centers to the phenanthroline unit of **1**, making the formation of square planar complexes very unlikely due to steric reasons. When **1** and (bpy)Pd(NO_3)$_2$ were mixed in CD_3CN:D_2O (1:1), the quantitative formation of a monomer ring was observed. The monomeric ring structure was confirmed by ^1H NMR, ^{13}C NMR, elemental analysis, and ESI mass spectroscopy. Subsequent addition of $Cu(I)^+$ led to the formation of a doubly interlocking catenane, which is analogous to 3^{10+}, with bpy on each Pd(II). The NMR observation showed that this reaction was also quantitative within the mixing time. This procedure shows the potentiality of reversible ring closing and opening

processes for constructing interlocking rings, in analogy with previous work.[5] The generation of the same doubly interlocking structure by the different two methods strongly suggests that these complexes are formed under thermodynamic control.



Scheme 3. The second approach for the preparation of doubly interlocking [2]catenanes via preformed ring structure

3-12 Formation of diastereomeric mixture by anion exchange with chiral anion

The doubly interlocking structure has topological chirality. In the formation process of $\mathbf{3}^{10+}$, the two enantiomers were generated as a racemic mixture. The following experiment strongly supported this chirality by the formation of diastereomemic mixture with chiral phosphate anions. After one nitrate was exchanged by chiral phosphate anion (potassium (*S*)-(-)-1,1-Binaphthyl-2,2'-diyl phosphate, 1 equivalent), each signals divided into two parts (Figure 7), whose ratio was estimated as 1: 1 by ^{1}H NMR integral ratio.

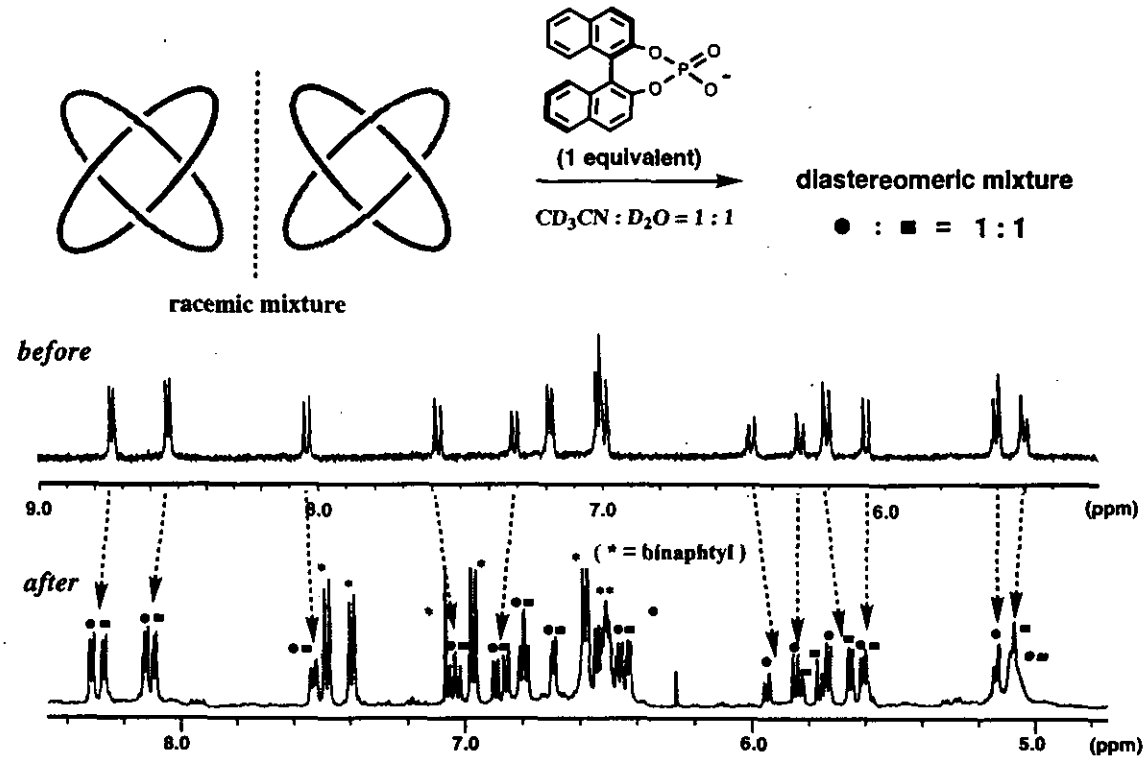


Figure 7. Spectroscopic observation of formation of diastereomeric mixture by anion exchange: (Before) compound 3^{10+} only (as racemate) (After) Each signals were divided into two parts, respectively.

3-13 Chiral induction by chiral palladium metal centers

By ^1H NMR observation, the reaction of precursor 2^+ and chiral metal center **6** gave two sets of the signal patterns, each of which is quite similar to that of compound 3^{10+}. This similarity suggests that those products also have doubly interlocking structure and these two products are diastereomeric mixture in 3 : 1 ratio (Figure 8).

This chiral induction deserved special attention. It does not seem that the chiral metal moiety **6** make such an effective chiral induction because it does not have a considerable asymmetric environment. However if each metal units would cause the slight energy difference (e.g. 0.2 - 0.5 kcal / mol), after the complexation, the whole energy difference could be large enough (e.g. 0.2 x 4 = 0.8 kcal / mol) to induce such the diastereomeric ratio.

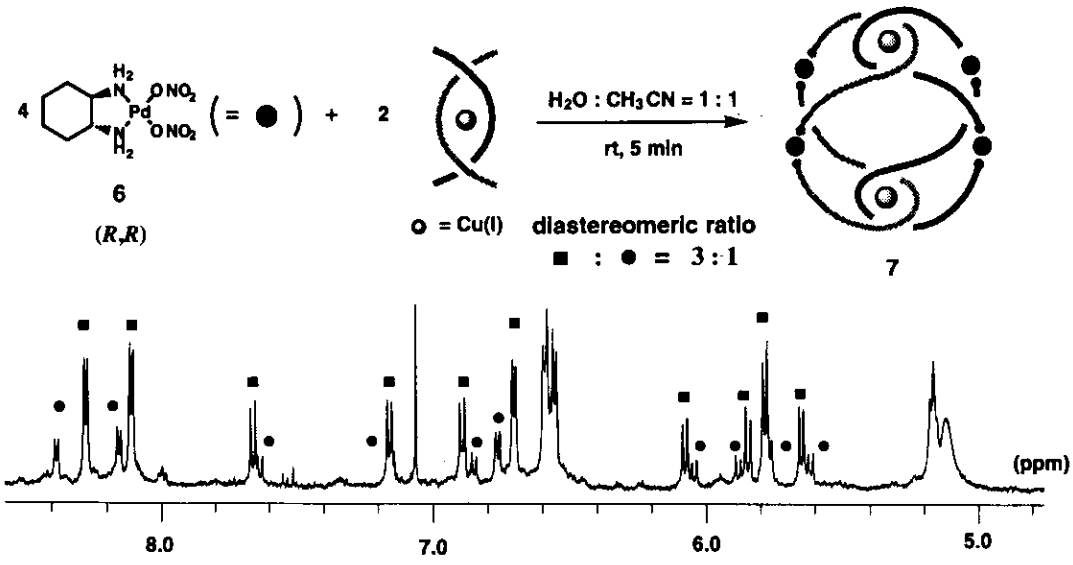


Figure 8. Chiral induction by the complexation of Pd(II) and precursor 2^{+}: Two sets of signals (solid circle and solid square) are ascribed to doubly interlocking structure.

When this diastereomeric mixture was employed to the CD (Circular Dichroism) measurement, remarkable negative Cotton effect was observed at 356 nm ($\Delta\varepsilon$ = -19.6 $dm^3 \cdot mol^{-1} \cdot cm^{-1}$) and 479 nm ($\Delta\varepsilon$ = -6.3 $dm^3 \cdot mol^{-1} \cdot cm^{-1}$) in Figure 9. Especially, absorption band at 479 nm is assigned to metal to ligand charge transfer effect (MLCT). This negative Cotton effect was owing to the molecular chirality[13-15] of the compound 3^{10+} since compound **6** itself does not have remarkable absorption bond around this region.

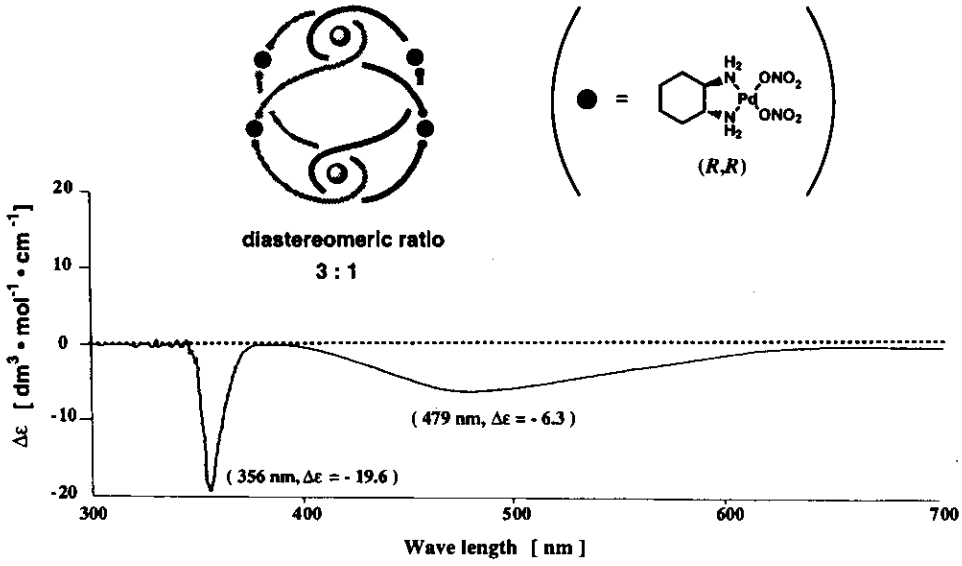


Figure 9. Circular dichroism (CD) measurement of diastereomeric mixture (ratio: 3 : 1): Negative Cotton effect was observed at 479 nm ($\Delta\varepsilon$ = -6.3 $dm^3 \cdot mol^{-1} \cdot cm^{-1}$) and 356 nm ($\Delta\varepsilon$ = -19.6 $dm^3 \cdot mol^{-1} \cdot cm^{-1}$). Conditions: CH_3CN : H_2O = 1:1, 25 °C

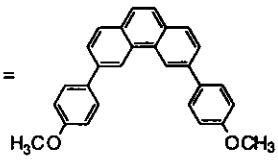
3-14 Electrochemical and electronic absorption spectroscopy properties

Catenane 3^{10+} (as PF_6 salt) displays interesting electrochemical and electronic absorption spectroscopy properties (Table 2). Cyclic voltammetry measurements showed that the redox potential of 3^{10+} (Cu^{II} / Cu^{I} = + 0.74 V) was relatively high compared to that of $Cu(dap)_2^+$ compound (Cu^{II} / Cu^{I} = 0.63 V; dap = 2,9-di(*p*-anisyl)-1,10-phenanthroline). In agreement with this high potential, a modest red shift was observed in UV-Vis spectroscopy when visible absorption band of catenane 3^{10+} (λ_{max} = 442 nm, ε = 2400 $mol^{-1} \cdot L \cdot cm^{-1}$) was compared to that of $Cu(dap)_2^+$ (λ_{max} = 435 nm, ε = 3140 $mol^{-1} \cdot L \cdot cm^{-1}$). These high redox potential and red shift property were ascribed to the presence of the positively charged Pd(II) metal in its frameworks.

