

## VII-G Molecular Self-assembly Through Coordination

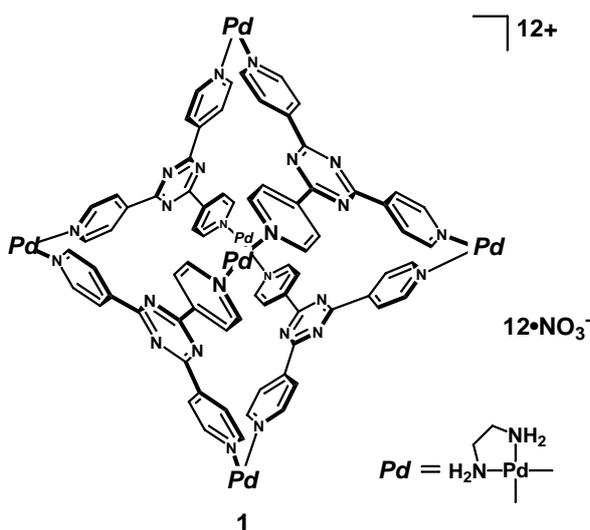
Molecular self-assembly refers to the spontaneous generation of well-defined structures from component molecules under a well-defined set of conditions. Since 1990, we have been studying the self-assembly of discrete structures based on coordination chemistry, where coordinate bonds induce the generation of defined structures. Studies during 1998-1999 are focused on the self-assembly of such three dimensional systems as cages, capsules, tubes, bowls, and 3D-interlocked molecules. Our strategy is characterized by the use of a cis-protected Pd(II) unit as a convergent block for molecular assembly, providing 90 degree coordination angle.

### VII-G-1 Encapsulation of Large, Neutral Molecules in a Self-Assembled Nanocage Incorporating Six Palladium(II) Ions

KUSUKAWA, Takahiro; FUJITA, Makoto

[*Angew. Chem., Int. Ed. Engl.* **37**, 3142 (1998)]

Cage compound **1** encapsulates as many as four molecules of *o*-carborane (8 Å in diameter). A large guest, 1,3,5-tri-*tert*-butylbenzene, once encapsulated by thermally-activated slippage, cannot escape from the cavity at room temperature since its dimension is slightly larger than that of the cavity window.



### VII-G-2 "Ship-in-a-Bottle" Formation of Stable Hydrophobic Dimers of *cis*-Azobenzene and -Stilbene Derivatives in a Self-assembled Coordination Nanocage

KUSUKAWA, Takahiro; FUJITA, Makoto

[*J. Am. Chem. Soc.* **121**, 1397 (1998)]

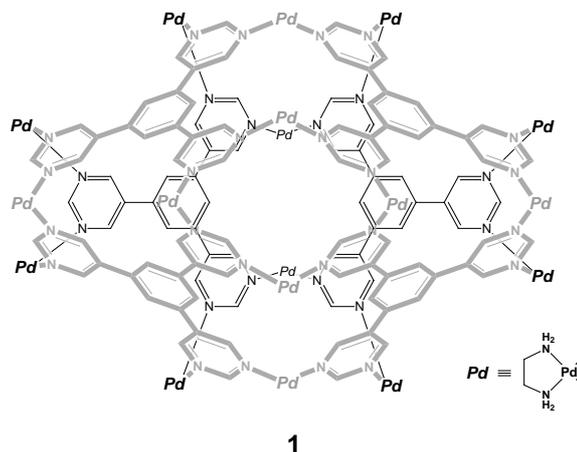
Nano-sized coordination cage **1** (see compound **1** in VII-G-1) has been shown to enclathrate large neutral guest molecules. Here we report the selective enclathration of "C-shaped" molecules such as *cis*-azobenzene and -stilbene derivatives by cage **1**. These guest molecules are enclathrated in the cavity through the "ship-in-a-bottle assembly" into a hydrophobically interacted dimer. The hydrophobic dimers of azobenzene derivatives are considerably stabilized and do not undergo *cis-trans* isomerization.

