# Accounts

## Supramolecular Self-Assembly of Macrocycles, Catenanes, and Cages through Coordination of Pyridine-Based Ligands to Transition Metals

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Recent developments in the study of the transition-metal mediated supramolecular self-assembly are reviewed. Focus is on the self-assembly of macrocycles, catenanes, and cages from (en)Pd($NO_3$)$_2$ (**1**) and pyridine-based bridging ligands. Coordination of linear 4,4′-bipyridine on the cis coordination site of palladium complex gives a macrocyclic square supramolecule, whereas macrocyclic dinuclear Pd(II) complexes self-assemble from **1** and flexible bridging ligands. Unprecedented formation of catenanes through rapid slippage of two preformed molecular rings can be achieved by exploiting the labile character of a Pd(II)-linked macrocycle: i.e., a macrocycle assembling from **1** and $PyCH_2C_6H_4CH_2Py$ exists in rapid equilibrium with its catenated dimer and the equilibrium is strongly pushed toward the catenane ($> 99 : 1$) in a polar media. The combination of **1** with tridentate ligands gives three-dimensional cagelike hosts. A spherical $M_3L_2$ complex organizes from **1** and a flexible tridentate ligand only in the presence of specific guests providing a model for induced fit. On the other hand, a nanometer-sized hollow supramolecule self-assembles from four rigid tridentate ligands held together by six protected Pd complex **1**.

In biological systems, the organization of well-defined structures such as the double helices of DNA is frequently induced by hydrogen bonds and other weak interactions. The application of this mechanism to artificial systems provides the concept of *supramolecular self-assembly*,[1—3] which is a term for the spontaneous generation of a well-defined supramolecular architecture from component molecules under a well-defined set of conditions. In earlier studies on the supramolecular self-assembly, hydrogen bonds were most frequently employed as they are in all biological systems.[4] In the 1980s, however, incorporation of *coordinate* bonds into the supramolecular self-assembly triggered the development of an entirely new field in which organic and inorganic chemistries are completely scrambled.[5—7] Earlier and important examples of such works involve $\beta$-cyclodextrin rotaxane with Co(III) coordinated stoppers (1981),[8] Cu(I)-templated synthesis of catenanes (1983),[5a,9] Cu(II)-linked macrocycles (1984),[10] and Cu(I)-directed assembly of double helicates (1987) (Chart 1).[11] In the 1990s, the metal directed self-assembly has been showing remarkable potentials to construct supramolecular architectures such as helices,[5d,11,12] grids,[13] boxes,[14] rods,[15] tubes,[16] interlocked systems,[5a,9] and so on.[5—7] These works emphasize that coordinate bonds are the most useful bonds in supramolecular self-assembly due to their versatile geometrical modes (e.g., linear, trigonal, square planar, tetrahedral) in bond formations and their moderate to high bond strengths.

In the late 1980s, we also planned the transition metal-based self-assembly of supramolecules. While extensive studies had been made on the self-assembly of helical structures at that time, we paid our own attention to *macrocycles* as the target structure. Prior to our study, there were several reports on macrocycles containing transition metals in their backbones. For example, Shaw and others prepared macrocyclic mononuclear Ir(I), Pt(II), and Pd(II) complexes[17] and dinuclear Rh(I) complexes[18] during the systematic study of the complexation of transition metals with $Ph_2P(CH_2)_nPPh_2$ ($n > 4$). No binding properties were reported for these molecules. Probably the first example of inorganic macrocycles designed as synthetic receptors is Maverick's dinuclear Cu(II) complex (1984) assembled from Cu(II) ions and ligands with two bis($\beta$-diketone) coordination sites and an aromatic spacer.[10a] Employment of a 2,7-naphthylene spacer made the cavity of their complex large enough to recognize small cyclic diamines such as DABCO.[10b,10c,10d]

We designed a macrocyclic structure that could be a synthetic receptor according to a very simple basic concept shown in Scheme 1. We paid our particular attention to the coordination geometry of a square planar transition metal because *it involves a right angle which organic chemists had never employed to construct their target structures.* Thus, Scheme 1 clearly illustrates that, when the right angle of a square planer transition metal is combined with a liner bidentate ligand, a macrocyclic square supramolecule assembles.

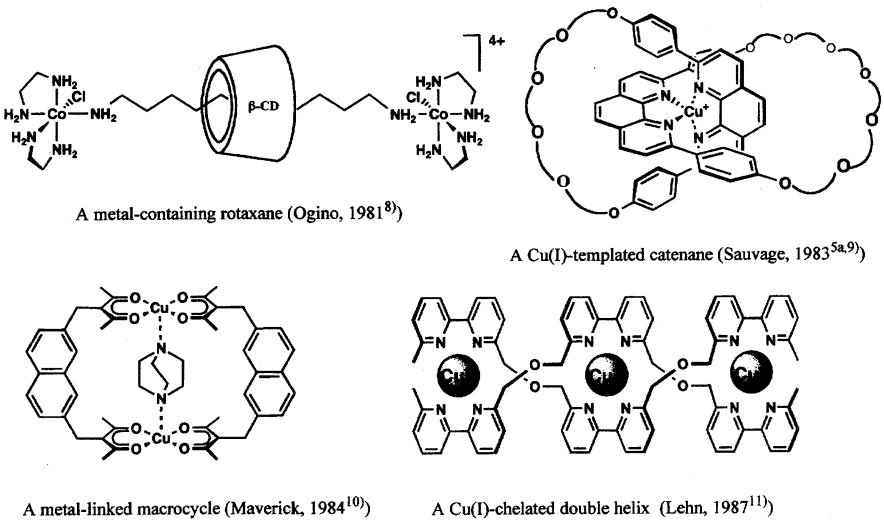
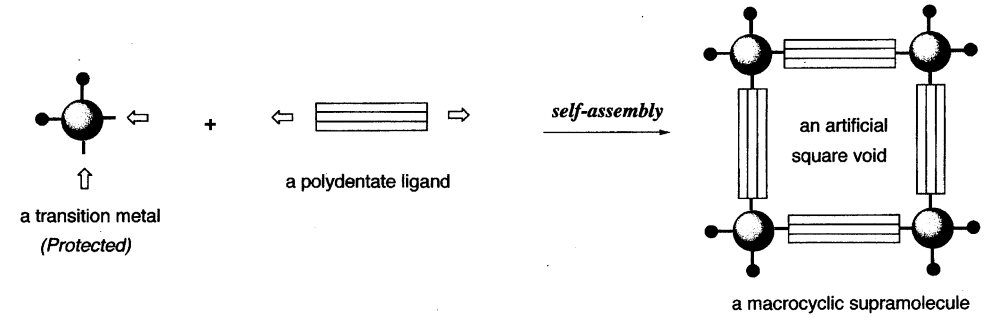



Chart 1. Earlier examples of supramolecular complexes.