Table 2. Electrochemical and electronic absorption spectroscopy properties

	Cu^{II} / Cu^{I} (V vs SCE)	λ_{max} (nm)	ε ($mol^{-1} \cdot L \cdot cm^{-1}$)
catenane 3^{10+}	**+ 0.74**	**442**	**3140**
$Cu(dap)_2^+$	**+ 0.63**	**435**	**2400**

dap =



2,9-di(*p*-anisyl)-1,10-phenanthroline

Solvent : CH_3CN
$c = 5.0 \times 10^{-4}$ ($mol \cdot L^{-1}$)
Bu_4NBF_4 (0.1 M)
Working electrode : Pt
Reference electrode : SCE

3-15 Conclusion

The combination of template strategy and self-assembly made it possible to synthesize the doubly interlocking [2]catenanes with high efficiency. This new strategy has enormous potential to apply to various multicomponent systems. And the formation of the same structures by the different path way indicated that the interlocking structures were constructed as the result of thermodynamic control.

Furthermore, the chiral induction by using chiral sources deserved special attention. The induction ability of each part is not so strong, however, total preferential effect produced the huge driving force to generating one of a diastereomer.

3-16 Experimental Section

The synthesis of 2,9-bis[4-(4-pyridylmethyl)phenyl]-1,10-phenanthroline 1 To a THF (80 mL) solution of diisopropylamine (3.7 mL, 26.4 mmol), *n*-BuLi (16.5 mL, 26.4 mmol, 1.6 M in hexane) was added at 0 °C over 5 min. After the reaction mixture was stirred for 10 min at 0 °C, 4-methylpyridine (2.3 mL, 24 mmol) was added at the same temperature, then the mixture was stirred for 15 min at 0 °C. A THF solution of $ZnCl_2$ (53 mL, 26.4 mmol, 0.5 M in THF) was added at 0 °C, then insoluble white materials were formed. To this mixture, $PdCl_2(PPh_3)_2$ (350 mg, 0.5 mmol) and 2,9-bis(4-bromophenyl)-1,10-phenanthroline (1.96 g, 4.00 mmol) were added, then the color of the solution turned into purple. The reaction mixture was stirred for 3 days at reflux temperature (85 °C). After the mixture was cooled down to room temperature, ethylenediamine (5 mL) and H_2O (10 mL) were added and stirred for 3 h. The solution was extracted with chloroform (100 mL x 2) and then the combined organic layers was dried over $MgSO_4$, filtered, and evaporated to dryness to give a crude product (3.64 g). The crude product was purified by column chromatography (silica gel, $CHCl_3$: 2% MeOH) to give the titled compound as pale yellow crystal (1.44 g, 2.8 mmol, 70% yield). ^1H NMR (500 MHz, $CDCl_3$, TMS as internal standard) δ 8.53 (d, J = 5.9 Hz, 4 H, Py$H\alpha$), 8.40 (d, J = 8.3 Hz, 4 H, PhHm), 8.31 (d, J = 8.3 Hz, 2 H, H_4 and H_7), 8.12 (d, J = 8.3 Hz, 2 H, H_3 and H_8), 7.79 (s, 2 H, H_5 and H_6), 7.39 (d, J = 8.3 Hz, 4 H, PhHo), 7.16 (d, J = 5.9 Hz, 4 H, Py$H\beta$), 4.08 (s, 4 H, CH_2); ^{13}C NMR (126 MHz, $CDCl_3$, TMS as internal standard) δ 156.50 (*C*q), 149.92 (*C*H), 149.90 (*C*q), 146.14 (*C*q), 140.18 (*C*q), 138.14 (*C*q), 136.96 (*C*H), 129.67 (*C*H), 128.08 (*C*H), 127.94 (*C*q), 126.04 (*C*H), 124.30 (CH), 119.93 (*C*H), 41.03 (CH_2); IR (KBr, cm^{-1}) 3646.2, 3586.4, 3333.7, 3282.6, 1621.1, 1608.5, 1586.3, 1490.9, 1435.9, 840.9, 739.7, 558.4.; mp 89.0 - 91.5 °C; HR-MS (EI) Calcld for $C_{36}H_{26}N_4(M^+)$, 514.2178. Found 514.2171.

Synthesis of doubly interlocking [2]catenane 3 To a acetonitrile solution (0.5 mL) of 2,9-bis[4-(4-pyridylmethyl)phenyl]-1,10-phenanthroline **1** (31 mg, 0.06 mmol), tetrakis(acetonitrile)-copper(I) hexafluorophosphate (11 mg, 0.03 mmol) was added at 25 °C under Argon atmosphere. This red brown solution was stirred for 20 min to give the catenane precursor **2**. To the reaction mixture, an aqueous solution (1 mL) of ethylenediamine palladium nitrate (18 mg, 0.06 mmol) was added at 25 °C. The mixture was stirred for 20 min. To the reaction mixture, an aqueous KPF_6 (0.3 M, 2 mL) was added to give red-brown precipitates, and then it was stirred for

4 h at room temperature. The red-brown solids were filtered, dried to give the titled compound (60 mg, 92%). Physical data of catenane $\mathbf{3}^{10+}$ (as PF_6 salt): ^1H NMR (400 MHz, D_2O, 80 °C, TMS as internal standard) δ 8.73 (d, J = 6.4 Hz, 4 H, Py$H\alpha$), 8.53 (d, J = 6.4 Hz, 4 H, Ph$H\alpha'$), 8.03 (d, J = 8.3 Hz, 2 H, H_4), 7.57 (d, J = 8.3 Hz, 2 H, H_3), 7.31 (d, 2 H, J = 8.0 Hz, H_7), 7.18 (d, J = 6.4 Hz, 4 H, Py$H\beta$), 7.01 (d, J = 6.4 Hz, 4 H, Py$H\beta'$), 6.99 (d, J = 8.3 Hz, 4 H, PhHm), 6.47 (d, J = 8.8 Hz, 2 H, H_5), 6.30 (d, J = 8.8 Hz, 2 H, H_6), 6.20 (d, J = 8.3 Hz, 4 H, PhHo), 6.06 (d, 2 H, J = 8.0 Hz, H_8), 5.60 (d, J = 8.0 Hz, 4 H, PhHm'), 5.50 (d, J = 7.8 Hz, 4 H, PhHo'), 3.58 (d, J = 15.6 Hz, 2 H, CHb), 3.37 (d, 2 H, J = 13.4 Hz, CHa), 3.12 (d, J = 13.4 Hz, 2 H, CHa'), 2.89 (d, J = 15.6 Hz, 2 H, CHb'), 2.75 - 2.70 (broad two singlets, 8 H, -CH_2CH_2-); ^{13}C NMR (CD_3CN, 126 MHz, TMS as external standard); 154.91, 154.85, 151.24, 151.16, 142.37, 142.33, 139.01, 137.03, 136.95, 136.45, 136.28, 136.14, 129.13, 128.13, 127.65, 127.49, 127.32, 127.12, 126.64, 126.52, 126.48, 126.27, 125.42, 124.79, 124.41, 122.73, 39.99, 39.65, 39.47, 39.10. IR (KBr, cm^{-1}) 3021.3, 2939.3, 2922.9, 1596.9, 1587.3, 1569.0, 1558.4, 1489.9, 1414.7, 846.7, 792.7, 781.1, 749.3; ESI-MS (CH_3CN) *m/z* (relative intensity) 1289.1 {[**3** - $(PF_6^-)_3]^{3+}$, 47%}, 930.4 {[**3** - $(PF_6^-)_4]^{4+}$, 98%}, 715.3 {[**3** - $(PF_6^-)_5]^{5+}$, 100%. Anal. Calcd for $\mathbf{3}^{10+} \cdot (H_2O)_{3.5}$, ($C_{76}H_{75}CuF_{30}N_{12}O_{3.5}P_5Pd_2$): C, 41.24; H, 3.41; N, 7.59.; Found: C, 40.89; H, 3.05; N, 7.54.

The synthesis of bpy-protected Pd monomeric ring compound Under nitrogen atmosphere, it was reacted by an CH_3CN (1.5 mL) solution of ligand **1** (31 mg, 0.06 mmol) and an aqueous solution (1.5 mL) of bpy-protected palladium complex (byp(Pd)$(ONO_2)_2$) (23.1 mg, 0.06 mmol). This solution was stirred at 25 °C for 2 h. To the red brown solution, an aqueous KPF_6 (2 mL, 213 mg) was added to form red brown precipitate. This reaction mixture was stirred for 12 h. The precipitate was filtered and dried to give the titled compounds as brown solids (46 mg, 0.044 mmol, 73% yield). Physical data of monomeric ring (as PF_6 salt): ^1H NMR (500 MHz, DMSO-d_6, TMS as external standard) δ 8.76 (d-like, J = 6.1 Hz, 4 H, Py$H\alpha$), 8.33 (d, J = 8.1 Hz, 2 H, bpyH_3), 8.12 (d, J = 8.3 Hz, 2 H, H_4 and H_7), 8.06 (t-like, J = 8.1 Hz, J = 5.4 Hz, 2 H, bpyH_4), 7.82 (d, J = 8.3 Hz, 2 H, H_3 and H_8), 7.72 (d, J = 8.1 Hz, 4 H, PhHm), 7.34 (d-like, J = 6.1 Hz, 4 H, Py$H\beta$), 7.29 (t-like, J = 8.1 Hz, J = 5.4 Hz, 2 H, bpyH_5), 6.84 (d, J = 8.1 Hz, 4 H, PhHo), 6.70 (d, J = 5.4 Hz, 2 H, bpyH_6), 3.87 (s, 4 H, -CH_2-); ^{13}C NMR (DMSO-d_6, 126 MHz, TMS as external standard) 156.16, 155.88, 155.77, 151.44, 149.44, 144.95, 142.68, 140.00, 138.60, 137.06, 129.10, 128.99, 128.69, 128.35, 127.00, 125.89, 124.67, 119.92. mp 220 °C

dec. Anal. Calcd for $C_{46}H_{34}F_{12}N_6P_2Pd \cdot 0.5(CHCl_3)$: C, 49.56; H, 3.09; N, 7.46. Found: C, 49.22; H, 3.02; N, 7.59.: ESI-MS (CH_3CN) *m/z* (relative intensity) 921.4 {[M - (PF_6^-)]$^+$, 100%}, 388.2 {[M - (PF_6^-)$_2$]$^{2+}$, 44%}.

