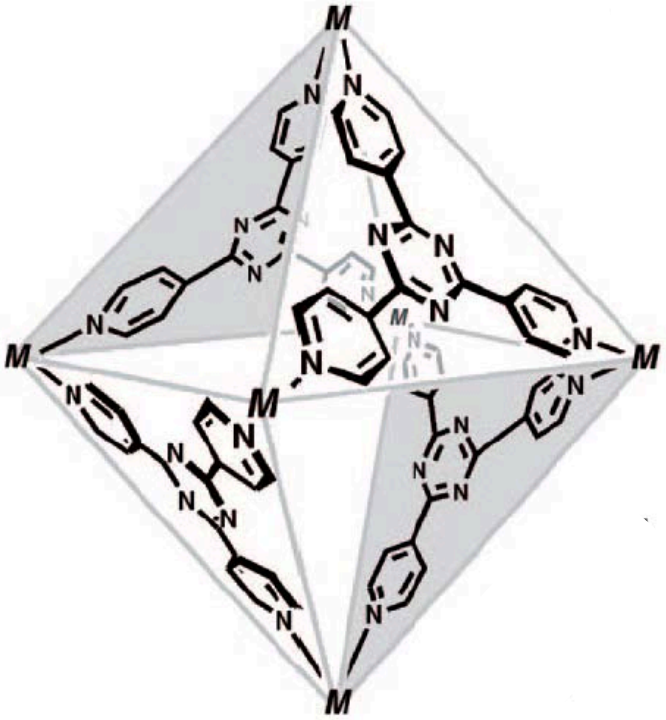
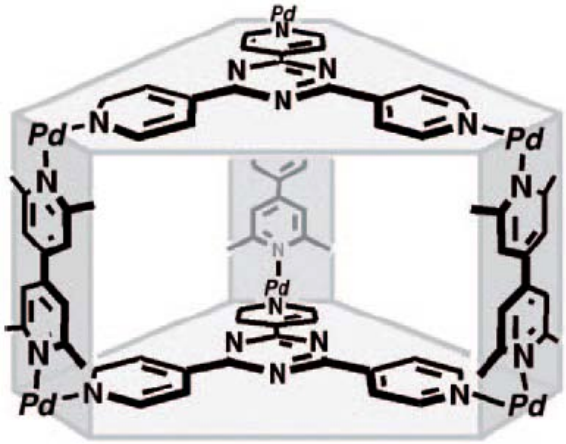
The Career of Makoto Fujita





Kai Xi

MacMillan Group Meeting

Feb 9th, 2011

Education and Career

Makoto Fujita (藤田　誠)

■ Education

B.S.: Chiba University (1980)

M.S.: Chiba University (1982)

Ph.D.: Tokyo Institute of Technology (1987)

■ Independent Career

Assistant Professor: Chiba University (1988 - 1994)

Associate Professor: Chiba University (1994 - 1997)

Associate Professor: Institute of Molecular Science (1997 - 1999)

Professor: Nagoya University (1999 - 2002)

Professor: The University of Tokyo (2002 - present)

東京大学
THE UNIVERSITY OF TOKYO

Project Leader: Core Research of Evolutional Science & Technology
of Japan Science and Technology Corporation (1997- present)

Achievements and Awards

■ Achievements

A pioneer in the field of supramolecular chemistry

Great impact on material science, nanotechnology, polymer science, organic chemistry etc.

nearly 300 publications H-Index = 62

Makoto Fujita (藤田　誠)

■ Awards

2010: The JSCC Award, Japan

2006: G.W.Wheland Award (Chicago University Lectureship Award)

2003: Nagoya Silver Medal

2001: Japan IBM Award

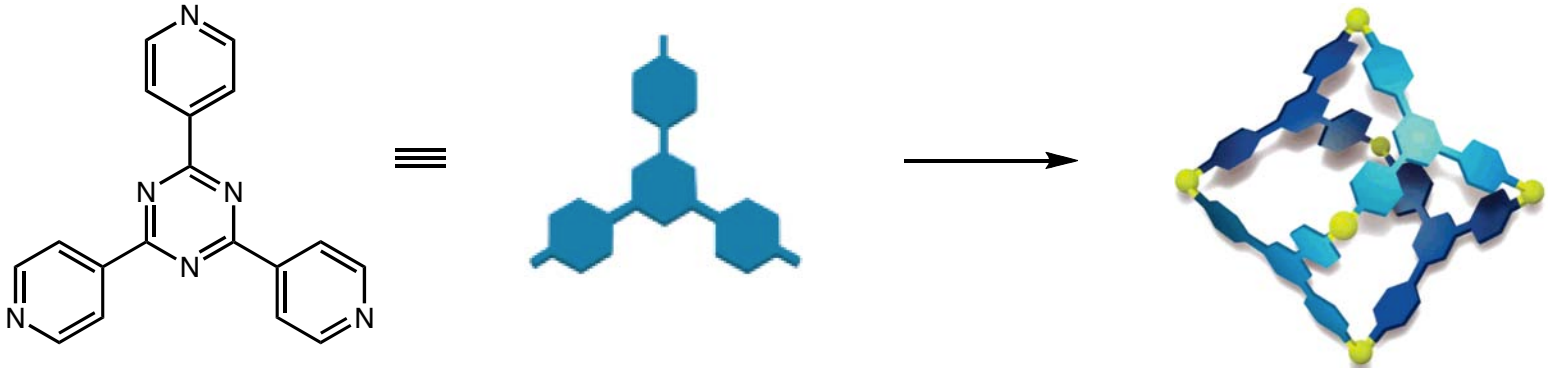
2000: Division Award of Chemical Society of Japan (Organic Chemistry)