Scheme 1. The concept of the supramolecular self-assembly of square macrocycles mediated by a protected, square-planar transition-metal.

The strategy of Scheme 1 is also characterized by the use of *protected* transition metals. The appropriate protection on a transition metal makes our strategy contrast strikingly with the general strategy of metal-directed assembly, in which naked metals have to be combined with more sophisticated ligands. In the first section of the present account, we disclose the self-assembly of macrocyclic supramolecules. Then, we deal with self-assembling catenanes (interlocked macrocycles). Finally, we expand the concept of Scheme 1 to three-dimensional systems and show self-assembling cage-like supramolecules that can encapsulate organic guests.[19]

**Self-Assembly of Pd(II)- (or Pt(II)-) Linked Macrocyclic Complexes Macrocyclic Tetranuclear Complexes: Molecular Squares.** According to the concept shown in Scheme 1, we first synthesized a macrocyclic tetranuclear complex **3** assembling from a cis-protected palladium(II) complex **1** and equimolar amount of 4,4′-bipyridine **2** (Eq. 1).[20] The procedure is quite simple: Two components are combined in water (or water–methanol) at ambient temperature and the quantitative self-assembly of macrocyclic complex **3** is observed. This complex is isolated as a pure precipitate in more than 90% yield by adding ethanol to the reaction mixture. The solution structure was strongly supported by NMR and electrospray ionization mass spectroscopy (ESI-MS). In addition, the solid structure of **3** was confirmed by X-ray crystallography, which showed the existence of an almost perfect square structure of **3** with face conformation of pyridine nuclei (Fig. 1).[21] The length of a

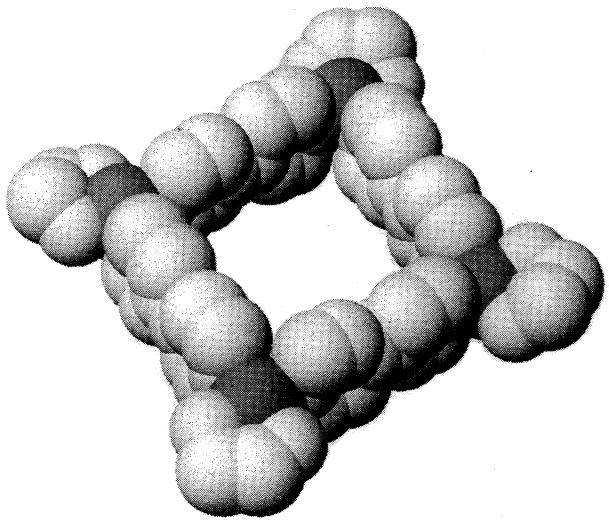
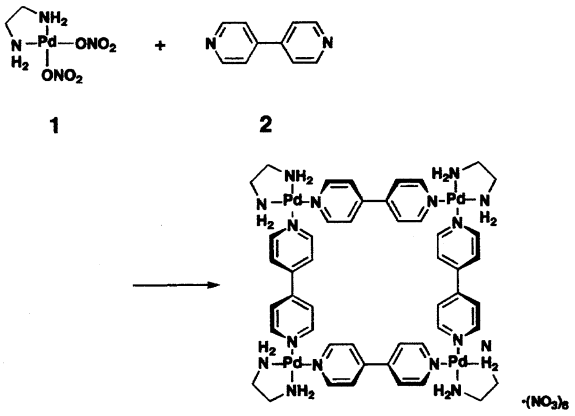


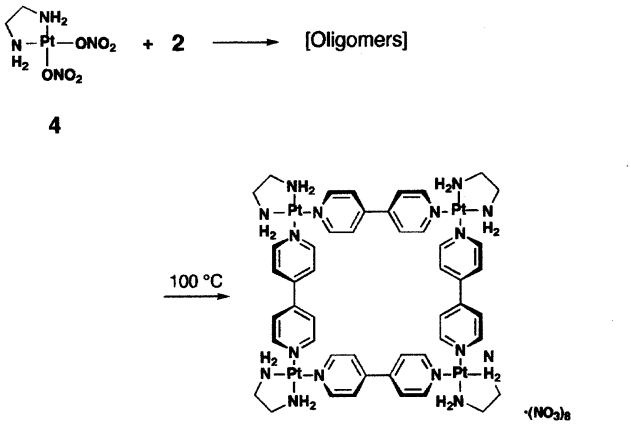
Fig. 1. The crystal structure of square complex **3**. The crystal was obtained as a clathrate complex with naphthalene, though neither the naphthalene molecules nor $NO_3^-$ ions were found due to high degree of disorder.

side of the cavity is approximately 8 Å; this corresponds to the diameter of the cavity of $\beta$-cyclodextrin. In water, complex **3** offers a hydrophobic cavity. Thus, we found the ability of **3** to recognize neutral aromatic compounds. For example, 1,3,5-trimethoxybenzene was recognized by **3** with a $K_a$ value of $7.5\times10^2$ (Table 1).[22]



**1** **2** **3** (1)

The platinum(II) counter part **5** was obtained in a quite different manner from those of the palladium(II) system. Since Pt(II)–Py bond is inert, treatment of (en)Pt($NO_3$)$_2$ (**4**) with 4, 4′-bpy (**2**) gave kinetically distributed oligomeric products. On heating the mixture at 100 °C, however, the oligomers were gradually transformed into the thermodynamically most stable **5** (Eq. 2). After a few weeks, the transformation was almost completed and **5** could be isolated as a pure material (81%). A significant difference in stability was found between **3** and **5**. Addition of **1** to **3** in $D_2O$ resulted in redistribution of products, giving a mixture of **3** and two acyclic components. In contrast, **5** was kept intact upon addition of **4**, because of the inertia of Pt(II)–Py bond under ordinary conditions.[23]



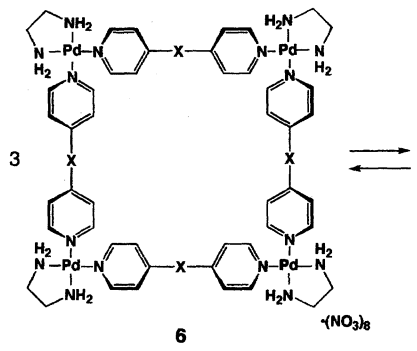
**4** **5** (2)

The square cavity of **3** can be expanded by the incorporation of aromatic spacers into the 4,4′-bpy skeleton. However, the assembly of expanded molecular squares **6** was accompanied by the formation of cyclic trimers **7** (Eq. 3).[21] Recently, phosphine analogs of **3** was reported by Stang.[24] Related square complexes in which metal ions provide the 90° angle at the four edges of the square were also reported by a few groups[25] after our publication.