### VII-G-3 A Nonmeter-Sized Hexahedral Coordination Capsule Assembled from 24 Components

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[*Nature* **398**, 794 (1999)]

Molecular capsules consist of closed, hollow frameworks within which encapsulated molecules are isolated from interaction with external molecules. In this environment, otherwise reactive molecules can be stabilized. Although some molecular capsules have been prepared by conventional synthetic chemistry, recent progress in non-covalent synthesis has allowed the creation of capsules held together by hydrogen bonds. Here we report the use of transition-metal based coordination chemistry to assemble a stable, nanometre-scale capsule **1** from 24 small components: 18 metal ions and six triangular ligands. The capsule is roughly hexahedral and comprises six edge-sharing triangles with two metal ions on each edge. This internal space has a volume of 900 Å and is fully closed to all but very small molecules.

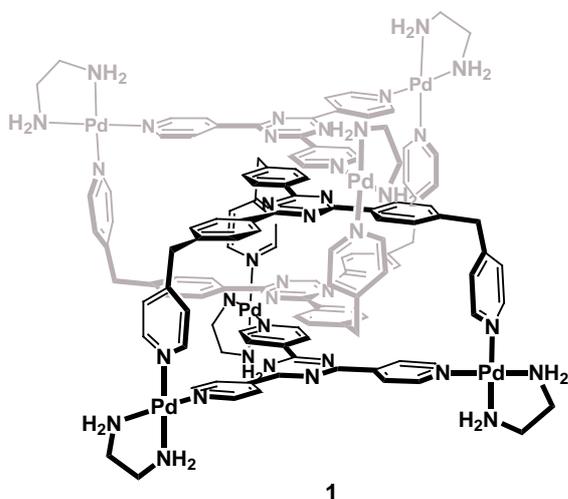


### VII-G-4 Spontaneous Assembly of Ten Components into a Two Interlocked, Identical Coordination Cages

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[*Nature* **400**, 52 (1999)]

Supermolecules consisting of interlinked ring-like molecules (catenanes) are an interesting target for chemical synthesis both for their intrinsic interest as non-covalently bound but robust assemblies and because of the perspective they offer on materials chemistry. Catenanes have been prepared by metal-ion templating and self-assembly through other non-covalent interactions. Here we report the synthesis of catenane **1** composed not of two interlocking rings but of two cages. This structure is prepared by metal-mediated self-assembly. The framework of each cage is assembled from five components: two tridentate ligands held together with three metal ions. Because each cage framework can bind an aromatic ring, two cage units will bind one another during their assembly process through the formation of a quadruple aromatic stack, giving rise to the ten-component interlocked supermolecule.

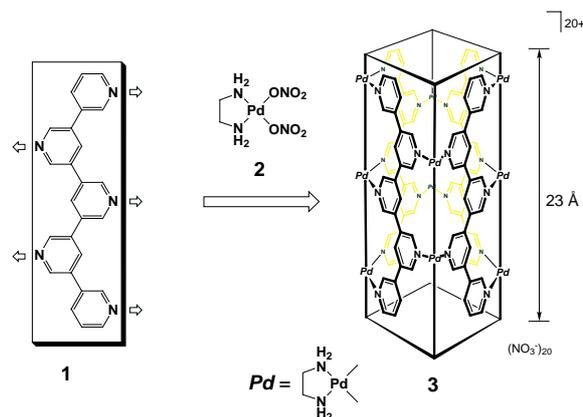


#### VII-G-5 Quantitative Formation of Coordination Nanotubes Templated by Rod-like Guests

AOYAGI, Masaru<sup>1</sup>; BIRADHA, Kumar<sup>2</sup>; FUJITA, Makoto  
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[*J. Am. Chem. Soc.* **121**, 7457 (1999)]