The synthesis of doubly locking [2]catenane analogue Under nitrogen atmosphere, was reacted the mixture of an CH_3CN (2 mL) solution of ligand **1** (21 mg, 0.04 mmol) and an aqueous solution (1 mL) of bpy-protected palladium complex (byp(Pd)(ONO_2)$_2$) (15.4 mg, 0.04 mmol). After stirred for 15 min, tetrakis(acetonitrile)copper(I) hexafluorophasphate (7.4 mg, 0.02 mmol) was added. The reaction mixture was stirred for 30 min at 25 ^oC. This solution was poured into an aqueous KPF_6 (148 mg, H_2O 1.5 mL). Immediately, red brown precipitate was formed. This reaction mixture was stirred for 1 h. Then, the precipitate was filtered and dried to give the titled compounds as brown solids (39 mg, 0.0083 mmol, 83% yield). ^1H NMR (500 MHz, D_2O, TMS as an external standard) δ 9.46 (d, *J* = 5.9 Hz, 2 H, Py*H*α1), 9.27 (d, *J* = 5.9 Hz, 2 H, Ph*H*α2), 9.20 (d, *J* = 6.1 Hz, 2 H, Py*H*α'1), 9.03 (d, *J* = 5.6 Hz, 2 H, Ph*H*α'2), 8.56 (d, *J* = 9.1 Hz, 2 H, bpyH_3), 8.54 (d, *J* = 10.7 Hz, 2 H, bpyH_3'), 8.47 (t, *J* = 8.7 Hz, 2 H, bpyH_5), 8.40 (t, *J* = 8.7 Hz, 2 H, bpyH_5'), 8.32 (d, *J* = 8.6 Hz, 2 H, H_4), 7.92 (d, *J* = 5.4 Hz, 2 H, Py*H*β1), 7.85 (d, *J* = 8.6 Hz, 2 H, H_3), 7.84 (broad signal, 2 H, Py*H*β'2), 7.74 (t, *J* = 7.5 Hz, 2 H, bpyH_4), 7.71 (d, *J* = 8.3 Hz, 2 H, H_7), 7.58 (t, *J* = 7.4 Hz, 2 H, bpyH_4'), 7.50 (d, *J* = 4.9 Hz, 2 H, bpyH_6), 7.43 (d, *J* = 5.9 Hz, 2 H, Py*H*β'1), 7.26 (d, *J* = 8.3 Hz, 4 H, Ph*H*m), 7.21 (d, *J* = 5.2 Hz, 2 H, Py*H*β'2), 7.11 (d, *J* = 4.9 Hz, 2 H, bpyH_6'), 6.58 (d, *J* = 9.0 Hz, 2 H, H_5), 6.55 (d, *J* = 8.8 Hz, 2 H, H_6), 6.52 (d, *J* = 8.3 Hz, 4 H, Ph*H*o), 6.40 (d, *J* = 8.1 Hz, 2 H, H_8), 5.85 (broad singlets, 8 H, Ph*H*o', Ph*H*m'), 3.92 (d, *J* = 15.6 Hz, 2 H, CH_b), 3.74 (d, *J* = 13.0 Hz, 2 H,CH_a), 3.46 (d, *J* = 13.1 Hz, 2 H,CH_a'), 3.32 (d, *J* = 15.4 Hz, 2 H, CH_b'). High Resolution ESI MS Calcd for [M-6(PF_6^-)]$^{6+}$ 635.9127, Found 635.9147. +2.0mmu, 3.1 ppm.

3-17 References and Notes

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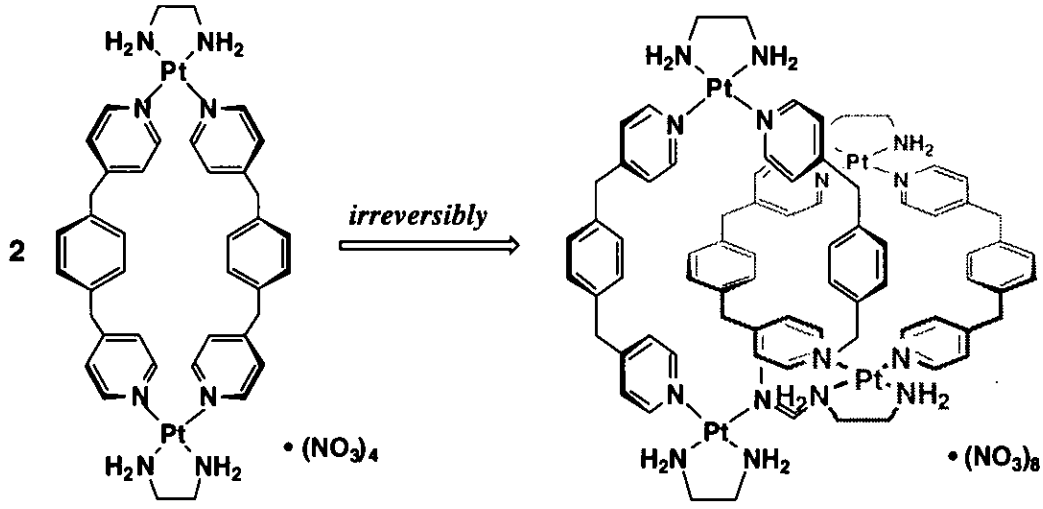
Chapter 4

A Molecular Lock. Synthesis and Characterization of Platinum Analogous [2]Catenane and Square Complex

J. Am. Chem. Soc. **1995**, *117*, 4175.

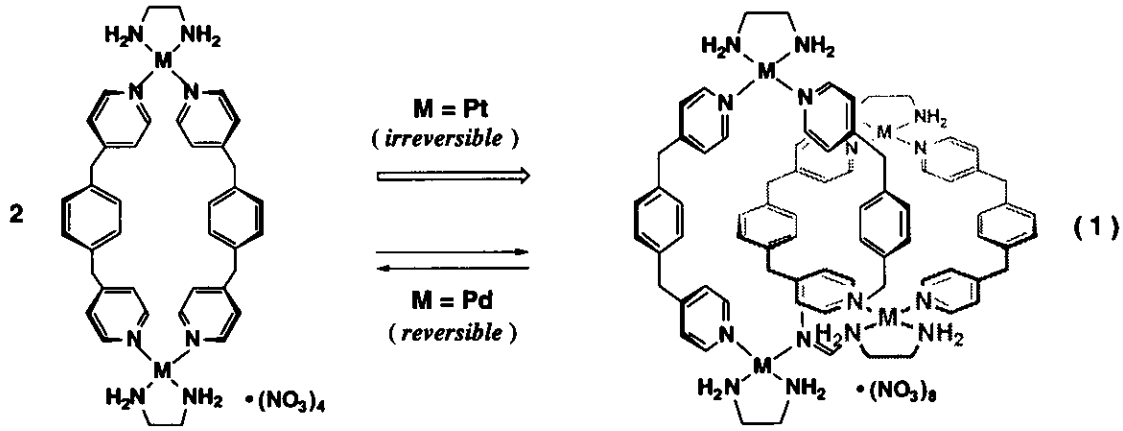
Abstract In this chapter, "a molecular lock" concept and its application to the synthesis of stable catenanes and square complexes are described. The molecular lock concept stems from the unique dual character of a Pt(II)-pyridine coordinate bond. That is, the Pt(II)-Py bond is inert under room temperature in water. However the bond becomes labile in highly polar media at elevated temperature. Due to this behavior, the Pt(II)-Py coordinate bond can be locked and released and, hence, is likened to a lock. By the incorporation of this Pt(II)-Py bond or " a molecular lock" into ring frameworks, the one-way formation of a [2]catenane is achieved. Application of molecular lock into the synthesis of kinetically stable tetranuclear square complex is also described.



4-1 Introduction

Interlocking ring structures continue to fascinate chemists, partly in expectation of serving molecular-scale devices.[1,2] Research in this area is now booming, mainly due to the recent development of templated synthetic strategies of Sauvage[3,4] and π-stacking-mediated self-assembly approaches of Stoddart.[5,6] In the proceeding chapter, the quantitative self-assembly of [2]catenane exploiting the labile nature of a palladium(II)-pyridine (Pd(II)-Py) coordinate bond is described.[7] There exists quite fast equilibration between monomeric ring **1b** and catenane **2b**. The presence of the equilibrium means that [2]catenane **2b**, once formed, easily dissociates into two separate rings.

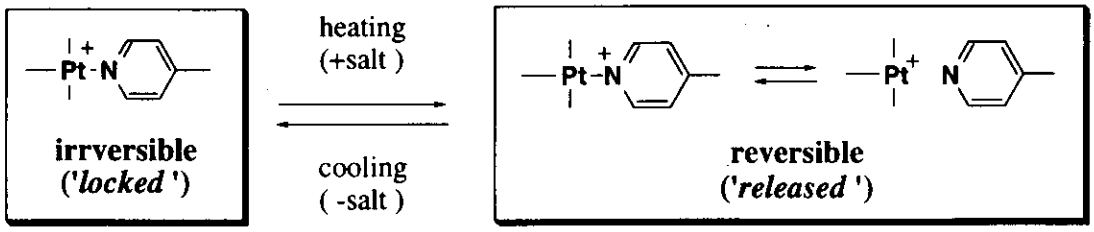
In contrast, if the labile coordinate bond can be frozen after the catenane formation, a complete catenane that would not dissociate into two rings will be obtained. Such a one-way formation of catenane **2a** is now achieved in a platinum(II) counterpart system, as described below.



1 (1a: M = Pt; 1b: M = Pd) 2

4-2 A molecular lock concept

Here the concept of a "molecular lock" is introduced exploiting the dual character of a platinum(II)-pyridine (Pt(II)-Py) coordinate bond. This bond can be likened to a lock since it is irreversible ("locked") under ordinary conditions but becomes reversible ("released") in highly polar media at elevated temperature (Scheme 1). Under forcing conditions, rapid dissociation of Pt(II)-Py bond would lead to self-assembly of thermodynamically stable products.