1994: Progress Award in Synthetic Organic Chemistry, Japan

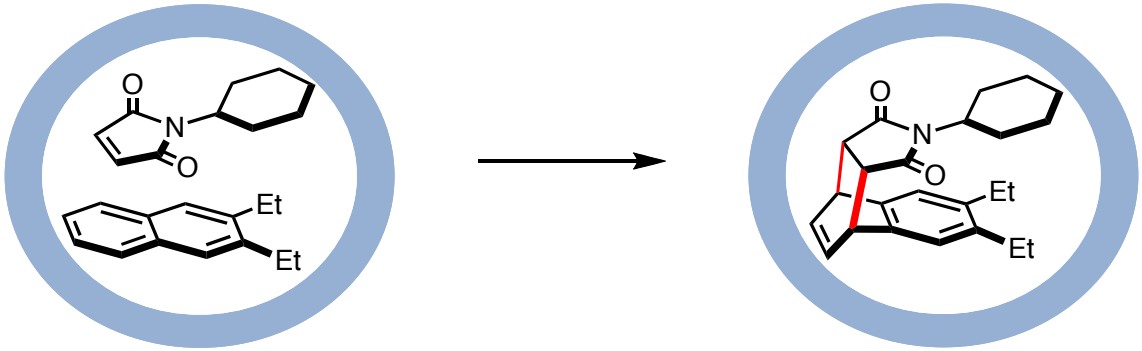
東京大学
THE UNIVERSITY OF TOKYO

Research Overview

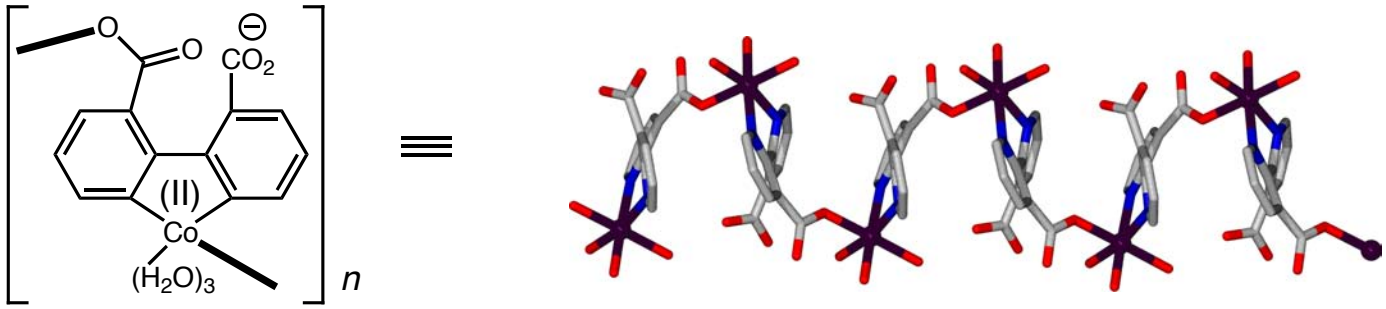
■ Develop self-assembling molecular systems utilizing transition metals ***fundamental tool***



■ Chemistry of isolated nano-space: *the "Functional Molecular Flasks"* ***finite assembly***

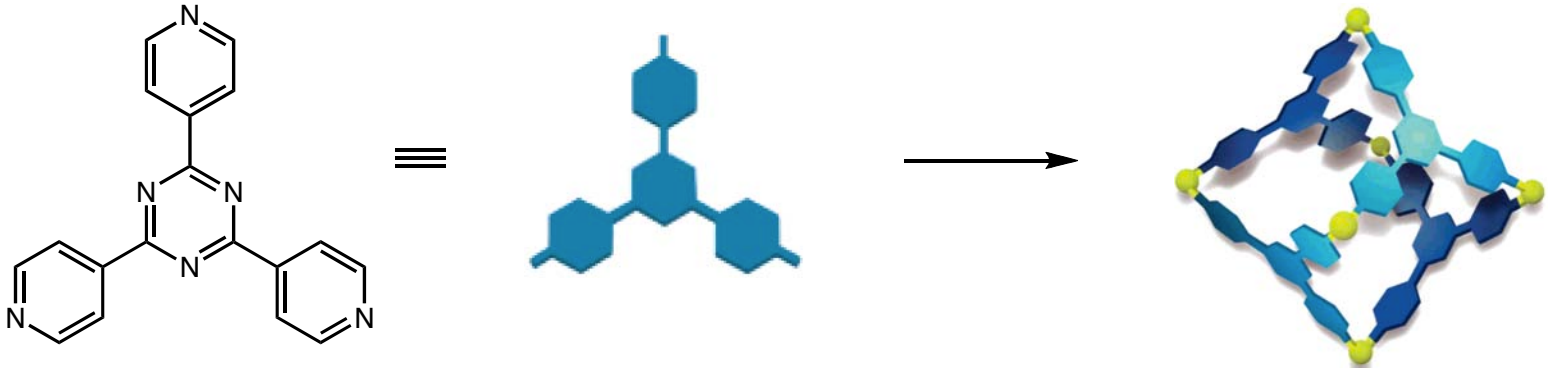


■ Coordination polymers: non-covalent polymers ***infinite assembly***

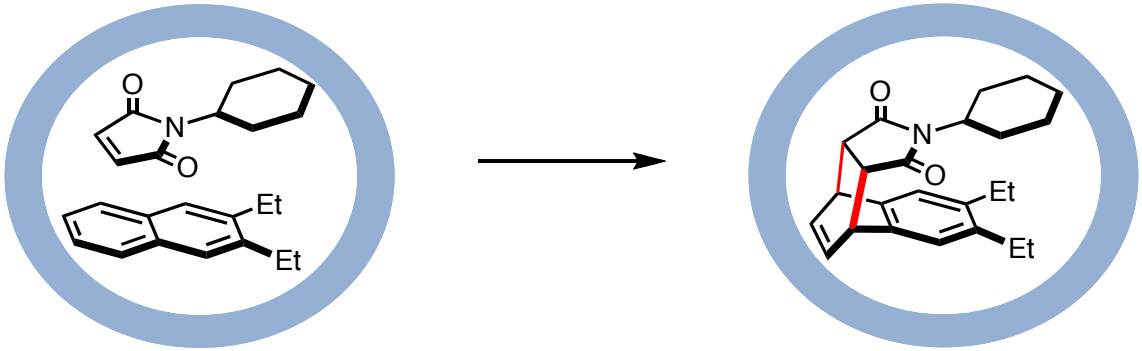


Research Overview

- Develop self-assembling molecular systems utilizing transition metals **fundamental tool**



- Chemistry of isolated nano-space: *the "Functional Molecular Flasks"* **finite assembly**



- Coordination polymers: non-covalent polymers **infinite assembly**

Supramolecular Chemistry – a Research Field beyond the Molecules

- Supramolecular chemistry focuses on the chemical systems made up of a discrete number of assembled molecular subunits or components.