Table 1. Association Constants between Self-Assembled Macrocycles and Various Guests

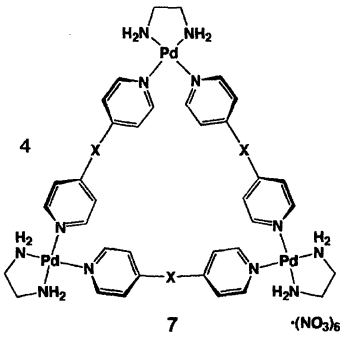
| Host | Guest | Association constant (L mol$^{-1}$) | Ref. |
|---|---|---|---|
| **3** | *N*-(2-Naphthyl)acetamide | 1800 | 26 |
| | 1,3,5-Trimethoxybenzene | 750 | 20 |
| | *p*-Dimethoxybenzene | 330 | 22 |
| | *m*-Dimethoxybenzene | 580 | 22 |
| | *o*-Dimethoxybenzene | 30 | 22 |
| | *p*-Bis(methoxymethyl)benzene | 10 | 22 |
| | 1,4-Dimethoxycyclohexane | N.C. | 22 |
| **5** | *p*-Dimethoxybenzene | 260 | 22 |
| | *m*-Dimethoxybenzene | 550 | 22 |
| | *o*-Dimethoxybenzene | 20 | 22 |
| **6b** | 1,3,5-Trimethoxybenzene | 420 | —[a] |
| | *p*-Dimethoxybenzene | 130 | —[a] |
| **11** | *p*-Dimethoxybenzene | 200 | 38 |
| | *p*-Dicyanobenzene | 201 | 38 |
| **12** | 1,3,5-Trimethoxybenzene | 2500 | 26 |
| | *p*-Dimethoxybenzene | 2680 | 26 |
| | *p*-Bis(methoxymethyl)benzene | 560 | 26 |
| | *p*-Dicyanobenzene | 80 | 26 |
| | *p*-Dinitrobenzene | 30 | 26 |

a) Unpublished results.



3 6 ·(NO$_3$)$_8$

a: X = -C≡C-; b: X = -CH=CH-; c: X = -C≡C-C≡C-; d: X = -C$_6$H$_4$-



4 7 ·(NO$_3$)$_6$ (3)

**Macrocyclic Dinuclear Complexes.** When flexible pyridine-based bidentate ligands were employed in place of **2**, macrocyclic dinuclear complexes were quantitatively obtained in most cases.[26—28] Examples given in Chart 2 show that our approach provides general and highly efficient syntheses of macrocycles. Some of their structures were fully characterized by X-ray crystallography (Fig. 2). Otherwise, fast atom bombardment mass spectrometry (FABMS) supported the macrocyclic structures. Even a ligand involving 3-pyridyl groups gave a dinuclear macrocycle (**16**).[29] It is particularly interesting that some of them showed unique ability for molecular recognition. For example, macrocycle **12** having two tetrafluorophenylene units showed remarkable molecular recognition ability for electron rich aromatic compounds. Thus, the association constant increased with increasing electron density of the guest molecules (Table 1). During the last several years, there have appeared a variety of self-assembling macrocycles from flexible ligands and naked transition metals.[30,31]

**Quantitative Self-Assembly of [2]Catenanes.** Interlocking molecular rings are termed catenanes.[32] The first synthesis of [2]catenane was achieved in 1960 by Wasserman,[33] though his synthetic strategy was statistical and the yield of the catenane was very poor. Later, the highly efficient formation of a catenane was realized in 1983 by the transition metal-template strategy of Sauvage.[5a,9] More recently, another highly efficient approach to catenanes was developed by Stoddart.[34] The self-assembly of organic aromatic systems through charge transfer interaction was shown to be highly effective to prepare catenanes. These pioneering works were followed by several catenane syntheses in the 1990s, most of which are mediated by amide hydrogen bond[35] or organometallic bond[36] formation.

Catenanes continue to fascinate chemists partly in expectation of serving as molecular-scale devices and machinery. On the other hand, catenanes are taking an important role in our biological systems. It is known that DNA large rings are frequently catenated. Surprisingly, *topoisomeraze II* catalyzes the dissociation and catenation of the DNA rings.[37] It seems very difficult to mimic such a biological transformation in artificial systems. However, the next section shows that supramolecular chemistry enables this transformation in an artificial system quite simply.

**Self-Assembly and Structure of [2]Catenanes.** We found that two-ring catenane ([2]catenane) **18** self-assembled from **1** and simple pyridine-based ligand **17** in water (Scheme 2).[38] Since the palladium–pyridine coordinate bond is reversible, rapid equilibrium between catenane **18** and monomer ring **11** was observed, and the equilibrium ratio of these components could be controlled by simply adjusting the concentration of the components. At higher concentrations, the equilibrium ratio shifted so that two molecules of **11** produce one molecule of catenane **18** according to Le Chatelier's law (Table 2).

The structure of **18** was confirmed by NMR and electrospray ionization mass spectromety (ESI-MS) as well as X-ray crystallographic study of Pt(II) analog **19** (Fig. 3).[39] In $^1$H NMR, the inside and outside ligands of catenane **18** were independently observed (Chart 3) consistent with the inhibition of internal rotation of the ring, as suggested by a tight aromatic contact in the crystal structure. Being surrounded by aromatic rings of another ring, the inside phenylene protons appear with marked high field shift ($\delta$=5.3).

**Thermodynamics and Mechanism of the Catenane Formation.** Even after the structure of catenane **18** was confirmed, we had two significant questions: *why* and *how* does this strange molecule spontaneously assemble? Concerning the first question (why?), we suggest that the assembly of the catenane is promoted by "double-differential complexation." That is, two molecular rings recognize each other in their cavities. The double-differential complexation produces a $\Delta G$ value approximately twice as much as simple molecular recognition, making the structure of the catenane stable enough to assemble quantitatively.

Such an interpretation is consistent with the remarkable medium effect on the equilibration. Less polar media pushed

Table 2. Concentration Effects on the Equilibrium Ratio of **18** and **11**[a]

| Concn/mM[b] | **18** : **11** |
|---|---|
| 1 | <1 : >99 |
| 2 | 11 : 89 |
| 5 | 38 : 62 |
| 10 | 59 : 41 |
| 20 | 75 : 25 |
| 50 | 91 : 10 |

a) Measured in $D_2O$ at room temperature. b) Net concentration of Pd(II).