Scheme 1. Schematic presentation of the molecular lock

Incorporation of the molecular lock into a macrocyclic backbone made it possible to irreversibly interlock two molecular rings. Thus, molecular ring **1a** involving the Pt(II)-Py bond is on the lock in water and is not in equilibrium with its catenated dimer **2a**, or any other structures. However, once the lock is "released" by adding $NaNO_3$ and heating at 100 °C, an equilibrium is strongly pushed toward the catenane by polar media. After self-assembling in a high yield, catenane **2a** is again locked up by cooling to room temperature and removing $NaNO_3$. This procedure completes molecular manipulation in which an organic architecture is built up by molecule-by-molecule.

4-3 Synthesis of [2]catenane by using molecular lock

Pyridine-based ligand **4** (0.1 mmol) was suspended in D_2O solution (4 mL) of ethylene-diamineplatinum(II) nitrate complex **3** (0.1 mmol) (Figure 1). Then, the mixture was heated at 100 °C. Ligand **4** gradually dissolved, and after 12 h, ^1H NMR showed highly efficient formation of molecular ring **1a** (Figure 1a). The formation of **1a** is kinetically controlled since the dissociation of the Pt(II)-Py bind under the reaction conditions is negligible. However, after sodium nitrate was added to the solution of **1a** ($[NO_3^-]$ = 5 M) and the solution was heated at 100 °C, a dramatic change in ^1H NMR spectroscopy was observed: Signals of **1a** were gradually transferred into those of **2a**, and the complete formation of **2a** was observed after 24 h (Figure 1b). It was confirmed that catenane **2a**, isolated as its perchlorate salt from the solution, did not dissociate any longer into **1a** in D_2O even at 100 °C. The physical data of these compounds were quite similar to those of Pd counterpart **2b** that has been reported previously.[7]

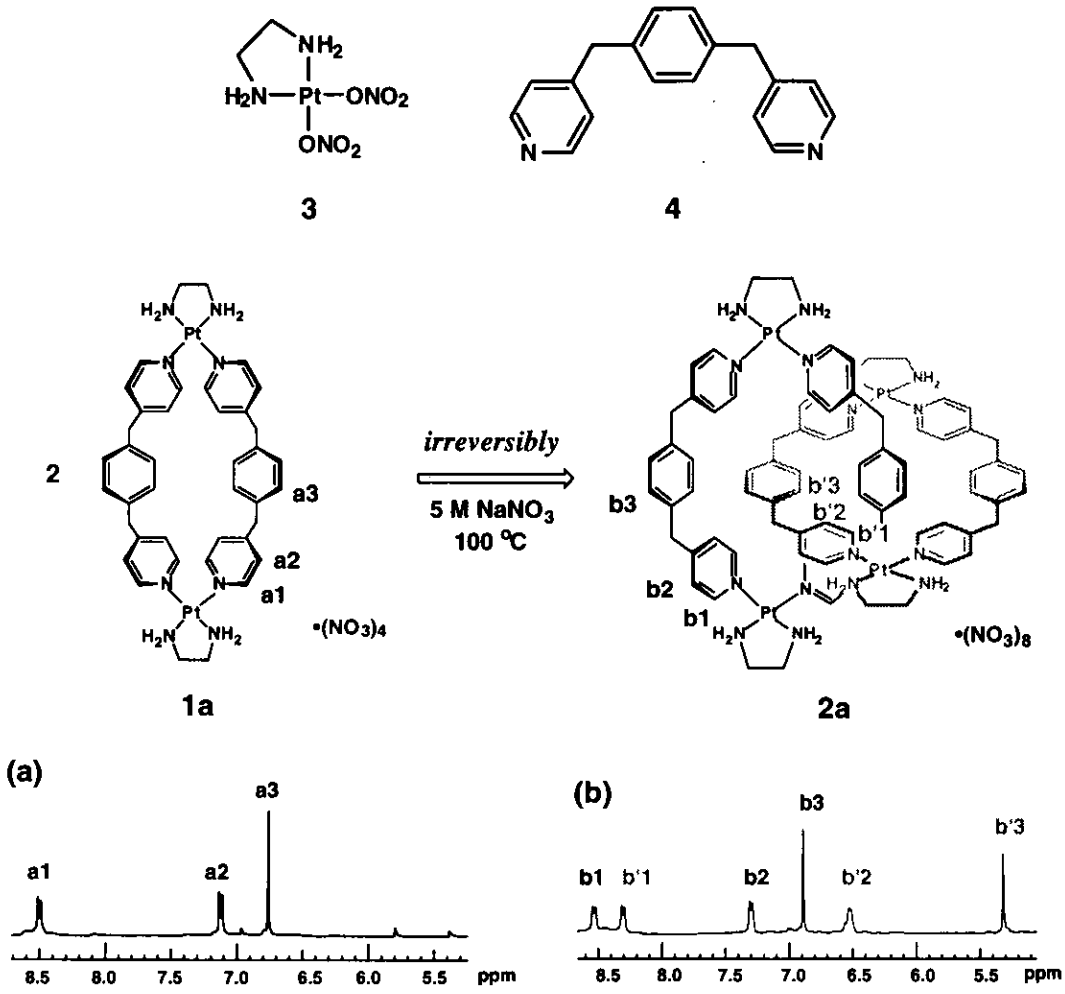


Figure 1. ^{1}H NMR observation (500 MHz, D_2O, TMS) of the transfer of **1a** into **2a** by releasing the molecular lock: Molecular ring **1a** (25 mM) was heated at 100 °C in D_2O solution of $NaNO_3$ (5 M). (a) After 0 h, signals a1, a2, and a3 are assigned as Py*H*α, Py*H*β, and C_6H_4 protons of **1a**, respectively. (b) After 24 h, signals b and b' are referred to the outside and inside ligands of **2a**, respectively.

The overall one-way transformation of **1a** into **2a** is schematically illustrated in Figure 2. Initially, a molecular ring is on the lock (A). The lock is then released by adding salt and heating (B), allowing the self-assembly of a catenated framework (C). Finally, this framework is locked by removing the salt and cooling (D).

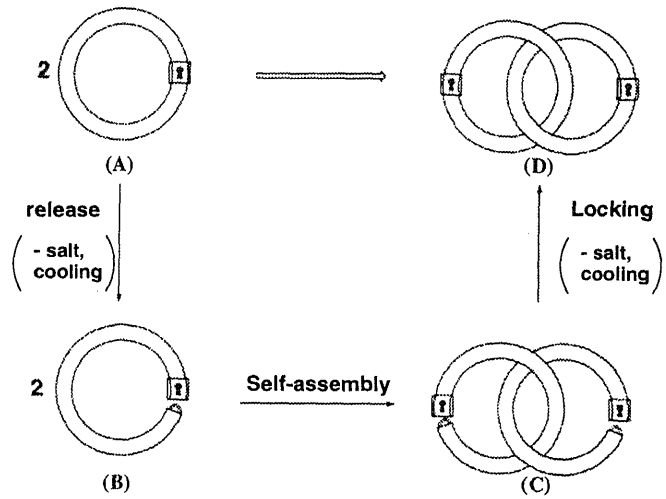


Figure 2. Irreversible formation of the [2]catenane from two complete rings by the use of the molecular lock

4-4 Crystal structure of [2]catenane 2a

Crystallography showed that the catenated structure of **2a** surely exists (Figure 3).[8] Single crystals were obtained from aqueous solution of [2]catenane **2a** (12.5 mM) containing $NaNO_3$ (5 M) by allowing the solution to stand at 15 °C for several days. It was found that boat-shaped two molecular rings interlock each other with edge-to-face aromatic-aromatic contact[9] that probably induces the self-assembly of the catenated structure in polar media. Counter-anion and water molecules of crystallization seem highly disordered since two NO_3^- ions and water molecules were missing in the crystallographic study even in the measurement at 173 K.

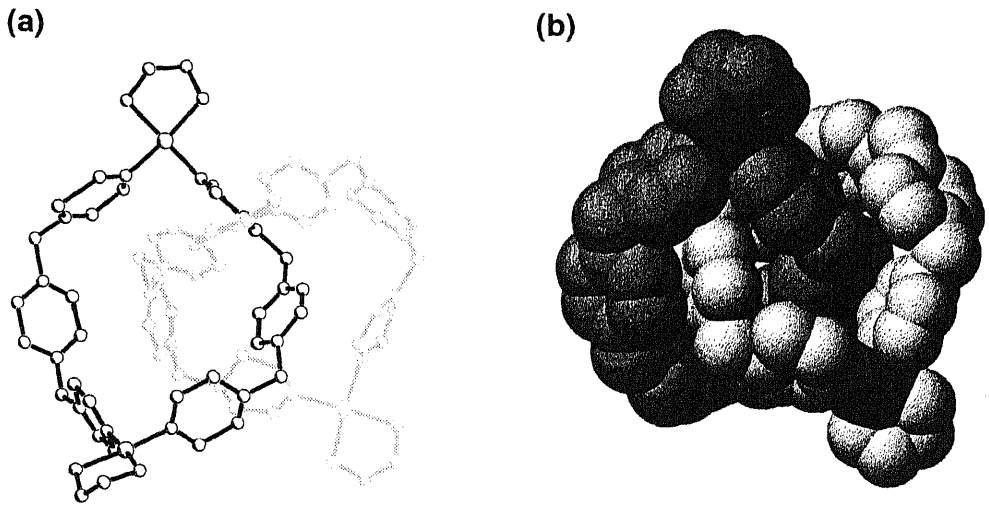


Figure 3. The crystal structure of catenane **2a**: (a) Ball-and-stick presentation and (b) CPK presentation

CPK presentation of catenane **2a** clearly indicates that some stabilization factor effectively work in order to generate and keep the catenane structure. The aromatic rings are nearly perpendicular to each other, suggesting CH-π interactions play an important role for the catenane conformation. Hydrophobic interactions should be also crucial for the catenane structure in the highly polar media such as H_2O. The doubly molecular recognition should be important in catenane conformation as mentioned in chapter 2.

4-5 Synthesis of square complex with molecular lock

The concept of the molecular lock was next applied to the preparation of the fully locked tetranuclear Pt(II) macrocycle **5a**. When platinum complex **3** was treated with 4,4'-bipyridine (1 mol equiv) in D_2O, an intractable oligomeric mixture was initially formed as kinetic products (Figure 5a). After the lock was released by addition of $NaNO_3$ and heating at 100 °C, the mixture was converged to the thermodynamically most favorable structure **5a** (Figure 4b), which was isolated in 50% yields as a locked form by adding $NaClO_4$. In the absence of $NaNO_3$, very slow transfer from kinetic products into **5a** was observed at 100 °C, however, more than a month was required to accomplish the transfer in a high yield.