Non-covalent forces: *hydrogen bonding, metal coordination, hydrophobic forces, van der Waals forces, electrostatic effects etc*

Johannes van der Waals
(1837 - 1923)

Existence of intermolecular forces

Hermann Emil Fischer
(1852 - 1919)

Enzyme-substrate interactions
Molecular recognition
Host-guest chemistry

Philosophical roots of supramolecular chemistry

Supramolecular Chemistry – a Research Field beyond the Molecules

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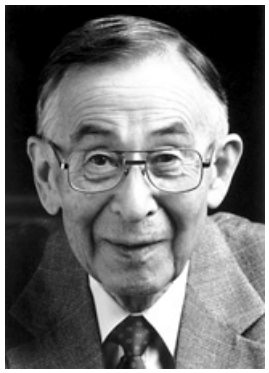
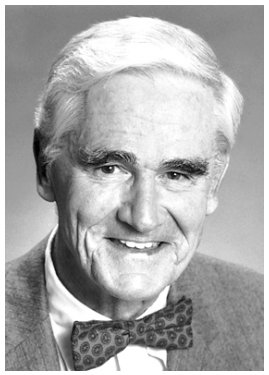


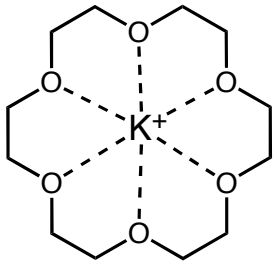
Charles John Pedersen
(1904 - 1989)



Donald James Cram
(1919 - 2001)

Jean-Marie Lehn
(1939 -)

1987



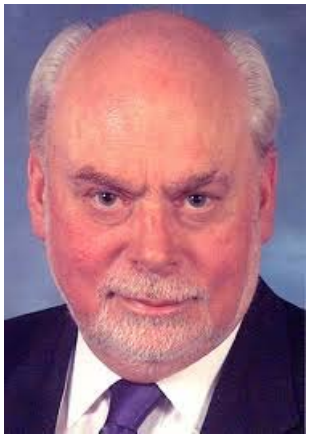
Development of crown ethers
Shape- and ion-selective receptors

Established the importance of supramolecular chemistry

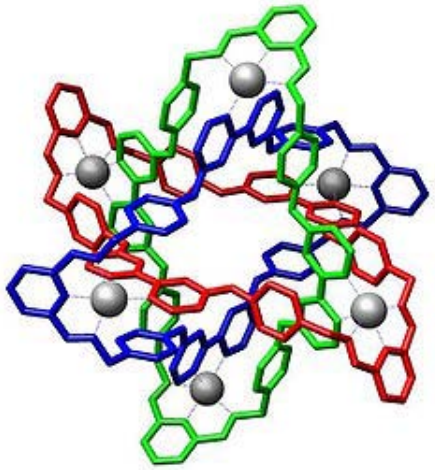
Supramolecular Chemistry – a Research Field beyond the Molecules

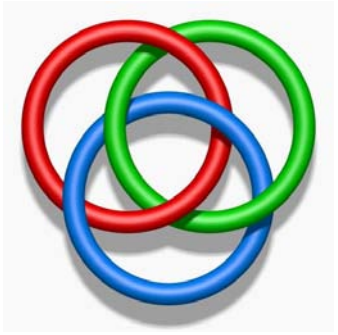
- Supramolecular chemistry focuses on the chemical systems made up of a discrete number of assembled molecular subunits or components.

Non-covalent forces: *hydrogen bonding, metal coordination, hydrophobic forces, van der Waals forces, electrostatic effects etc*



Sir (James) Fraser Stoddart
(1942 -)





Molecular Borromean ring

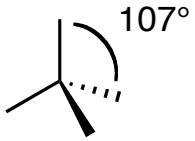
Highly complex self-assembled structure
Molecular Machinery

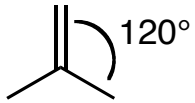
Application on nanotechnology, photo- and electo-chemistry etc.

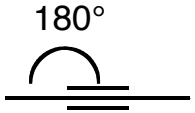
Chichak, K. S.; Cantrill, S. J.; Pease, A. R.; Chiu, S-H; Cave, G. W. V; Atwood, J. L.; Stoddard, J. F. *Science* **200**4, *304*, 1308.

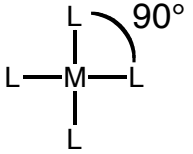
Square Complex - The Beginning

- How can we incorperate 90° angles in to organic framework?

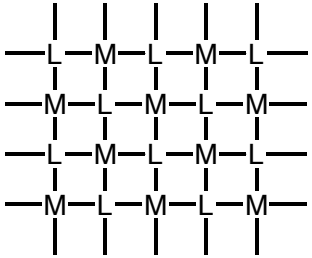


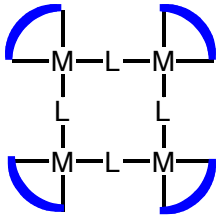


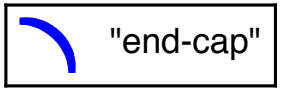




- How can we make a single square instead of infinite framework?