Molecular-based tubular structures have attracted considerable current interest because of their potential abilities for selective inclusion and transportation of ions and molecules and catalysis for specific chemical transformations, by exploiting the interior space of the tubes. In the present study, coordination nanotubes **3** are constructed by linking oligo(3,5-pyridine)s **1** with a cis-protected Pd(II) building block, (en)Pd(NO<sub>3</sub>)<sub>2</sub> (**2**, en = ethylenediamine). This transformation was in fact accomplished with the remarkable template effect of biphenyl derivatives. Thus, the reaction of **1** and **2** first resulted in the formation of uncharacterizable products. However, the addition of sodium 4,4'-biphenylene-dicarboxylate to the solution induced the smooth assembly of nanotubes **3** wherein four oligo(3,5-pyridine) molecules were held together with six to ten Pd(II) units. A nanotube structure templated by a guest was confirmed by an X-ray crystallographic analysis.

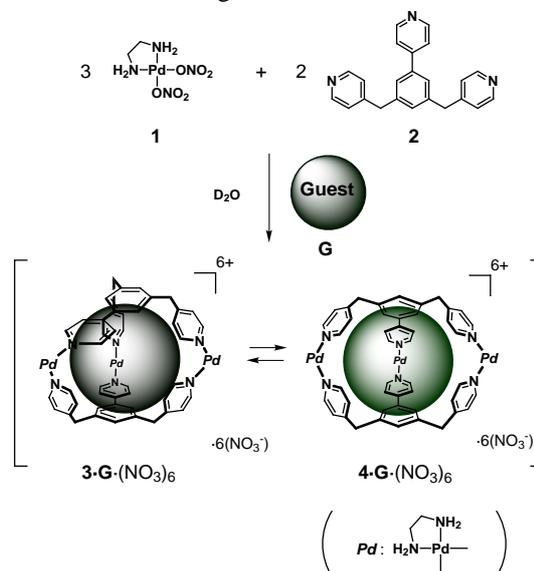


#### VII-G-6 Guest-Selected Formation of Pd(II)-Linked Cages from a Prototypical Dynamic Library

HIRAOKA, Shuichi<sup>1</sup>; FUJITA, Makoto  
(<sup>1</sup>CREST, *Jpn. Sci. Tech. Co. (JST)*)

[*J. Am. Chem. Soc.* in press]

Biological receptors modulate the shape and size of their recognition sites to bind substrate molecules, generating numerous receptor structures from which the most suitable one is selected (or induced-fit) by their substrates. Modeling such a system is particularly important to develop a new receptor design wherein artificial receptors are constructed through a selection process by their own guests. Although previous examples are dealing with the induced-fit control of receptor conformations, there are only several reports on the control of receptor linkages. Here we report the guest-selected formation of its optimal cage-like receptor from an equilibrium mixture of receptors. In the following scheme, Pd(II)-linked cages, **3** and **4**, and some oligomeric compounds, accessible from the same components **1** and **2**, are in equilibrium. From this thermodynamic mixture, each cage structure is selected upon the addition of appropriate guest molecules. This phenomenon is a prototype for "dynamic receptor library," which represents one of important goals in the field of molecular recognition.



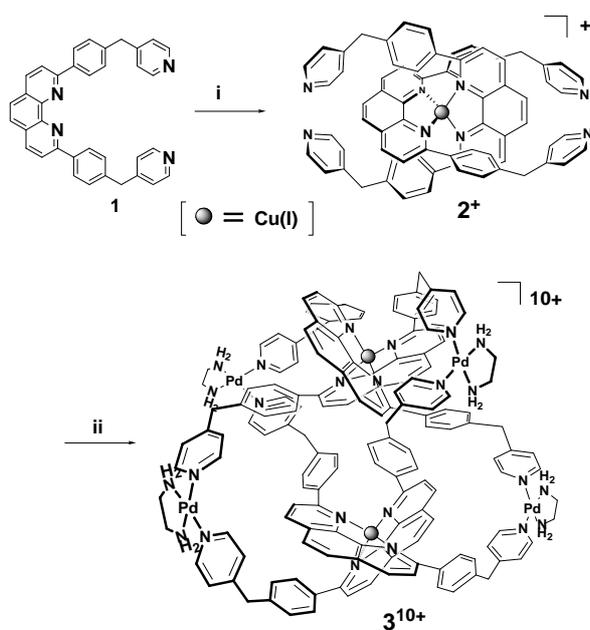
### VII-G-7 Quantitative and Spontaneous Formation of a Doubly Interlocking [2]Catenane using Copper(I) and Palladium(II) as Templating and Assembling Centers