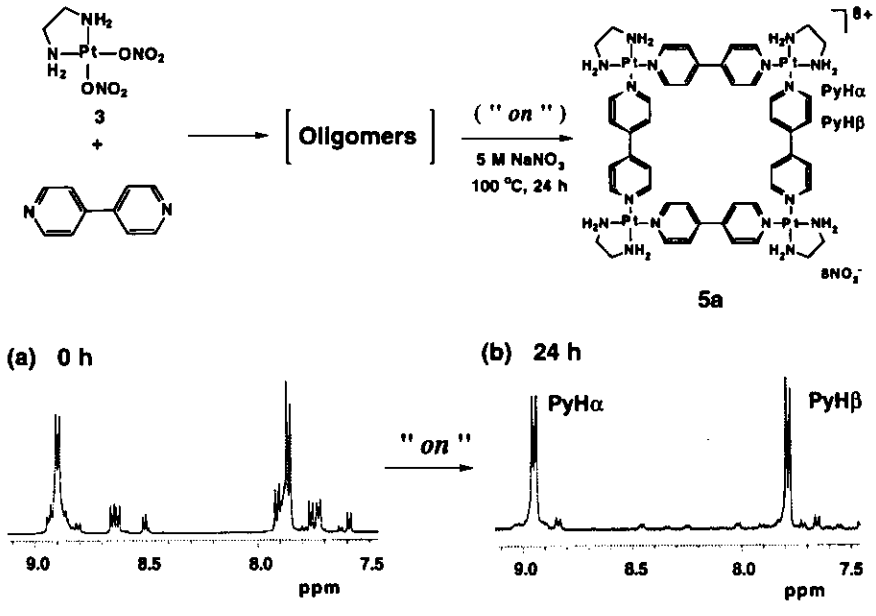


Figure 4. ^1H NMR observation (500 MHz, D_2O, TMS) of the transfer of an oligomeric mixture into **5a** by releasing the molecular lock: The oligomeric mixture given by mixing **3** (10 mM) and 4,4'-bipyridine (10 mM) was heated at 100 °C in D_2O solution of $NaNO_3$ (5 M). (a) After 0 h. (b) After 24 h. Doublet signals appearing at δ 8.82 and 7.78 are referred to the Py*H*α and Py*H*β protons of **5a**, respectively.

4-6 Stability of platinum containing catenane 5a

A significant difference between **5a** and a palladium (II) counterpart **5b**[10] was demonstrated by comparing their stability. Addition of (en)Pd(ONO_2)$_2$ (2.4 mol equiv) to **5b** in D_2O resulted in redistribution of products, giving a mixture of **5b** (ca. 50%) and two acyclic components having Pd:bpy = 1 : 2 and 2 : 3 stoichiometries (Figure 5b). In striking contrast, **5a** was kept intact upon addition of **3** since its structure had been locked (Figure 5a). Recently, it was found out that this Pt(II)-Py coordination bond has outstanding stability to acidic and basic conditions as discussed in the next chapter.

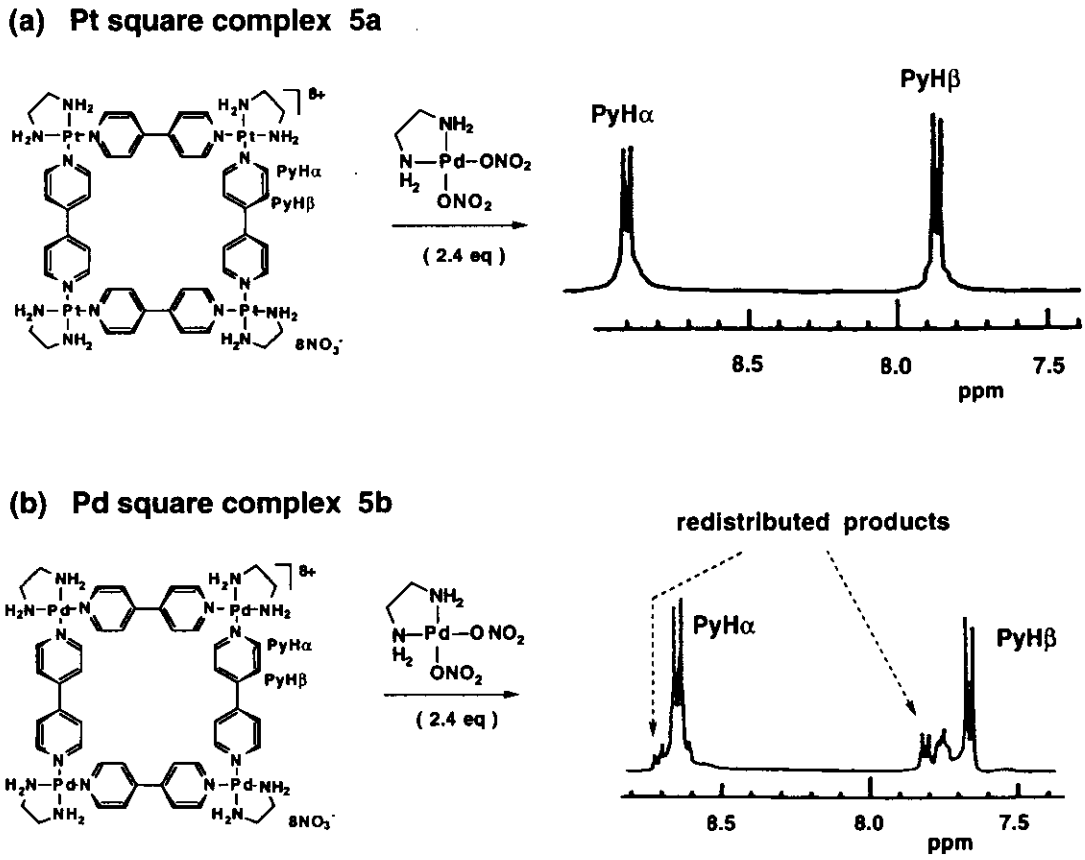


Figure 5. The stability of the tetranuclear complexes by ^{1}H NMR (500 MHz, D_2O, TMS): (a) Even by the addition of (en)Pd(ONO_2)$_2$, the square structure kept intact. (b) By the addition of (en)Pd(ONO_2)$_2$, some redistributed products were observed on ^{1}H NMR spectrum.

4-7 Conclusion

In conclusion, the irreversible formation of [2]catenane **2a** and tetranulear square complex **5b** were achieved by the incorporation of molecular lock into the ring frameworks. Because the Pt(II)-pyridine coordinate bond has remarkable stability, the catenane structure remains

unchanged under acidic and basic conditions in which palladium counterpart is easily decomposed. By controlling the reversibility of coordinate bond, we succeeded in the construction of kinetically stable structures via self-assembly process.

4-8 Experimental section

Synthesis of monomeric ring 1a A mixture of ethylenediamineplatium dichloride (98 mg, 0.300 mmol) and silver nitrate (102 mg, 0.600 mmol) in H_2O (6 mL) was stirred at 100 °C for 2 h in dark places. To this reaction mixture, an activated carbon was added, and this mixture was exposed by ultrasonic wave, then was filtered. To this filtrate (5 mL), 1,4-bis[(4-pyridyl)methyl]benzene (65 mg, 0.250 mmol) and H_2O (5 mL) were added. The concentration of [Pt^{2+}] was 25 mM. This mixture was stirred at 100 °C for 88 h to give monomeric platinum ring complex.

Self-assemble of catenane 2a In a sealed testing tube, H_2O (1.5 mL) was added to a (en)$PtCl_2$ (98 mg, 0.3 mmol) and a silver nitrate (102 mg, 0.6 mmol). This mixture was stirred at 100 °C for 2 h protected from light. After cooled to room temperature, an activated carbon was added and was exposed the ultrasound waves, then filtered. To this filtrate (1 mL), was added $NaNO_3$ (2.12 g). To this clear solution, 1,4-bis(4-pyridylmethyl)benzene (65 mg, 0.25 mmol) was added. This mixture was stirred at 100 °C for 24 h. The solvent was evaporated and residue was dried *in vacuo*.

Purification of this crude product by preparative thin layer chromatography (1N $NaNO_3$: MeOH = 1 : 3) followed by reprecipitation with aqueous $NaClO_4$ gave the product (43 mg, yield 30%, as ClO_4 salt) as white solid. ^1H NMR (D_2O, TMS/$CDCl_3$ as external standard) δ 8.55 (d-like, J = 6.6 Hz, 8 H, PyH_α), 8.30 (d-like, J = 6.6 Hz, 8 H, PyH'_α), 7.38 (d-like, J = 6.6 Hz, 8 H Py$H\beta$), 6.91 (s, 8 H, PhH), 6.59 (d-like, J = 6.6 Hz, 8 H, Py$H'\beta$), 5.34 (S, 8 H, -Ph'H-), 3.93 (s, 8 H, -CH_2-), 3.04 (s, 8 H, -CH'_2-), 2.83 (s, 16 H, -NCH_2CH_2N-); ^{13}C NMR (D_2O, TMS/$CDCl_3$ as external standard) δ 156.24 (*C*q), 154.98 (*C*q), 150.78 (*C*H), 150.67 (*C*H), 136.22(*C*q), 135.42 (*C*q), 129.72 (*C*H), 128.45 (*C*H), 127.27 (*C*H), 126.56(*C*H), 46.73 (CH_2), 46.65 (CH_2), 39.80 (CH_2), 39.57 (CH_2); FAB-MS (*m/z*) 2757 $[M-(ClO_4)]^+$, 2657 $[M-(ClO_4)-(HClO_4)]^+$, 2556 $[M-(ClO_4)-(HClO_4)_2]^+$; m.p. >250 °C (decomp.) Brief crystal data: Empirical formula, $C_{80}H_{96}N_{24}$ •$O_{24}Pt_4$ • xH_2O (x = ca. 4.0); formula weight, 2558.14; crystal color, habit, colorless,

prismatic; Lattice type, primitive; lattice parameters, a = 17.351(2), b = 23.520(2), and c = 26.219(3) Å, β = 92.22(1) °; V = 10691(1) Å^3