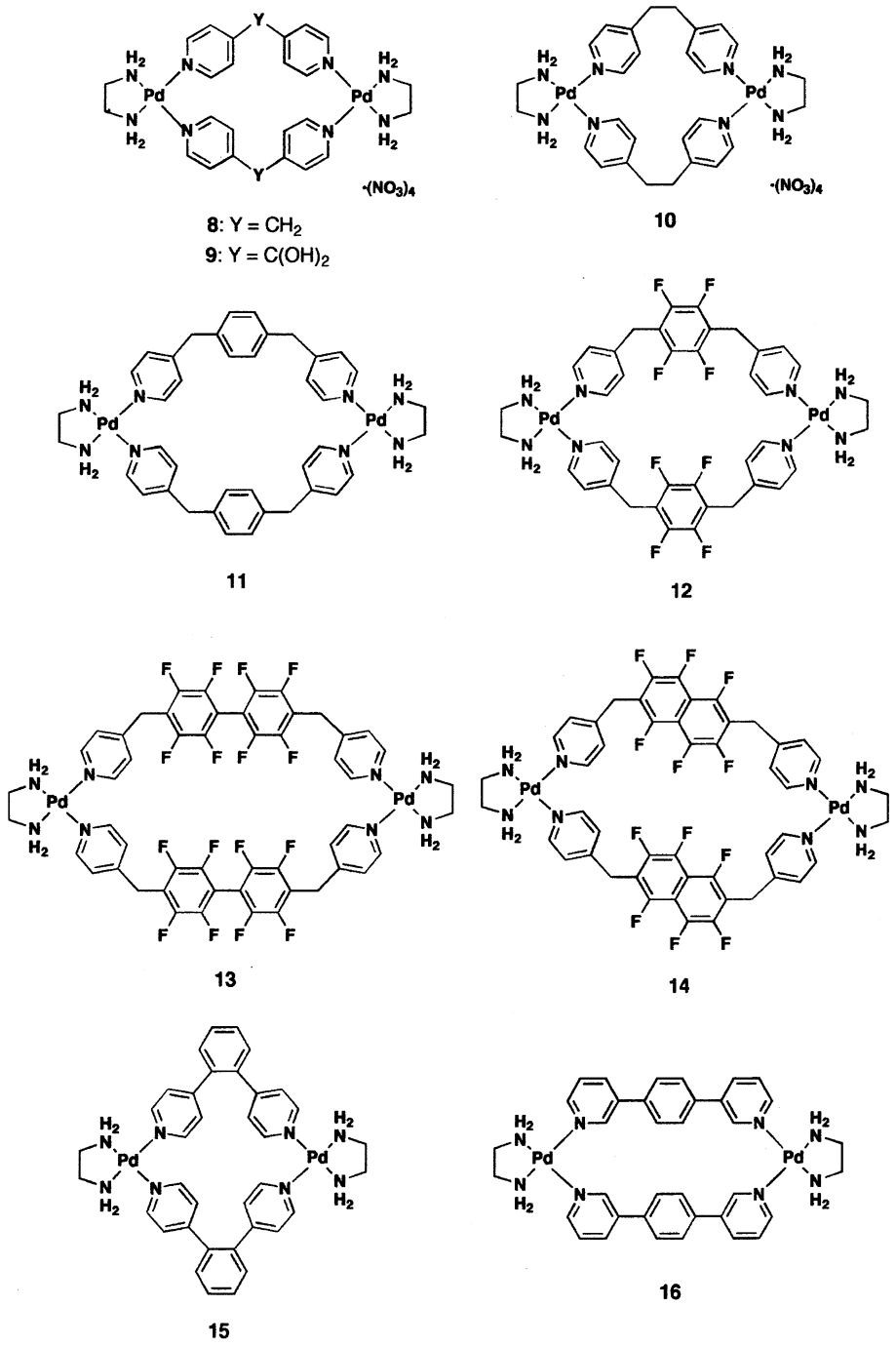



Chart 2. Examples of self-assembling macrocycles.

the equilibration toward monomer **11** because hydrophobic interaction was reduced in the less polar medium. In contrast, this equilibrium was strongly pushed toward catenane **18** by employing a more polar medium which enhances the hydrophobic interaction. Thus, in a 1 M $D_2O$ solution (1 M=1 mol $dm^{-3}$) of sodium nitrate, the catenane became an overwhelmingly dominant species (Table 3).[38]

The second question (how?) is concerned with the mechanism of the catenane formation through very rapid slippage of molecular rings. A conventional explanation for the catenane formation involves the dissociation of a ring at a Pd–N linkage, threading another ring on the thread, and reconnection of the ends of the thread. However, a few experiments negated this simple mechanism. For example, molecular ring **12** did not interlock with Stoddart's polyether ring **20**[35] in spite of the large thermodynamic advantage ($\Delta H$ 22 kJ $mol^{-1}$ by MM2) (Eq. 4). Alternatively, NMR techniques using truncated driven nuclear Overhauser effect (TOE) as well as a few experiments suggested that the rapid interconversion is explained in terms of ligand exchange between Pd–N bonds. That is, the proposed pathway leading to the catenane involves two sequential ligand exchanges between two molecular rings concomitant with a twisting of the rings around each other (Fig. 4).[40]