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[*J. Am. Chem. Soc.* in press]

A new strategy based on pure coordination chemistry has been used to construct a 4-crossing [2]catenane. The ligand **1** 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). The final complex **3** is a chiral species incorporating 4 ligands, 2 copper(I) and 4 palladium(II) centres. It has been characterized in solution and its structure has been evidenced by ESI-MS.



### VII-G-8 Flexible Coordination Networks with Fluorinated Backbones. Remarkable Ability for Made-to-Order Enclathration of Organic Molecules

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We have designed and prepared flexible ligands containing fluorinated aromatic rings: PyCH<sub>2</sub>-R<sub>f</sub>-CH<sub>2</sub>Py; Py = 4-pyridyl, R<sub>f</sub> = -C<sub>6</sub>F<sub>4</sub>-, -C<sub>6</sub>F<sub>4</sub>-C<sub>6</sub>F<sub>4</sub>-, and -C<sub>10</sub>F<sub>6</sub>-. Because of very weak intermolecular forces among fluorinated compounds, networks from these ligands and metal ions are not apt to be constricted or interpenetrated, but prefer to interact with guest molecules to form clathrate compounds. In these clathrate complexes,

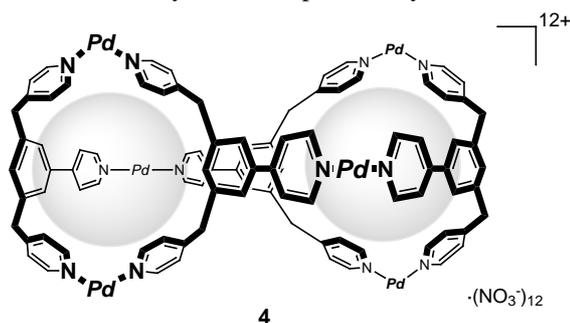
we have found that the network topologies are induced-fit by guest molecules owing to the flexibility of the ligand frameworks giving rise to 1D, 2D, and 3D structures with large cavities. Consequently, we have achieved “made-to-order” enclathration of a variety of organic guests with the flexible, fluorinated coordination networks.

### VII-G-9 Kinetic and Thermodynamic Aspects in the Substrate-Induced Assembly of Optimal Receptors from a Dynamic Library

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(<sup>1</sup>CREST, Jpn. Sci. Tech. Co. (JST); <sup>2</sup>Nagoya Univ.; <sup>3</sup>JSPS)

Pyridine functionalized C<sub>2v</sub> ligand **1** (see compound **2** in VII-G-6) has been recently shown to provide a mixture of more than two cage-like receptors upon complexation with (en)Pd<sup>2+</sup> coordination block. The mixture thus obtained can be termed as “dynamic receptor library” because appropriate substrates induce the assembly of their optimal receptors from the mixture. Further studies on this thermodynamic phenomenon have elucidated some important structural and mechanistic aspects.

We report here that, in addition to M<sub>3</sub>L<sub>2</sub> type receptors **2** and **3** (see compounds **3** and **4** in VII-G-6, respectively), dimeric M<sub>6</sub>L<sub>4</sub> cage **4** is involved in the equilibrium mixture. Interestingly, **2** and **3** interconvert via the dimeric M<sub>6</sub>L<sub>4</sub> form as revealed by a kinetic study. Furthermore, symmetrical M<sub>3</sub>L<sub>2</sub> cage **2** and M<sub>6</sub>L<sub>4</sub> dimer **4** are isolated and characterized by X-ray crystallography. These results emphasize how easily a variety of host frameworks with different connectivities and stoichiometries are generated from only one ligand component and how precisely the optimal receptor frameworks are selected from the equilibrated cage molecules or a “dynamic receptor library.”