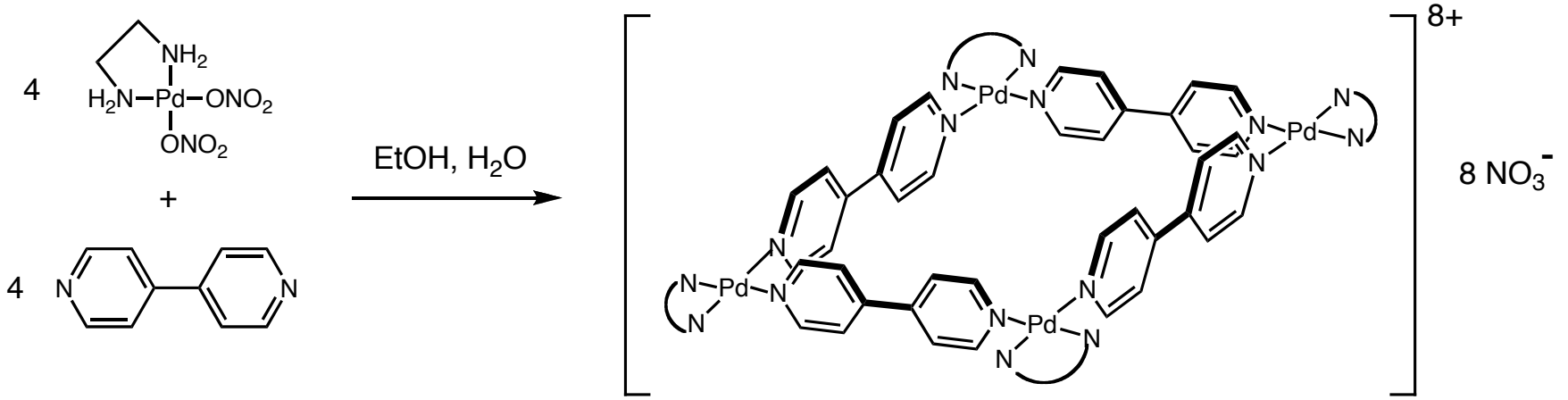




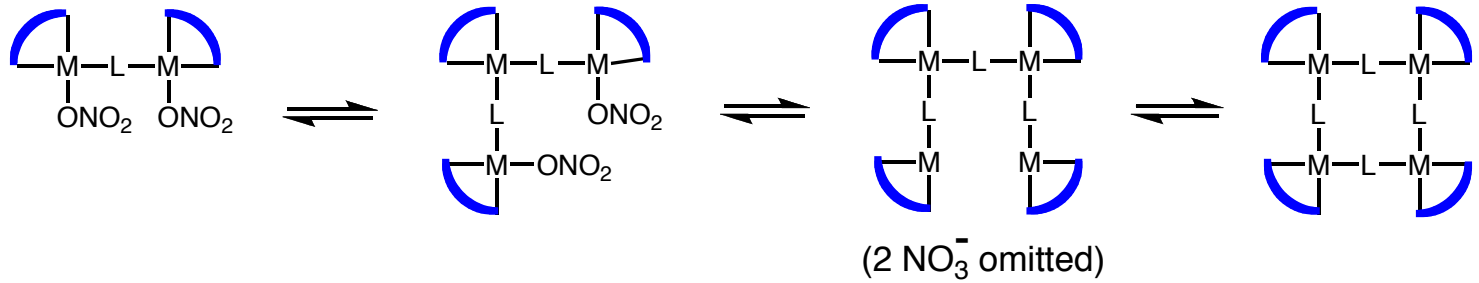


Square Complex - The Beginning

- All pyridine nuclei of the complex are completedly equivalent.
- Empirical formula predicted by CHN analysis is reproduced even if excess 4,4'-bpy is used.



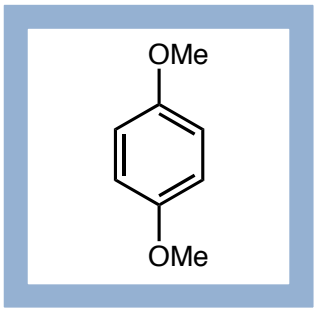
- Intermediates observed when 4,4'-bpy was portionwise added.

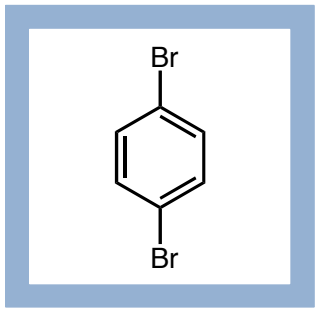


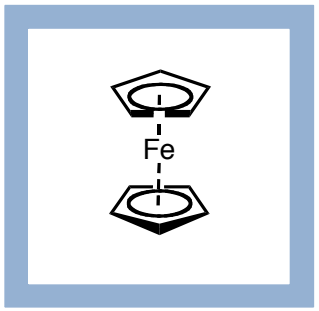
Fujita, M.; Yazaki, J.; Ogura, K. *J. Am. Chem. Soc.* **1990**, *112*, 5645.

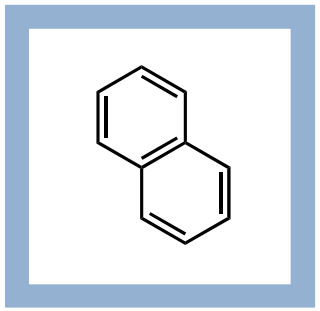
X-ray Crystal Structure of the Square Complex

■ Some aromatic molecules can be recognized and form a complex.