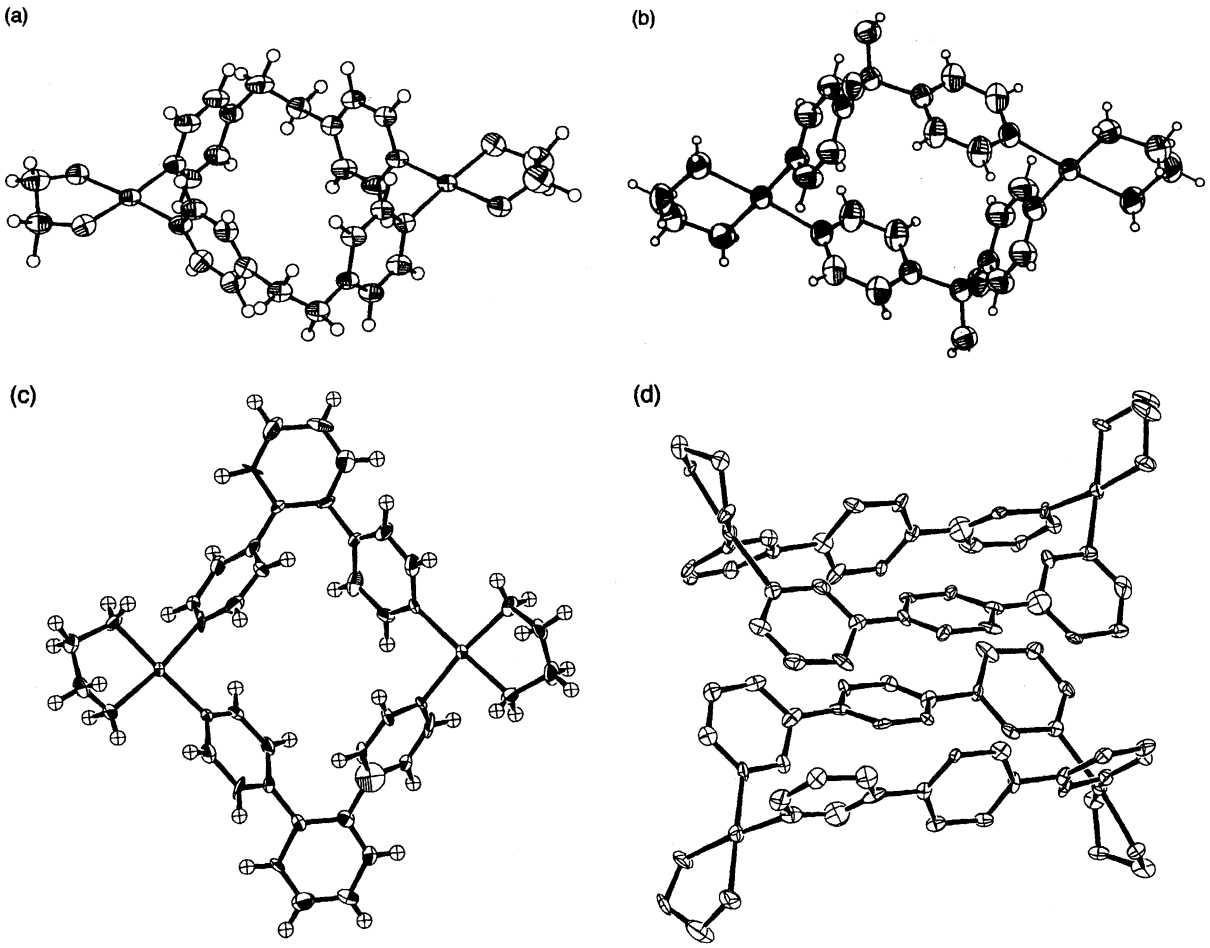
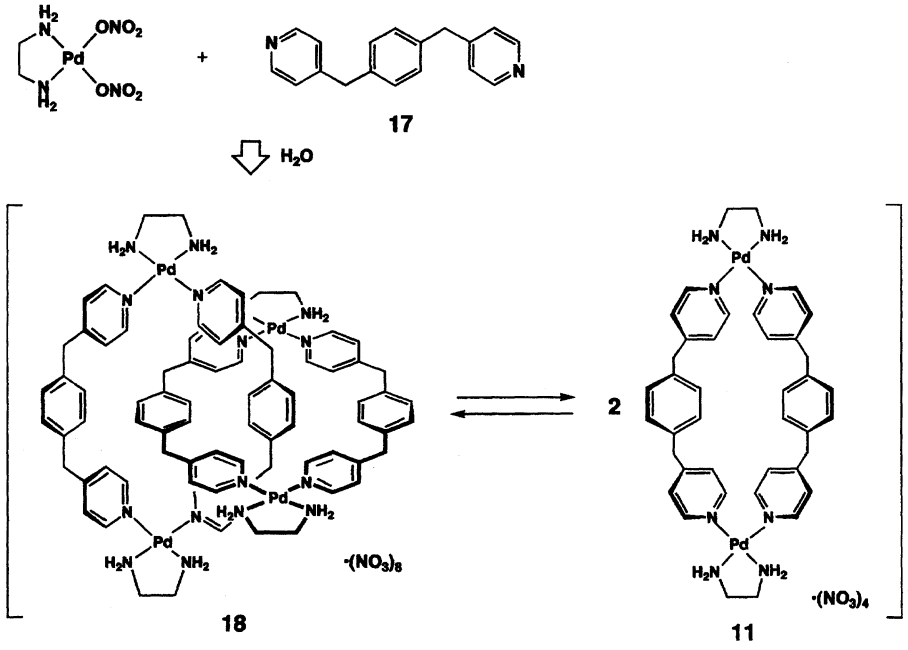



Fig. 2. Crystal structures of self-assembling dinuclear macrocyclic complexes: (a) **8**; (b) **10**; (c) **15**; (d) **16**. Two crystallographically independent molecules were found in the solid structure of **16** (d).




Scheme 2. Self-assembly of [2]catenane **18**.

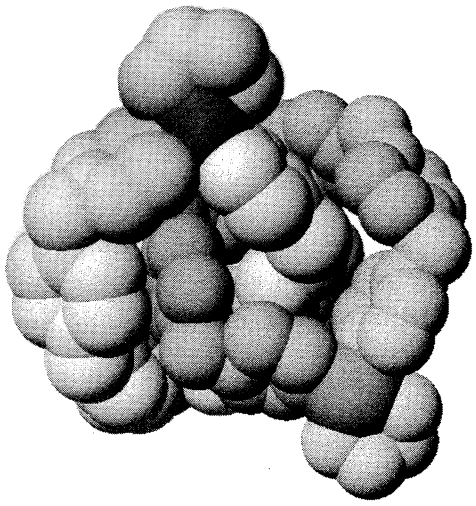
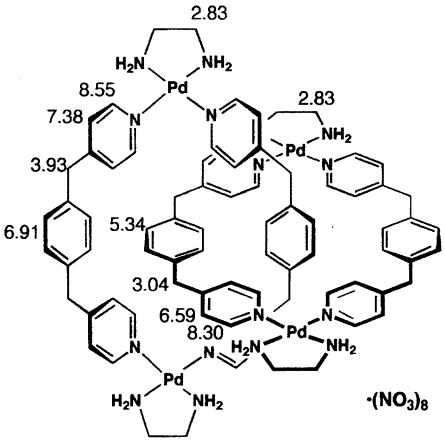
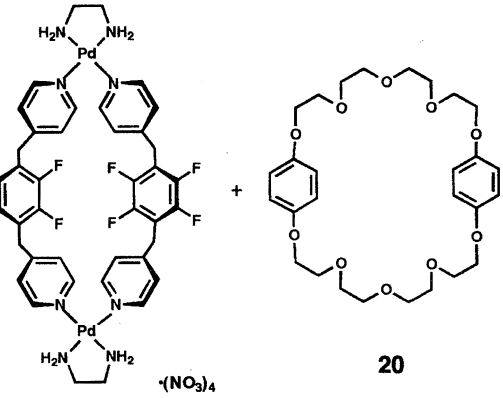


Fig. 3. The crystal structure of Pt(II) catenane **19**.