Synthesis of tetranuclear complex. A mixture of ethylenediamineplatinum dichloride (91 mg, 0.28 mmol) and silver nitrate (95 mg, 0.56 mmol) in D_2O (4 mL) was stirred for 2 h at 100 °C in dark places. An activated carbon was added. Then, the mixture was exposed with ultrasound wave and filtered. The mixture of the filtrate (3 mL) and 4,4-bipyridine (33 mg, 0.21 mmol) was stirred at 100 °C for 24 h. To this reaction mixture (2 mL), sodium nitrate (854 mg) was added. This mixture was stirred at 100 °C for 24 h. To the reaction mixture (1.5 mL), aqueous solution (5 mL) of sodium perchlorate (1.05 g) was added to form precipitates. The reaction mixture was stirred at room temperature overnight. This reaction mixture was filtered. The residue was dried *in vacuo* to give the titled product as white solid (33 mg, yield 45%). ^{1}H NMR (270 MHz, D_2O, TMS as external standard) δ 8.55 (d-like, J = 6.6 Hz, 8 H, Py$H\alpha$), 8.30 (d-like, J = 6.6 Hz, 8 H, Py$H\alpha$'), 7.38 (d-like, J = 6.6 Hz, 8 H, Py$H\beta$), 6.91 (s, 8 H, PhH), 6.59 (d-like, J = 6.6 Hz, 8 H, Py$H\beta$'), 5.34 (s, 8 H, PhH'), 3.93 (s, 8 H, CH_2), 3.04 (s, 8 H, CH'_2), 2.83 (s, 16 H, -NCH_2CH_2N-). ^{13}C NMR (67 MHz, D_2O, TMS as external standard) δ 156.24 (*C*q), 154.98 (*C*q), 150.78 (*C*H), 150.67 (*C*H), 136.22 (*C*q), 135.42 (*C*q), 129.72 (*C*H), 128.45 (*C*H), 127.27 (CH), 126.56 (C*H*), 46.73 (CH_2), 46.65 (CH_2), 39.80 (CH_2), 39.57 (CH_2). m.p. > 250 °C (decomp). FAB MS (*m/z*, as ClO_4 salt) 2757 [M - (ClO_4)]$^+$, 2657 [M - (ClO_4) - ($HClO_4$)]$^+$, 2557 [M - (ClO_4) - ($HClO_4$)$_2$]$^+$.

Crystallographic experimental details:

A. Crystal Data

Empirical Formula	$C_{80}H_{96}N_{24}Pt_4$
Formula Weight	2558.14
Crystal Color, Habit	colorless, prismatic
Crystal Dimensions	0.25 X 0.20 X 0.50 mm
Crystal System	monoclinic
Lattice Type	Primitive
No. Reflections Used for Unit Cell Determination (2θ range)	3(44.0 - 45.7 °)
Omega Scan Peak Width at Half-height	0.22 °
Lattice Parameters	a = 17.351(2) *Å*

	b = 23.520(2) Å
	c = 26.219(3) Å
	β = 92.22(1) °
	V = 10691(1) $Å^3$
Space Group	$P2_1/n$ (#14)
Z value	4
D_{calc}	1.589 g/cm^3
F_{000}	4992.00
μ(CuKα)	98.15 cm^{-1}

B. Intensity Measurements

Diffractometer	Rigaku AFC5S
Radiation	CuKα (λ = 1.54178 Å)
	graphite monochromated
Attenuator	Ni Foil (Factors = 1.00, 3.57, 12.70, 45.11)
Take-off Angle	6.0 °
Detector Aperture	9.0 mm horizontal
	13.0 mm vertical
Crystal to Detector Distance	258 mm
Temperature	-173.0 °C
Scan Type	ω-2θ
Scan Rate	32.0°/min (in w) - up to 3 scans
Scan Width	(1.00 + 0.30 tan θ) °
$2\theta_{max}$	121.9 °
No. of Reflections Measured	Total: 16145
	Unique: 15533 (R_{int} = 0.099)
Corrections	Lorentz-polarization
Absorption	(trans. factors: 0.9218 - 1.0857)

C. Structure Solution and Refinement

Structure Solution	Direct MethodsRefinement
Full-matrix least-squares	
Function Minimized	$\Sigma\omega(\|Fo\| - \|Fc\|)^2$
Least Squares Weights	$1/[\sigma^2(Fo)] = 4Fo^2/[\sigma^2(Fo^2)]$
p-factor	0.04
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (I>3.00σ(I))	4157
No. Variables	937
Reflection/Parameter Ratio	4.44
Residuals: R; Rw	0.116; 0.161

Goodness of Fit Indicator	3.51
Max Shift/Error in Final Cycle	4.09
Maximun Peak in Final Diff. Map	3.08 $e^-/Å^3$
Mininum peak in Final Diff. Map	-1.35 $e^-/Å^3$

Selected geometrical data Selected bond length (a): Pt(1)-N(3), 2.08(6); Pt(1)-N(4), 1.98(6); Pt(2)-N(5), 2.02(7); Pt(2)-N(6), 2.10(6); Pt(3)-N(10), 2.10(7); Pt(3)-N(11), 2.1(1); Pt(4)-N(15), 2.08(6); Pt(4)-N(16), 2.07(6). **Selected bond angles (deg)**: N(3)-Pt(1)-N(4), 92(2); N(7)-Pt(2)-N(8), 91(3); N(10)-Pt(3)-N(11), 91(3); N(15)-Pt(4)-N(16), 91(2). **Selected torsion angles (deg)**: N(4)-Pt(1)-N(3)-C(3), -125; N(3)-Pt(1)-N(4)-C(38), 129; N(8)-Pt(2)-N(7)-C(17), 92; N(7)-Pt(2)-N(8)-C(23), 95; N(11)-Pt(3)-N(10)-C(78), -76; N(10)-Pt(3)-N(11)-C(41), -54; N(15)-Pt(4)-N(16)-C(63), 120; N(16)-Pt(4)-N(15)-C(58), 130.

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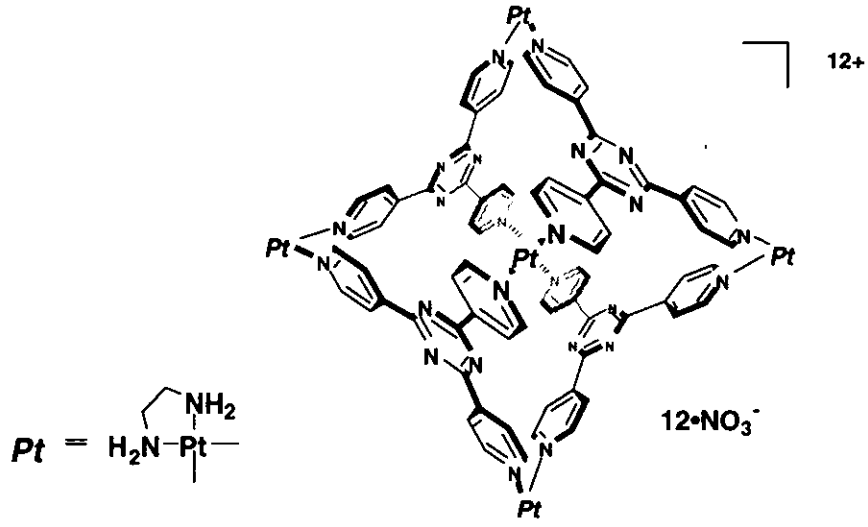
Chapter 5

A Thermally Switchable Molecular Lock. The Guest-Templated Synthesis of a Kinetically Stable Nano-Sized Cage

J. Am. Chem. Soc. **1998**, *117*, 8561.

Abstract: In this chapter, the molecular lock concept is applied to a nano-sized cage complex. As introduced in proceeding chapter, the reversibility of Pt(II)-pyridine coordinate bond can be controlled to labile bond from inert one by external stimuli. Such a switchable chemical bond is termed as "Molecular Lock" since self-assembled chemical structures can be "released" or "locked" by turning "on" or "off" the stimuli.

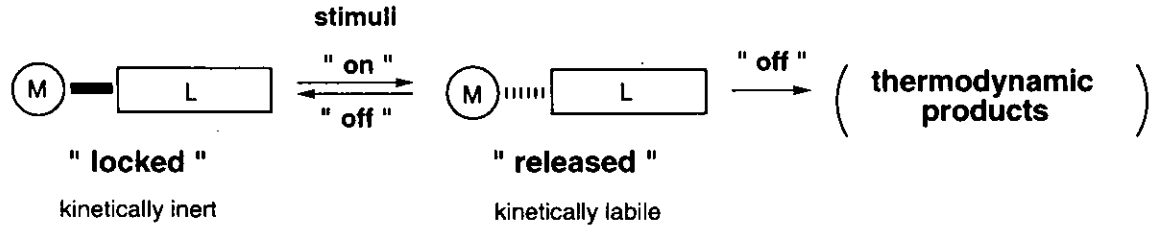
By incorporating Pt(II)-Py bond into the vicinity of a cage structure, a kinetically stable nano-sized cage complex was obtained. A suitable guest molecule showed remarkable template effect for the generation of the cage compound. In addition, the assembled complex was revealed to have remarkable stability toward acidic and basic conditions.



5-1 Introduction

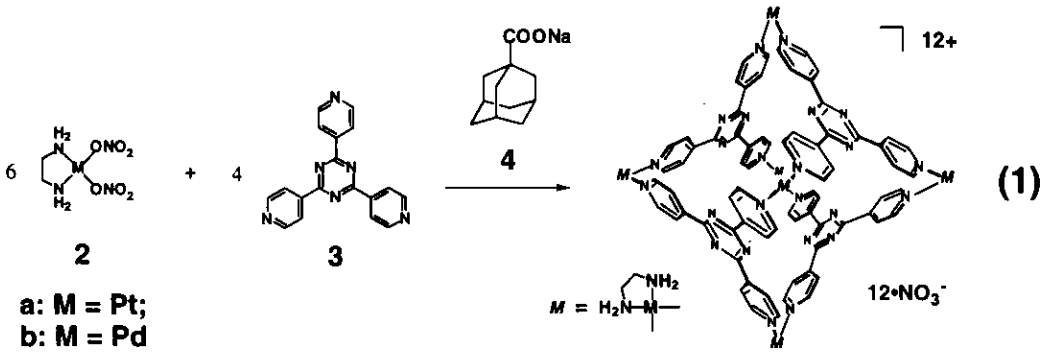
Recently, transition metals have been employed for the rational design and efficient construction of highly ordered supramolecular structures. However, such metal-containing supramolecules are, in general, labile and not tolerant under forcing conditions (e.g., acidic, basic, or nucleophilic conditions) because they self-assemble as a result of thermodynamic equilibration.