### VII-G-10 Dynamic Behavior of Rod-like Guest Accommodated in Coordination Nanotubes

AOYAGI, Masaru<sup>1</sup>; FUJITA, Makoto  
(<sup>1</sup>GUAS)

Oligo(3,5-pyridine) ligands **1** self-assemble into coordination nanotubes **2** with the aid of remarkable template effect of rod-like guest (For the structures of **1** and **2**, see those of **1** and **3** in VII-G-5, respectively). Studies on the dynamic behavior of guest molecules accommodated in the tubes are particularly interesting

because guests are expected to move only in a one-dimensional way within a tightly fitted tubular space and such a restricted guest motion would lead to novel functions of tubular molecules: *e.g.*, shape-selective molecular transportation and (catalytic) chemical transformation. Here, we report NMR studies on the dynamic motion of the guests accommodated in the coordination nanotube. Guest molecules are found to shuttle in the tube without turning their head and tail at room temperature, but intermolecularly exchange at elevated temperature.

### VII-G-11 Wacker Oxidation in an Aqueous Phase Through the Reversed Phase-Transfer Catalysis of a Self-Assembled Nanocage

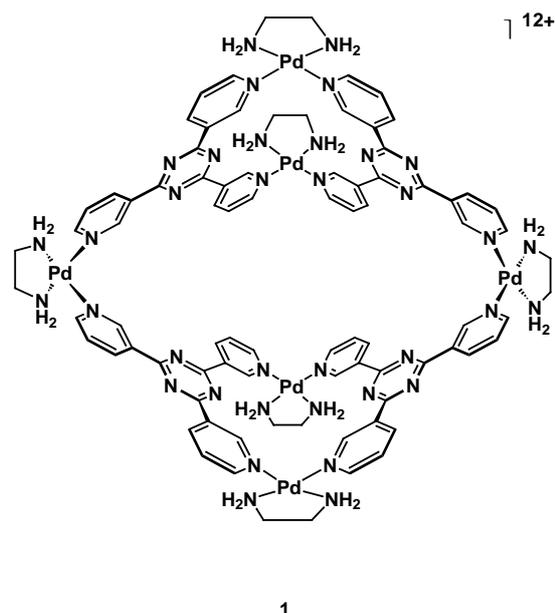
ITO, Hirokazu<sup>1</sup>; KUSUKAWA, Takahiro; FUJITA, Makoto  
(<sup>1</sup>GUAS)

Chemical transformation in aqueous media is a current trend in synthetic chemistry in view of developing clean technology. One of the best approaches to water-based reactions is to develop reversed phase-transfer catalysts which bring organic substrates into aqueous phase, let them react with aqueous reagents, and take out products from the aqueous phase. This paper reports that the coordination nanocage **1** (see compound **1** in VII-G-1) shows the reversed phase-transfer catalysis toward Wacker oxidation of olefins which is a typical Pd(II)-promoted catalytic reaction. Thus, styrene is effectively and catalytically oxidized to acetophenone (86% yield) by treating it with aqueous solution of (en)Pd(NO<sub>3</sub>)<sub>2</sub> (10 mol%) and cage **1** (10 mol%).

### VII-G-12 Hydrophobic Assembling of a Coordination Nanobowl into a Dimeric Capsule Which can Accommodate upto Six Large Organic Molecules

YU, Shu-Yan<sup>1</sup>; KUSUKAWA, Takahiro; KUMAR, Biradha<sup>1</sup>; FUJITA, Makoto  
(<sup>1</sup>JSPS)