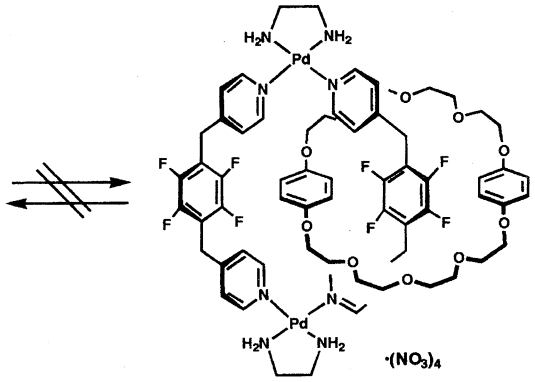



**18**

Chart 3. $^1$H NMR chemical shift ($\delta$, ppm) of **18** in $D_2O$ at room temperature.

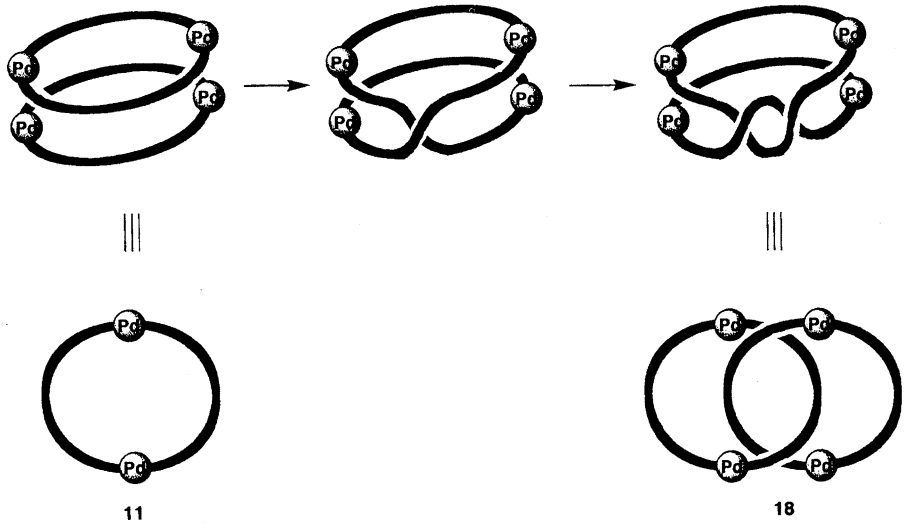



**12** **20**




(4)

**A Molecular Lock** We have discussed the unprecedented equilibration between a catenane and two component rings. However, the presence of the equilibrium means that catenane **18** once formed easily dissociates into two separate rings **11**. If the labile coordinate bond can be frozen after the catenane assembles, a complete catenane that never dissociates into two rings can be obtained. Such a one-way formation of a catenane was achieved in a platinum(II) counterpart system (Eq. 5) using the concept of "molecular lock."[37]



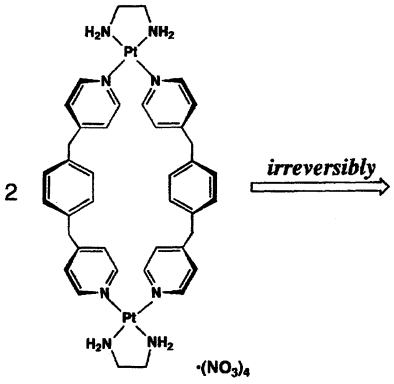
**11** **18**

Fig. 4. Topological presentation of the mechanism for the rapid slippage of molecular rings via ligand exchange.

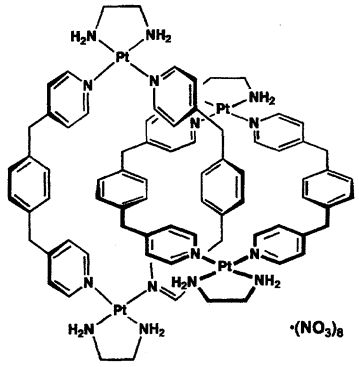
Table 3. Medium Effects on the Equilibrium Ratio of **18** and **11**[a]

| Medium | Guest[b]/mol equiv | **18** : **11** |
|---|---|---|
| 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*-methoxyphenyl)acetate.




**21**



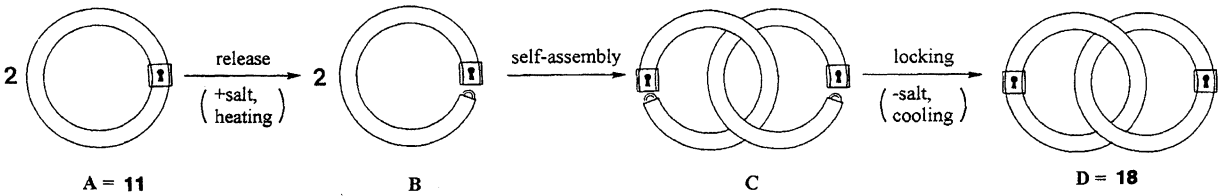

**19** (5)

The concept of "molecular lock" stems from the exploitation of the dual character of the Pt(II)–Py bond. This bond can be likened to a lock because it is irreversible ('locked') under ordinary conditions but becomes reversible ('released') in a highly polar medium at high temperature. Incorporation of the molecular lock into a macrocyclic framework made it possible to irreversibly interlock two molecular rings. In Scheme 3, molecular ring **21** is initially on the lock (**A**). The lock is then released by adding a salt ($NaNO_3$) and heating at 100 °C (**B**), allowing the self-assembly of a catenated framework (**C**). Finally, this framework is locked by removing the salt and cooling (**D**). This chemical manipulation of molecular rings was successfully accomplished and we obtained locked catenane **19** in a high yield.

**Self-Assembly of 3D Cagelike Hosts.** Macrocycles are two-dimensional receptors. On the other hand, three-dimensional receptors are provided by hollow, cagelike molecules. The door of the chemistry of the 3D receptors was opened in the 1970s by three-dimensional chelating compounds or cryptands.[41] Later, various cage- and bowl-like complexes with a 3D void have been prepared,[42,43] and these compounds often showed remarkably high molecular recognition ability. One of the most striking studies that definitely differentiates the 3D cavity from the 2D system is the chemistry of carcerands developed by D. J. Cram.[43,44] A guest molecule encapsulated in the carcerand was completely isolated from the outside and an otherwise extremely unstable molecule can exist with a long lifetime in the 3D cavity at room temperature.[44] Stereoisomerism in the 3D cavity of carcerand was recently reported.[45] Thus chemists can expect the development of new chemistry in chemically created endohedral fields inside the 3D receptors.