If the self-assembled structures can be converted into kinetically inert structures, supramolecules in thermodynamic equilibration can be trapped as kinetically stable forms. Such a conversion is achieved by exploiting the dual character of a Pt(II)-pyridine coordinate bond which is inert but temporally becomes labile by thermal stimuli. Such a Pt(II)-pyridine can be termed as "molecular lock" because the reversibility is controlled by external stimuli. By incorporation of the molecular lock, a thermodynamic equilibrium structure can be trapped (or locked) to a kinetically stable form by turning off the stimuli.[1]



The quantitative self-assembly of cage structure **1b** has been already reported (Equation 1).[2] This complex encapsulates four bulky guest molecules such as adamantane carboxylate in the cavity. In this chapter, the thermally switchable molecular lock, i.e., Pt(II)-pyridine bond, is incorporated into its frameworks.[2,3] Under thermal stimuli, the molecular lock is released and the equilibrated structure of Pt(II) contained within cage **1a** was generated from six metals **2a** and four ligands **3** with the aid of a large template guest.[4] By turning off the thermal stimuli, the cage framework was locked. Subsequently, empty cage **1a** was isolated in a high yield by removing the template guest molecules. Normally, supramolecules self-assembled through weak interactions are labile and not tolerant under forcing conditions,[5] however, nanocage **1a** was shown to be very

stable enough to retain its structure under acidic and basic conditions because its framework is "locked."



Cage complex 1

5-2 Synthesis of cage-like complex 1a by molecular lock

The high yield synthesis of Pt(II) cage complex **1a** was achieved with the aid of the remarkable template effect of a large guest, sodium adamantanecarboxylate **4**. When ligand **3** (0.06 mmol) was treated with **2a** (0.09 mmol) in D_2O (18 mL), a kinetically distributed oligomer mixture was formed at first (NMR chart (a) in Figure 1). After being heated at 100 °C for 24 h, components were slightly converged into a thermodynamically stable cage structure **1a** (NMR chart (b) in Figure 1), but the conversion was too slow to give **1a** in a reasonable yield. To make the cage structure more stable, sodium adamantanecarboxylate **4** (0.06 mmol, 4 equiv to **1a**), which is a suitable guest for palladium(II)-linked derivative **1b**,[3] was added and the solution was stirred at 100 °C for additional 24 h. As a result, we found that the addition of guest **4** induced the smooth, high yield formation of **1a** (NMR chart (c) in Figure 1). Guest signals were highly upfield-shifted due to the inclusion in the cavity ($\Delta\delta$ -0.6 – -2.1 ppm); the host-guest ratio was estimated to be 1:4 by NMR as observed in the palladium complex.[2]

The role of the template **4** is more clarified by the following experiments. The original mixture was heated for additional several days in the absence of **4**, but no significant change in the NMR was observed. Sodium acetate did not show any template effects, suggesting that neither sodium cation nor carboxylate ion induces the assembly of **1a**. The formation of cage **1a** was not accelerated significantly under acidic conditions (HNO_3).

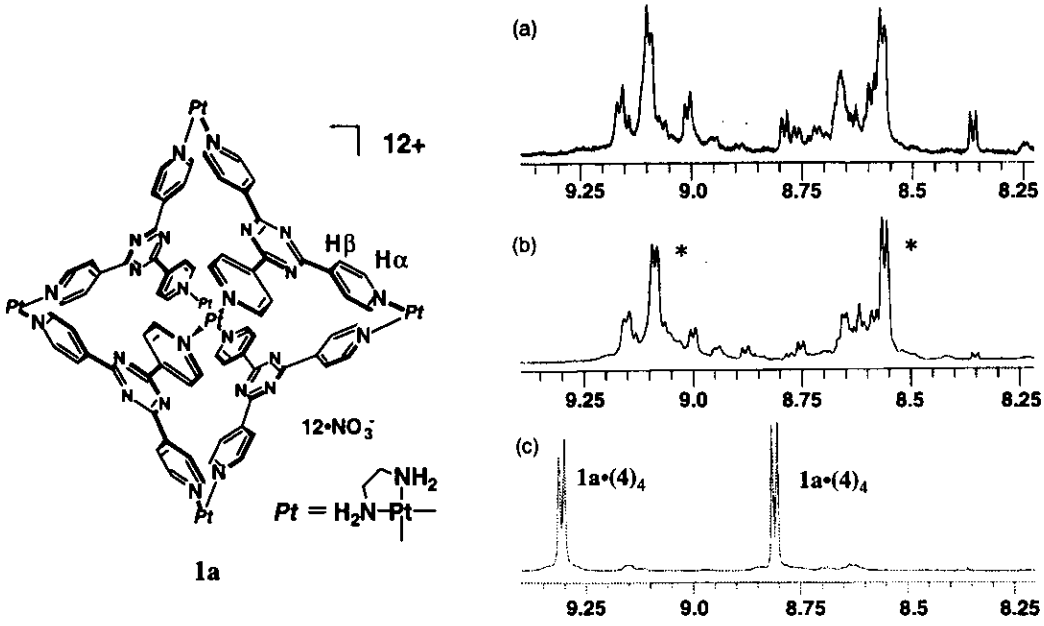


Figure 1. The ^{1}H NMR observation of the guest template synthesis of **1a** (500 MHz, D_2O, 25 °C, TMS as an external standard): (a) A kinetically distributed oligomer mixture (b) After heated for 24 h at 100 °C: Main peaks (*) at δ 9.08 and 8.56 were assignable to **1a**, which are slightly upfield shifted (by ~0.05 ppm) from those of guest-free **1a** presumably due to some interactions with other oligomer components (c) After heated for 24 h at 100 °C in the presence of guest **4** (4 equiv): Signals at δ 9.16 and 8.63 are assigned to **1a**•$(4)_4$ and slightly downfield shifted from those of guest-librated **1a**.

5-3 Confirmation of cage structure 1a

Physical properties and binding behavior of **1a** are quite similar to those of palladium analogue **1b**. The cage **1a** structure was fully assigned by ^{1}H NMR, ^{13}C NMR and elemental analysis. Furthermore, the ESI MS indicated the molecular weight of the target cage compound.[6] The signals at 1361.1, 984.9, and 759.0 in the spectrum were corresponding to [M - $(PF_6)_3$]$^{3+}$, [M - $(PF_6)_4$]$^{4+}$, and [M - $(PF_6)_5$]$^{5+}$, respectively. Signals at {[M - $(PF_6)_n$] • $(CH_3CN)_m$ }$^{n+}$ were also observed, suggesting the accommodation of the solvent molecules in the cavity of the cage complex. It was also suggested that the one or two molecules were removed in the course of an analytical process.

5-4 Removal of the template molecules from the cage

The guest-templated assembly of cage **1a** is a model for "*induced-fit*" since the guest induced the organization of its own receptor.[7,8] Usually, a receptor framework organized by induced-fit will be lost when the guest is removed. In contrast, receptor **1a** did not lose its cage structure by removing the guest because the Pt(II)-py bond in **1a** was locked after the self-

assembly event. Guest **4** which was included in the cavity of **1a** was easily removed as its acid form by acidification of the aqueous solution of **1a**•$(4)_4$ with HNO_3 followed by extraction with chloroform (Figure 1d). To the resulting aqueous solution of empty cage **1a**, excess amount of aq KPF_6 was added to precipitate pure **1a** as a PF_6 salt in 68% yield. The structure was fully assigned by ^1H, ^{13}C NMR and elemental analysis. Neutral compounds such as toluene, methoxybenzenes, and adamantane were also encapsulated by host **1b**, but they did not show any template effects for the assembly of **1a**.

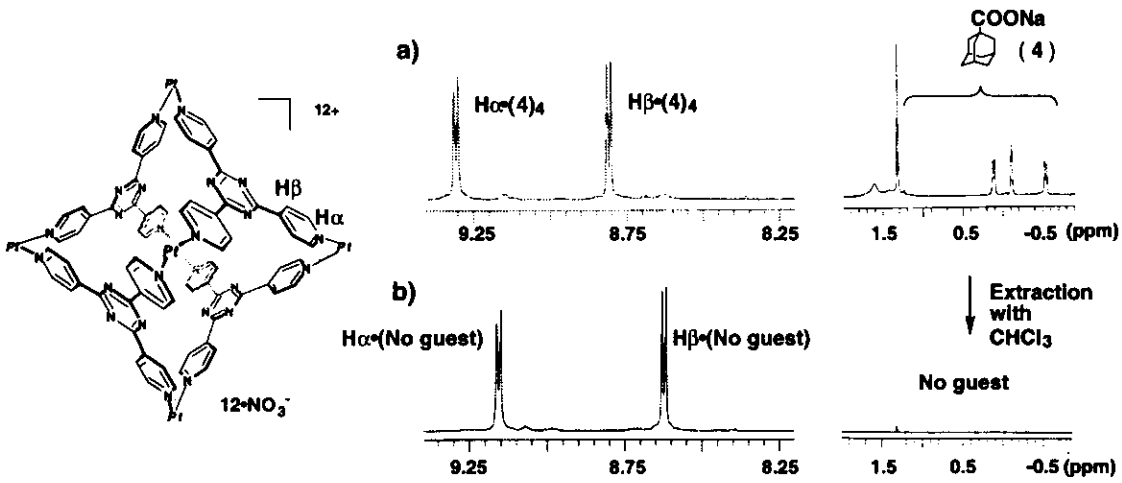


Figure 2. ^1H NMR (500 MHz, D_2O, TMS, pH >1): a) Peaks around 0 ppm were ascribed to encapsulated guest molecules. Cage **1a** included four guest molecules inside the cavity. b) Extraction with $CHCl_3$ removed all the guest compounds.

5-5 Remarkable stability of 1a towards acidic, basic, and nucleophilic conditions

The kinetic stability of **1a** deserves special attention. Surprisingly, nanocage **1a** is tolerant to <pH 1 or >pH 11 conditions at room temperature. Thus, an acid (HNO_3), a base (K_2CO_3), or even a strong nucleophile (NEt_3) did not destroy the framework of **1a**. Such a remarkable stability toward acidic and basic conditions stands in sharp contrast to that of hitherto known metal-containing supramolecules which normally decompose under such conditions. Actually, palladium(II) counterpart **1b** immediately decomposed by adding HNO_3[9] as an acid or NEt_3 as nucleophilic base. In acidic conditions, protonated ligand (**3** • $3H^+$) was observed as the major products by ^1H NMR. On the other hand, a fine precipitate was formed upon addition of NEt_3. The ^1H NMR measurement showed that a complicated mixture was resulted (Figure 3b).