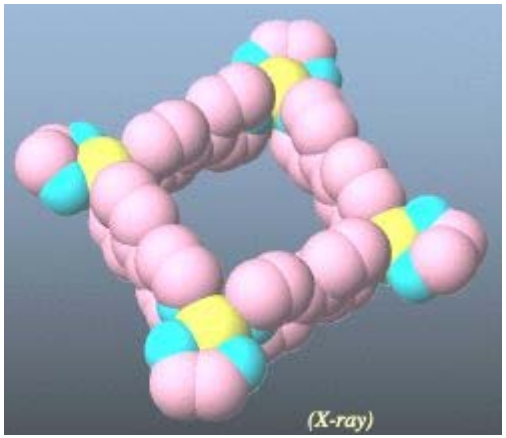








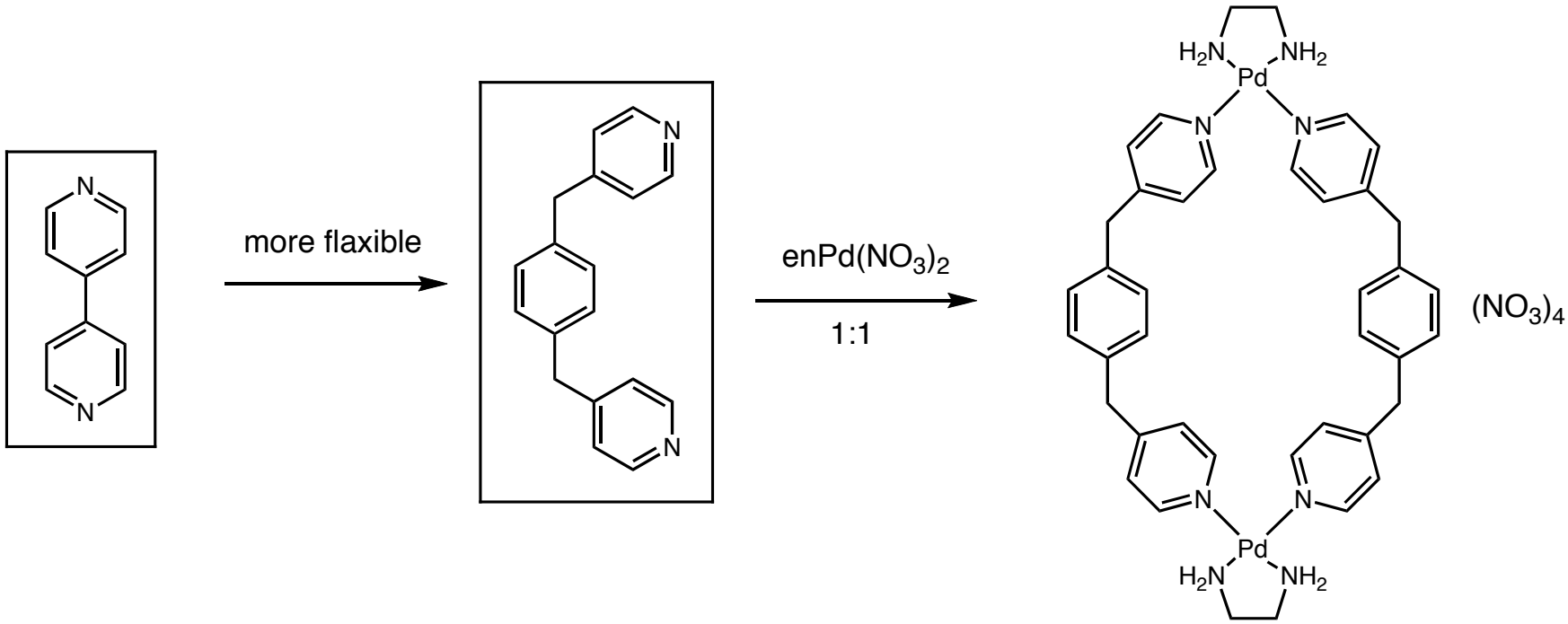
■ X-ray crystal structure is determined from the naphthlene complex.



Fujita, M.; Sasaki, O.; Mitsuhashi, T.; Fujita, T.; Yazaki, J.; Yamaguchi, K.; Ogura, K. *J. Chem. Soc., Chem. Commun.* **1996**, 1535.

Formation of Catenane

- What will happen if the ligand change from rigid to flexible?



Fujita, M.; Ibukuro, F.; Hagihara, H.; Ogura, K. *Nature* **1994**, *367*, 720.

Formation of Catenane

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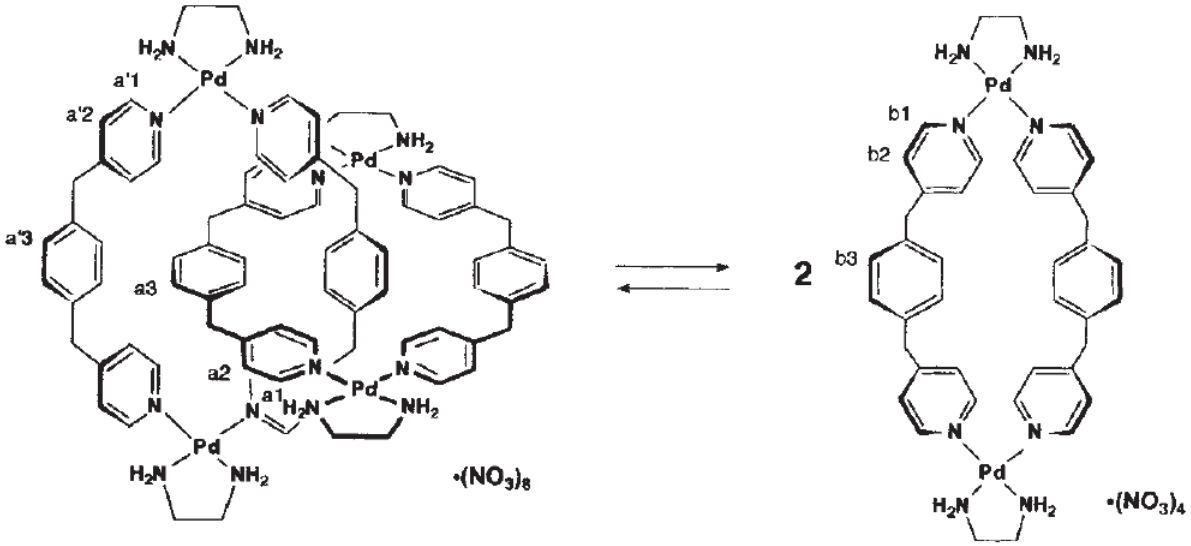
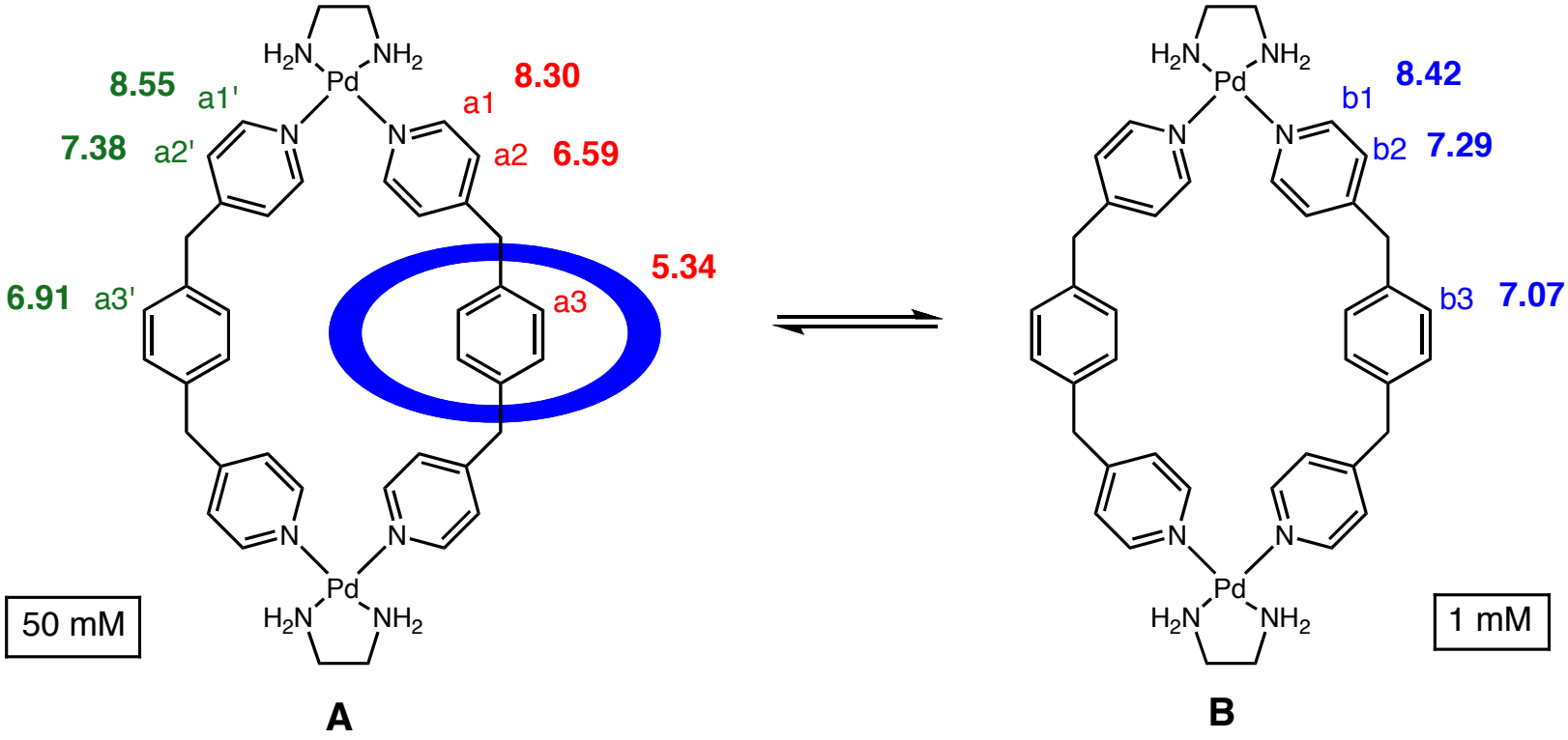