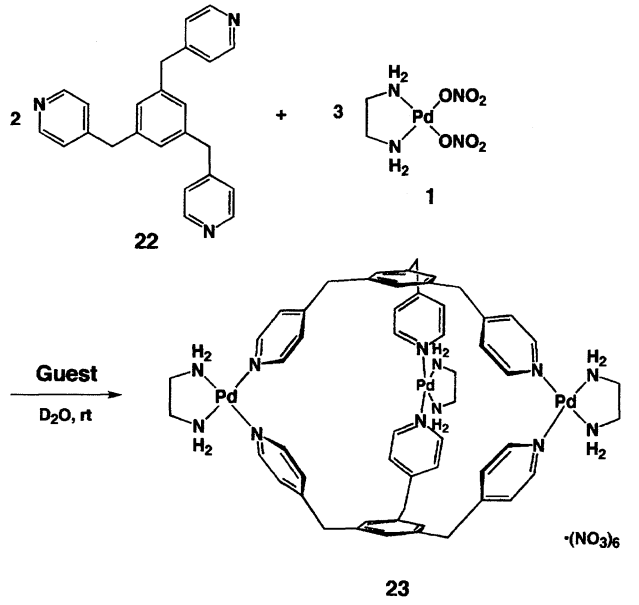
Despite their remarkable potential ability, however, difficulties encountered in their syntheses extremely limit the development of the chemistry of the 3D compounds. Again the following section emphasizes that the metal-directed self-assembly provides a very efficient approach to 3D receptors. Recent examples of self-assembling 3D compounds involve Saalfrank's adamantane-like aggregates,[46] Rebek's hydrogen bonded spherical dimers,[47] and Lehn's cylindrical complex.[14]

**Guest-Induced Assembly of an $M_3L_2$ Cagelike Complex: Induced-Fit Molecular Recognition.**[48] The self-assembly of macrocycles using protected Pd(II) complex **1** was applied to a three-dimensional system. Thus, the reaction of the cis-protected palladium(II) and tridentate ligand **22** in a 3 : 2 stoichiometry was examined in expectation of the assembly of cagelike supramolecule **23** (Eq. 6). We found that the self-assembly of **23** is quite different from that of other supramolecules because **23** is assembled only in the presence of an appropriate guest. Namely, an intractable mixture of oligomeric products is obtained in the absence of a guest molecule. However, the addition of an appropriate



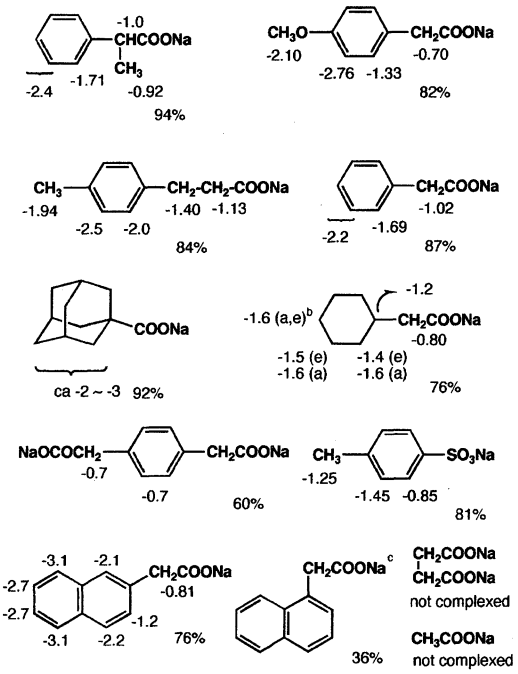

Scheme 3. Schematic presentation of the irreversible formation of a catenane from two complete rings using a "molecular lock".

guest induces the assembly of cagelike complex **23**. For example, the addition of sodium (*p*-methoxyphenyl)acetate to the oligomer mixtures induced the formation of a 1 : 1 host–guest complex which was isolated in 94% yield. The guest-induced assembly of **23** was monitored by a time-dependent $^1$H NMR measurement. The high upfield shift of guest signals in NMR ($\Delta\delta$: up to ca. 3 ppm) supports the encapsulation of the guests in the cavity. NMR titration experiments showed 1 : 1 complexation between **23** and various organic carboxylates. The relative ability of these guests to induce the assembly of **23** was estimated from NMR yields of the 1 : 1 host–guest complexes (Chart 4). The results shown in Chart 4 demonstrate that bulky substituents, whose sizes are comparable to that of the cavity of **23**, are so effective as to induce the self-assembly of **23**. Thus, the guest-induced assembly of **23** provides an entire model for "induced-fit" molecular recognition because the recognition site of a receptor organizes in the presence of specific guests. A macrocyclic complex showing similar behavior was recently reported.[49]



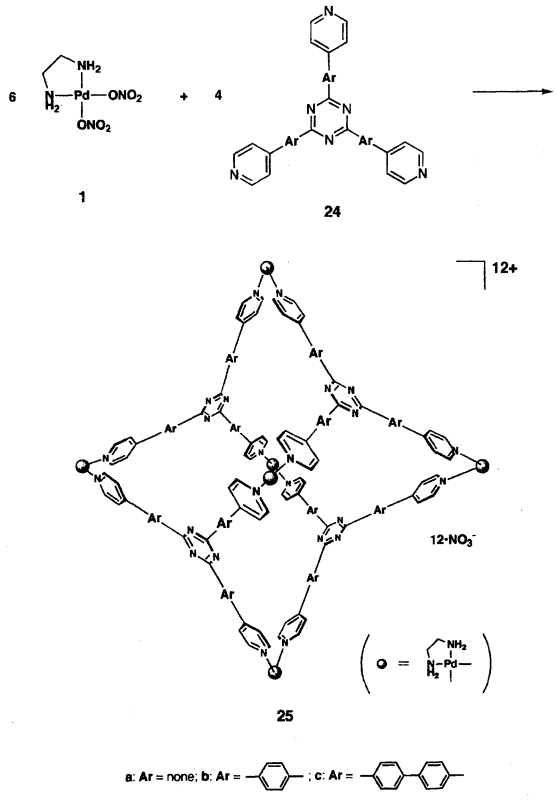

(6)

**Self-Assembly of Hollow, Nanosized $M_6L_4$ Complexes: Molecular-Based Ultrafine Particles.**[50] Precise control of nanometer-scale structures has become one of the most important subjects in both physics and chemistry.[51–53] Of many nano-scale materials, ultrafine particles are of intense interest from a materials science point of view because they are expected to show unique properties which fine particles have never possessed. Usually, ultrafine particles are prepared by grinding fine particles. In contrast, we constructured molecular-based ultrafine particles through supramolecular self-assembly from ten simple molecules by simply extending our basic concept (Scheme 1) to a three-dimensional system. Thus, nanometer-scale supramolecule with adamantane-like symmetric framework (**25a**) was assembled from six molecules of **1** and four molecules of 2,4,6-tri-4-pyridy-1,3,5-triazine (**24a**) (Eq. 7).




a) The NMR yield of **23** is determined at $[\mathbf{22}]_0$=2 mM, $[\mathbf{1}]_0$=3 mM, and [guest]=1.5 mM. The negative values present upfield shift ($\Delta\delta$ in ppm) in $^1$H NMR measured at $[\mathbf{22}]_0$=6 mM, $[\mathbf{1}]_0$=9 mM, and [guest]=1.5 mM: at these conditions, $\Delta\delta$ values of the guests (except $C_6H_4(COONa)_2$) were saturated. b) Axial and equatorial protons are donated by a and e, respectively. c) $\Delta\delta$ values could not be analyzed due to overlap with uncharacterized signals.