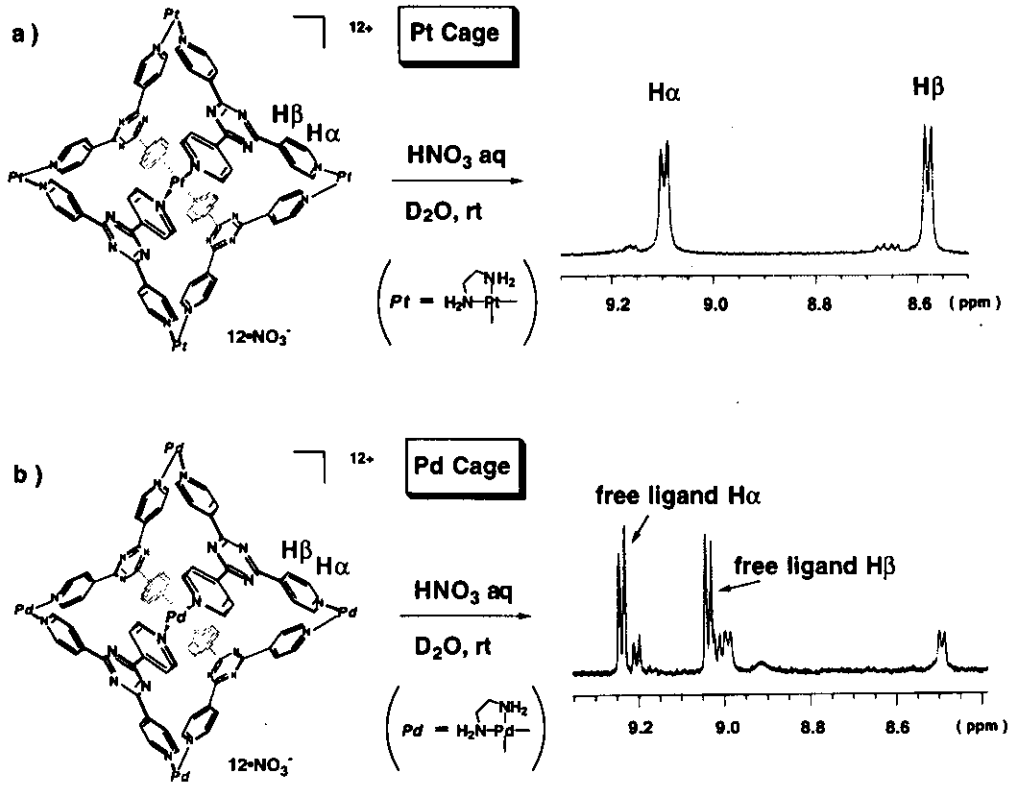


Figure 3. The difference of the stability of cage compound **1a** (Pt complex) and its relative **1b** (Pd analogue) towards acidic conditions: a) [Pt complex]; Even under pH<1 conditions, the cage structure remained unchanged for 12 h at room temperature. b) [Pd complex]; The two major peaks were assigned to protonated aziridine ligands, respectively. The observation showed that cage structure was easily decomposed under the acidic conditions. Spectroscopic experiment was done with ^{1}H NMR (500 MHz, D_2O,TMS).

5-6 pH-responsible host-guest system

The stability of **1a** toward acid and base made it possible to design a pH responsible host-guest system.[9] In D_2O solution, *N*, *N*-dimethylaniline (**5**) was effectively bound in the cavity of **1a** in a host:guset = 1:4 ratio. The complexation was supported by the significant upfield shift of guest protons in ^{1}H NMR ($\Delta\delta$ = ca. -1.0 ppm for aromatic protons and -0.8 ppm for methyl protons). However, cage **1a** immediately liberated **5** when the solution was acidified (<pH 1) with HNO_3. In NMR, the guest signals of free **5**•H^+ was observed upon acidification. The decapsulation of **5** from **1a** was probably due to decreased hydrophobic interaction as well as cationic repulsion between the host and the guest. The liberated guest again came back into the cavity of **1a** when the solution was treated with K_2CO_3 (pH 11). Thus, we achieved the complete switching of the binding property of cage **1a** by pH control.

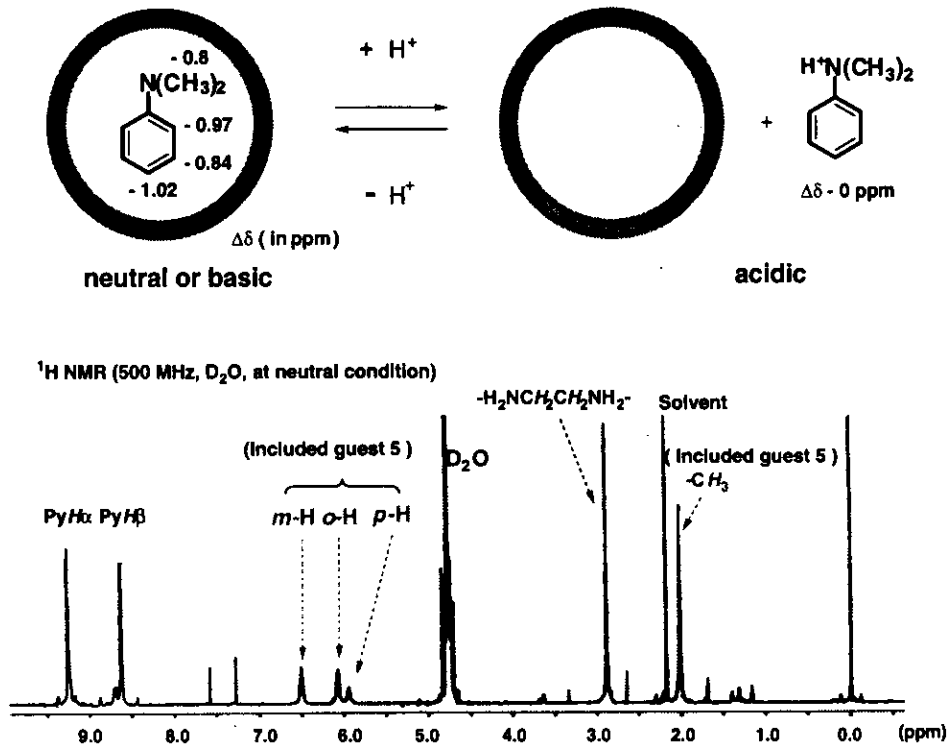


Figure 4. pH-responsible host-guest system: The nucleophilic guest was included into the cavity under neutral conditions. Highly upfield shift was detected by ^{1}H NMR (500 MHz, D_2O, TMS). In contrast, no upfield shift was observed under acidic conditions.

5-7 Conclusion

In this chapter, the author found that highly efficient self-assembly of stable nano-sized cage complex **1a**, which was converted into an inert (kinetically stable) form by turning off the thermal stimuli. These interesting results are due to the dual character of a Pt(II)-pyridine coordinate bond. Namely, the Pt(II)-pyridine bond is inert, but becomes labile by thermal stimuli.

Molecular lock concept is based on the fact that reversibility of coordination bond can be controlled by an external stimuli (i.e. heat, light, and electronic). Application of this molecular lock concept for constructing other discrete structures as well as the development of photo- and electrochemically switchable molecular locks will bring a valuable development to supramolecular chemistry.

5-8 Experimental section

Synthesis of guest-included cage complex 1a In D_2O (10 mL), ethylenediamine platinum (II) chloride (33 mg, 0.10 mmol) and silver nitrate (34 mg, 0.2 mmol) was heated at 100 °C for 2h in dark place. After an addition of activated charcoal, the mixture was filtered. To the filtrate

(9 mL), 1,3,5-tripyridylaziridine (19 mg, 0.06 mmol) was added. This mixture was heated at 100 °C for 24 h. To the mixture (8 mL), aqueous solution (8 mL) of sodium 1-adamantane-carboxylate (10.6 mg, 0.02 mmol) was added, then the reaction mixture was heated at 100 °C for 24 h to give the cage complex including the four guest molecules. ^{1}H NMR (500 MHz, D_2O, TMS as external standard) δ 9.32 (d-like, J = 6.8 Hz, 24 H), 8.80 (d-like, J = 6.8 Hz, 24 H), 2.82 (s, 24 H), 1.35 (s, 24 H), 0.08 (d, J = 12.9 Hz, 12 H), -0.12 (s, 12 H), -0.49 (d, J = 12.9 Hz, 12 H).

Anion exchange and isolation To the water solution of **1a**•(**4**)$_4$ (0.83 mM, 16 mL, 0.0133 mmol), aqueous HNO_3 (0.316 M, 350 μL, 0.11 mmol) was added. The water solution was washed by $CHCl_3$ (20 mL x 2) to remove **4** as acid form. These procedures gave cage complex that no guest molecules were encapsulated. To the water phase, KPF_6 aqueous solution (147 mg, 0.80 mmol, 0.27 M) was added, then the mixture was stirred for 17 h at room temperature. EtOH was added to the mixture, and the precipitate was filtered to give pale yellow powder of PF_6 salt of **1a** (40 mg, 87%). ^{1}H NMR (500 MHz, D_2O, TMS as external standard) δ 9.16 (d-like, J = 6.8 Hz, 24 H), 8.63 (d-like, J = 6.8 Hz, 24 H), 2.82 (s, 24 H); ^{13}C NMR (125 MHz, D_2O, TMS as external standard) δ 170.5 (*C*q), 153.9 (*C*H), 146.1 (*C*q), 126.7 (*C*H), 48.7 (*C*H); IR (KBr, cm^{-1}) 3401, 3060, 1622, 1575, 1527, 1377, 833, 813, 680, 559; mp 225 °C dec.; Anal. Calcd for $C_{84}H_{84}F_{72}P_{12}Pt_6$•$(H_2O)_8$•$(C_2H_5OH)_2$: C, 22.28; H, 2.38; N, 10.63. Found C, 22.36; H, 2.69; N, 10.34. ESI MS (CH_3CN) *m/z* 1361.1 $[M - (PF_6)_3]^{3+}$, 984.9 $[M - (PF_6)_4]^{4+}$, 759.0 $[M - (PF_6)_5]^{5+}$

Guest inclusion experiment The solution of guest-free complex **1a** was prepared by the method mentioned above. To this solution (2 mL, 1.66 mM), *N*,*N*-dimethylaniline (8.3 mM, 800 μL) was added to give the guest-included cage complex. The encapsulation occurred smoothly at room temperature within 5 min, and was observed by ^{1}H NMR or UV-vis spectroscopy. In the ^{1}H NMR, the signals assignable to guest molecules were highly shifted to upfield. In UV-Vis, outstanding absorption band appeared at 495 nm (ε = 433 L•mol^{-1}•cm^{-1}, D_2O).

pH-responsible host guest system To the solution (2 mL) of cage complex that has four molecules of N,N'-dimethylaniline in its cavity, dilute HNO_3 (0.316 M) was added until the solution became acidic (< pH 1). ^{1}H NMR observation showed the release of guest molecules from the cavity. To this solution, small amount of K_2CO_3 was added until the acidic condition turned into basic. By ^{1}H NMR, the guest molecules were included in the cage complex again.

The cage complex is stable enough to retain the structure under these conditions. These inclusion and release were also detected by UV-Vis spectroscopy.

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Okazaki,

January 7, 2000.

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