Fujita, M.; Ibukuro, F.; Hagihara, H.; Ogura, K. *Nature* **1994**, *367*, 720.

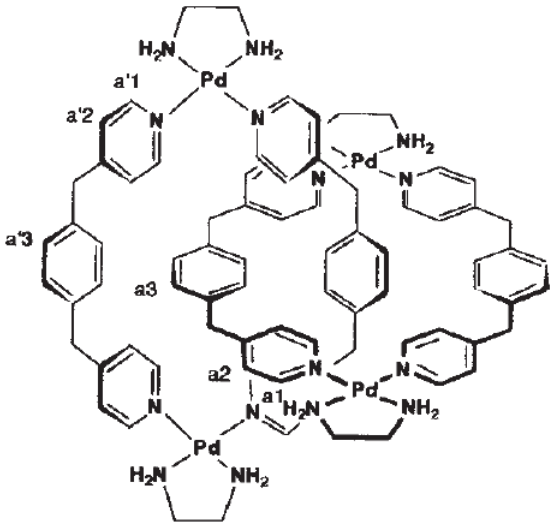
NMR Data Is Consistent with Catenane Structure

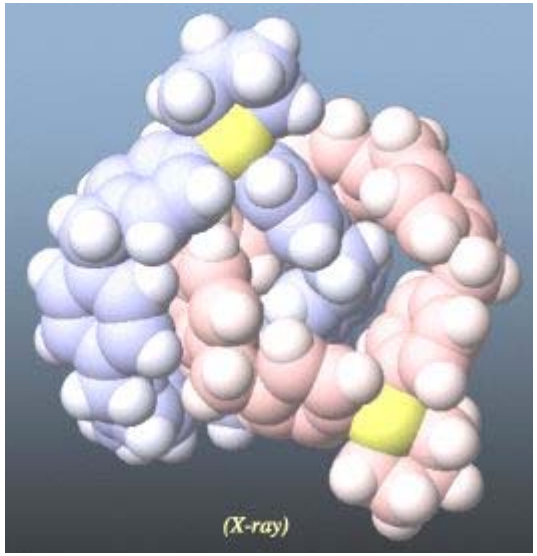
- Concentration plays an important role.



Fujita, M.; Ibukuro, F.; Hagihara, H.; Ogura, K. *Nature* **1994**, *367*, 720.

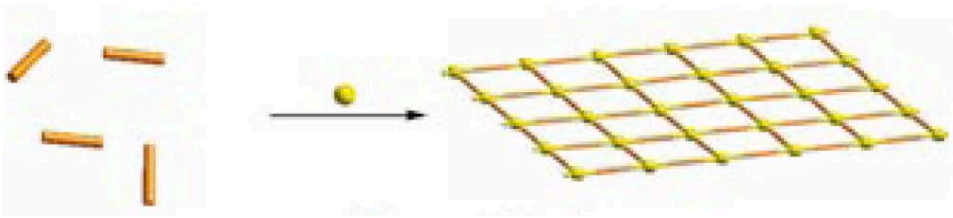
X-ray Crystal Structure of the Catenane

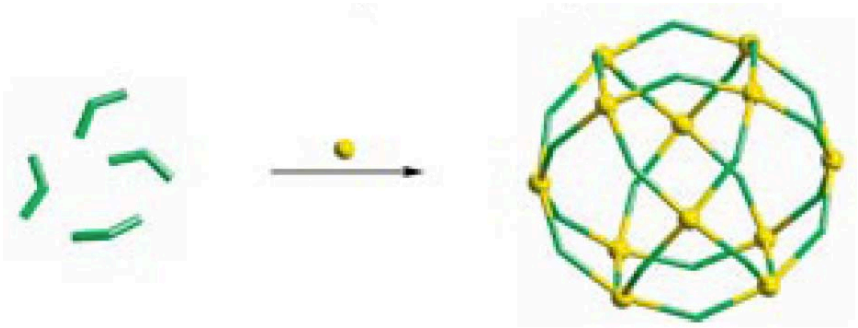


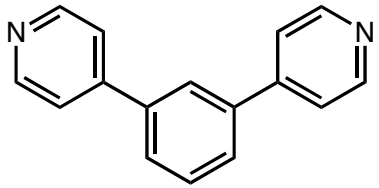


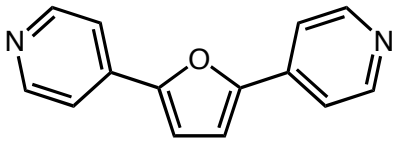
Self Assembly of Molecular Spheres

- Molecular spheres are formed from banana-shaped ligands.