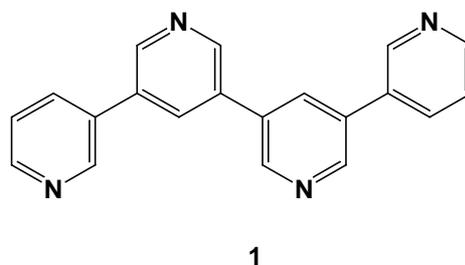
Dimerization of bowl-shaped molecules is an attractive approach to molecular capsules which are capable of accommodating organic molecules within their interior space. Both covalent and non-covalent dimers of bowl-shaped molecules have been studied during the last decade. Recently reported coordination nanobowl **1** provides a unique component for a dimeric capsule because the nature of the bowl is amphiphilic: *i.e.*, the open cavity of **1** is surrounded by 16 aromatic rings and thus hydrophobic, whereas the outside surface of the bowl is hydrophilic due to the exposure of six charged Pd(II) centers. Therefore, bowl **1** is expected to assemble in aqueous media into a dimeric capsule creating a large hydrophobic pocket inside the framework. Reported here is that such a dimeric structure assembles in a solid state accommodating as many as six neutral organic molecules. Spectroscopic studies elucidated that the same structure also exists even in solution.



### VII-G-13 Porous Coordination Polytubes

BIRADHA, Kumar<sup>1</sup>; AOYAGI, Masaru<sup>2</sup>; FUJITA, Makoto  
(<sup>1</sup>JSPS; <sup>2</sup>GUAS)

Despite great interest in porous coordination polymers assembled from metals and bridging ligands, there remains difficulty in predicting cavities in the polymer frameworks because of the frequently encountered unfavorable interpenetration of the networks. This problem can be solved by designing organic ligands which are unable to give interpenetrated networks. In this regard, use of a panel-like ligand such as **1** is attractive because its coordination assembly is expected to give polytube structures which are not allowed to interpenetrate. In this report we show that, upon treatment with a transition metal (CuI), ligand **1** assembles into polytube structures which accommodate organic guests in the tubular cavities. Interestingly, the polytube structures are templated by the guest employed; *i.e.*, two polytubes possessing different linkage connectivities with the accessible porosity of *ca.* 30–50% have been obtained by using different organic guests.



### VII-G-14 X-Ray And NMR Observation of Encapsulated Molecules in a Self-Assembled Coordination Nanocage

KUSUKAWA, Takahiro; FUJITA, Makoto

Nano-sized coordination cage **1** (see compound **1** in VII-G-1) has been shown to enclathrate “C-shaped” molecules such as *cis*-azobenzene and -stilben derivatives. The dimeric assembly of the guests was evidenced for a diaryl diketone guest **2**, by X-ray crystallography (Figure 1), which showed the formation of M and P helical conformations for the guest molecule. Due to the formation of a desymmetrized M/P meso dimeric structure, the  $^1\text{H-NMR}$  showed 12 signals for the pyridine protons of the triazine ligand. This observation indicated that the conformation of guest molecule **2** was fixed as a meso-dimeric form even in a solution.

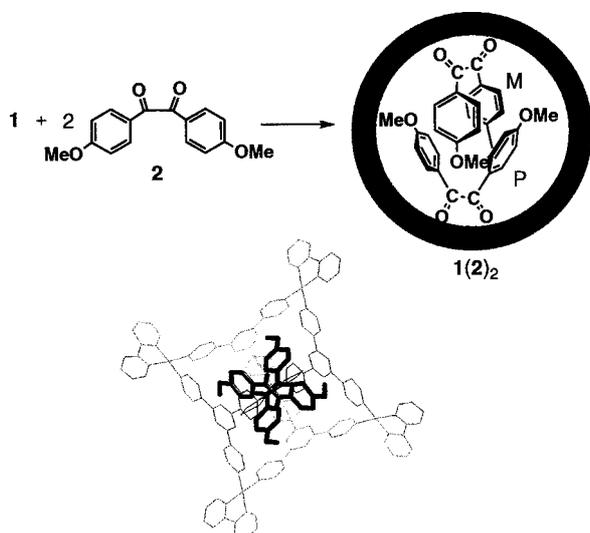


Figure 1. The crystal structure of **1(2)<sub>2</sub>**.