Chart 4. Guest-Induced Organization of **23**.[a]




(7)

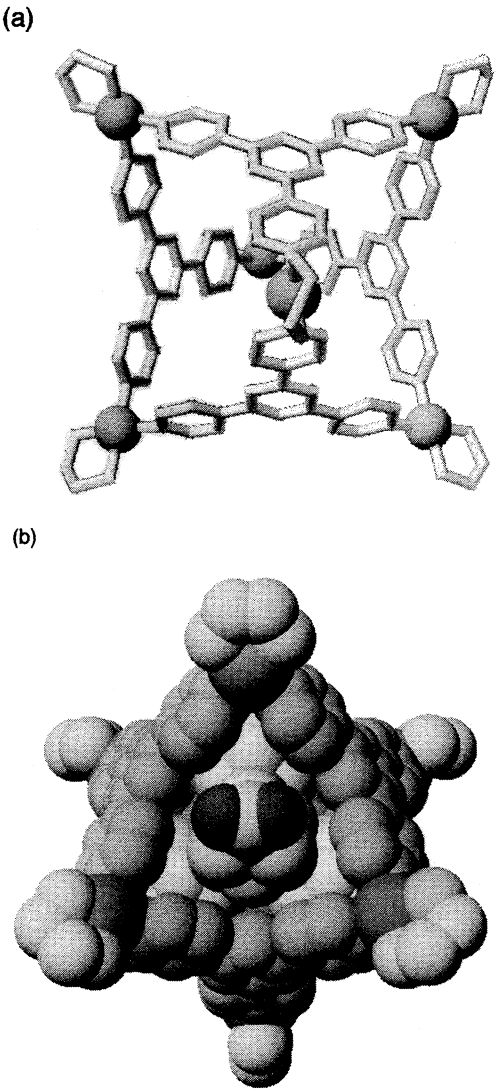



Fig. 5. The crystal structure of nanosized aggregate (**25a′**)·(**26**)$_4$. (a) Only the host framework is shown. (b) A view looking down the entrance of the nanosized cavity (a CPK presentation).

The structure of **25a** was confirmed by X-ray crystallography. Although **25a** itself was obtained as a single crystal, they were too unstable for any diffraction study. However, in the presence of 1-adamantanecarboxylate ion (**26**), relatively stable crystals of clathrate complex (**25a′**)·(**26**)$_4$ were obtained (**25a′**=**25a**–$NO_3^-$). The crystallography showed that the three dimensional **25a** structure really exists and four guest molecules are tightly encapsulated inside the nanosized cavity of **25a** (Fig. 5). A spectroscopic study based on NMR showed that the same host–guest aggregate (**25a′**)·(**26**)$_4$ was also organized even in an aqueous media.

Larger derivatives **25b,c** were accessible by employing phenylene- or biphenylene-bridged ligand **24b,c**. The molecular sizes of these molecules amount to several nanometers, which were in fact measured by a common laser light scattering method, showing their characteristics as particles.[50]

## Conclusion

Supramolecular self-assembly of macrocycles, hollow cages, and catenanes has been achieved through coordination of various bridging ligands on cis-protected palladium(II) that provides 90° for the construction of the supramolecular architectures. Throughout the present study, we have mainly employed cis-protected palladium(II) as a tool for supramolecular self-assembly. One might question "why palladium(II)?". Before closing this paper, a brief answer will be given.

In our basic concept (Scheme 1), we needed a stable transition metal with a square planar geometry and a suitable cis-protective group on the metal. Group 10 metals with a +II oxidation state ($Ni^{2+}$, $Pd^{2+}$, and $Pt^{2+}$) are the best candidates since they are very stable to air and water and always provide desired square planer geometry. In addition, cationic charge on metals is expected to produce the high water solubility of the self-assembled complex with a hydrophobic cavbity. We found that coordination on $Ni^{2+}$ was so labile that the ethylenediamine protective group dissociated during or after the desired self-assembly process. On the other hand, coordination $Pt^{2+}$ was so inert that pyridyl ligands would not dissociate under the ordinary conditions (though it temporarily dissociates in polar media at elevated temperature as already discussed). The best combination is ethylenediamine-protected palladium(II) and pyridyl ligands. The moderate lability of the coordinate bond on $Pd^{2+}$ is quite appropriate for our purpose. That is, ethylenediamine (an aliphatic chelating ligand) never dissociates from the metal whereas pyridyl ligands (aromatic monodentate ligands) are bonded reversibly to Pd(II). Probably, the success of this study is due to the finding of the best combination: an ethylenediamine protective group–palladium(II)–pyridyl ligands. More significantly, this combination makes the strategy of our work quite different from that of other metal-directed self-assembly systems.

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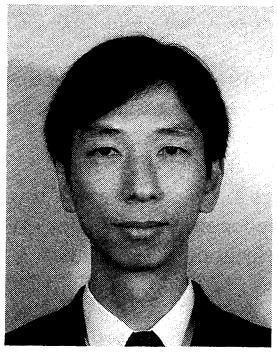
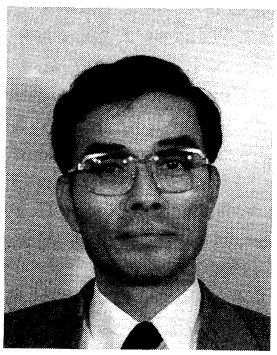


Makoto Fujita was born in Tokyo, Japan, on September 28, 1957. He completed his undergraduate study in 1980 and his Master's degree in 1982 at Chiba University. Then he moved to Sagami Chemical Research Center and joined the groups of Dr. Iwao Ojima, who is now a distinguished professor of New York State University at Stony Brook, and Dr. Tamejiro Hiyama, who is now a professor of Tokyo Institute of Technology. In 1987, he received his Ph. D. degree from Tokyo Institute of Technology on the highly selective reactions using silicon and zinc reagents. Then he joined the Ogura group at Chiba University as an assistant professor in 1988 and was promoted to an Lecturer in 1991 and to Associated Professor in 1994. He is a recipient of the Progress Award in Synthetic Organic Chemistry, Japan.



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