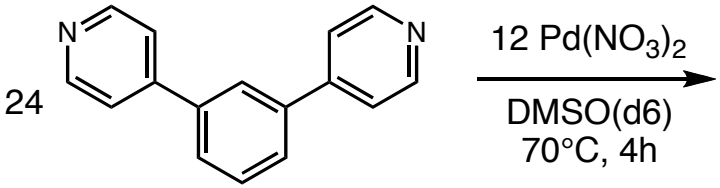


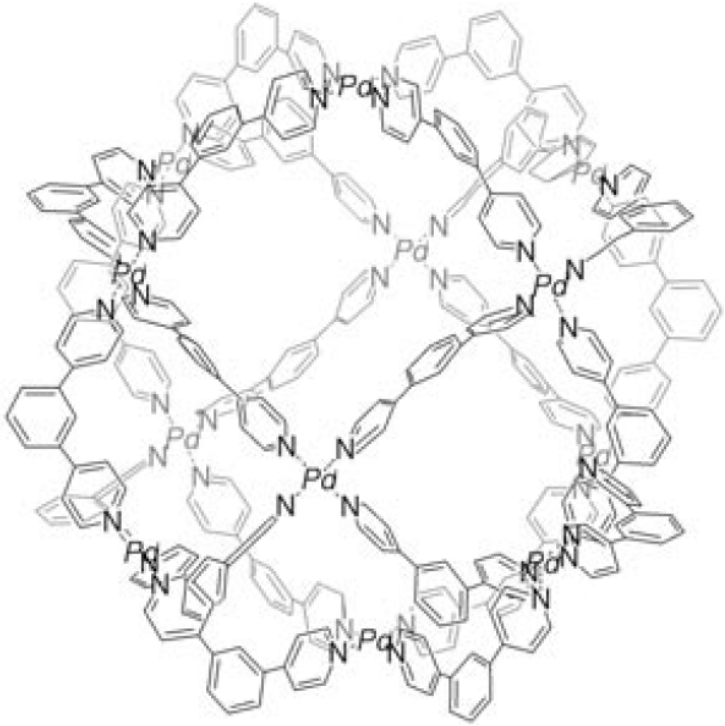


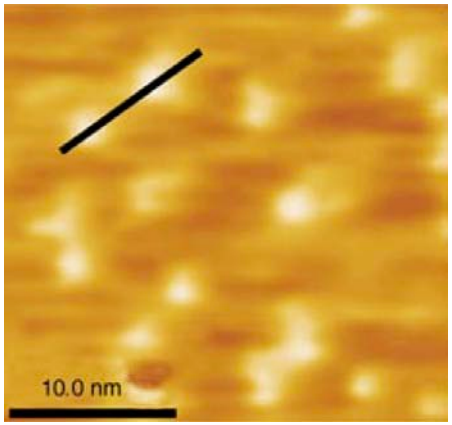


Tominaga, M.; Suzuki, K.; Kawano, M.; Kusukawa, T.; Ozeki, T.; Sakamoto, S.; Yamaguchi, K.; Fujita, M. *Angew. Chem., Int. Ed.* **2004**, *43*, 5621.

Self Assembly of Molecular Spheres





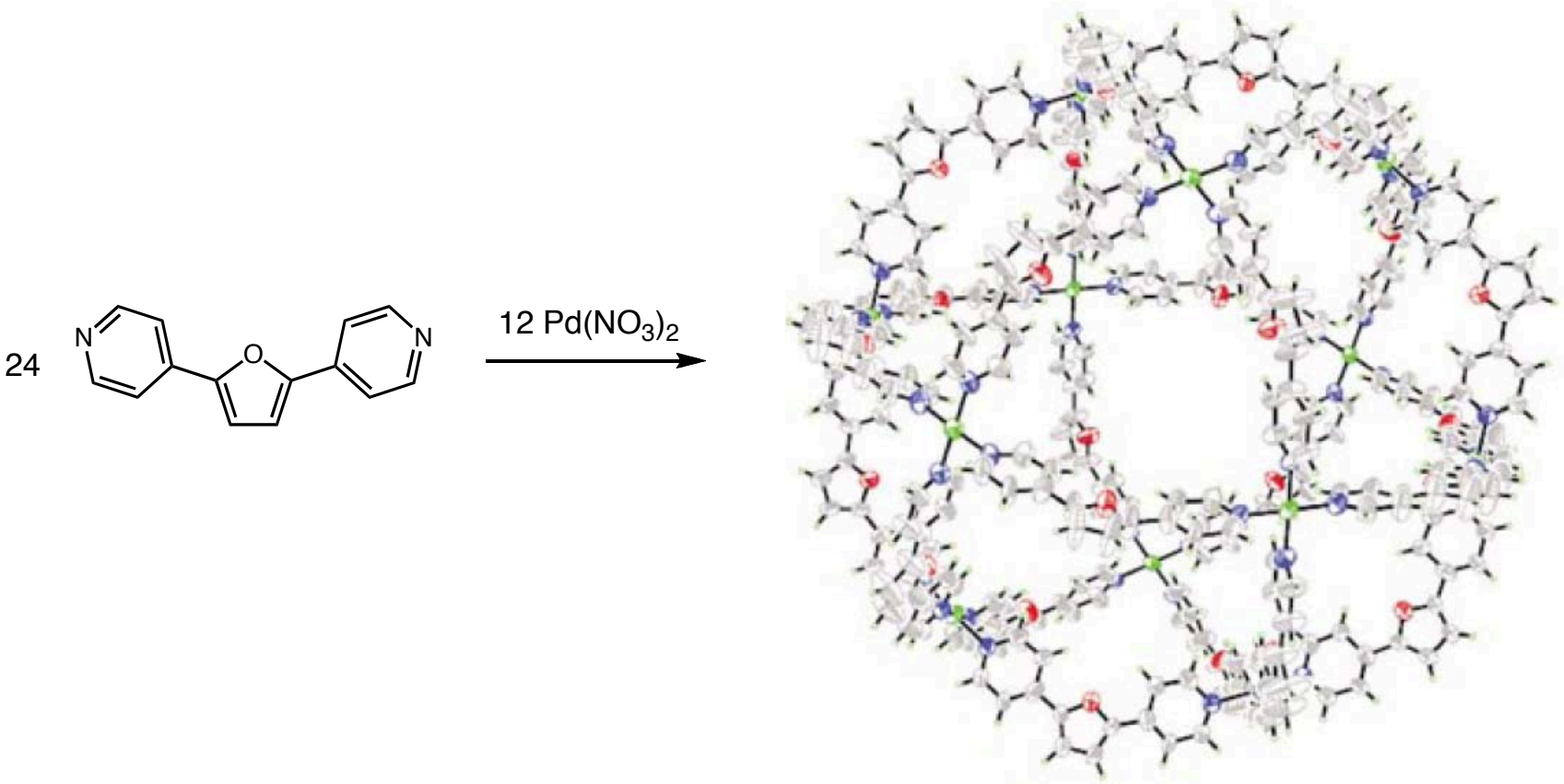


STM image of individual spheres (~ 3.5 nm)

Tominaga, M.; Suzuki, K.; Kawano, M.; Kusukawa, T.; Ozeki, T.; Sakamoto, S.; Yamaguchi, K.; Fujita, M. *Angew. Chem., Int. Ed.* **2004**, *43*, 5621.

Self Assembly of Molecular Spheres

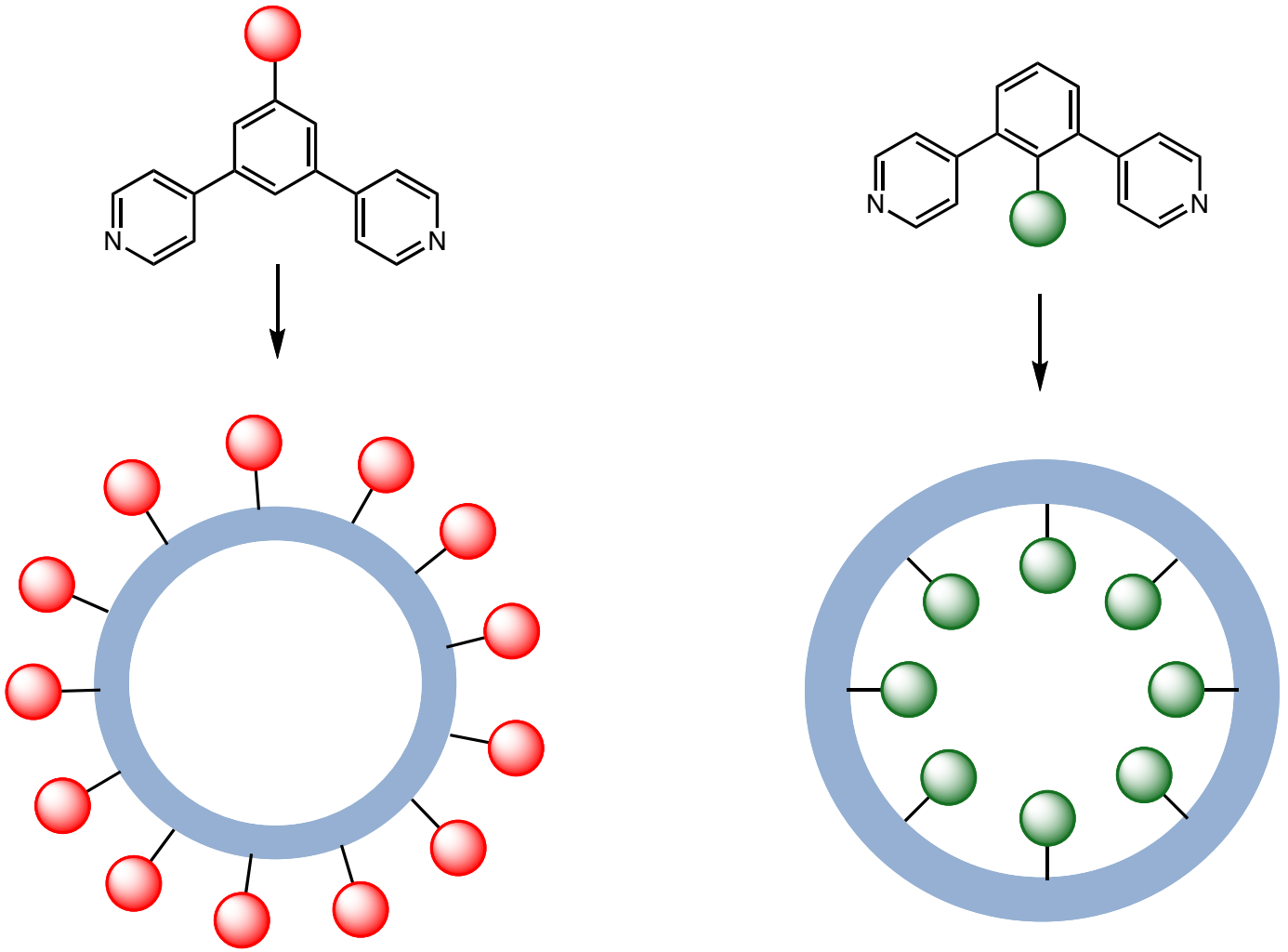
- Sturcture of molecular spheres are further confirmed by X-ray crystal structure.



Tominaga, M.; Suzuki, K.; Kawano, M.; Kusukawa, T.; Ozeki, T.; Sakamoto, S.; Yamaguchi, K.; Fujita, M. *Angew. Chem., Int. Ed.* **2004**, *43*, 5621.

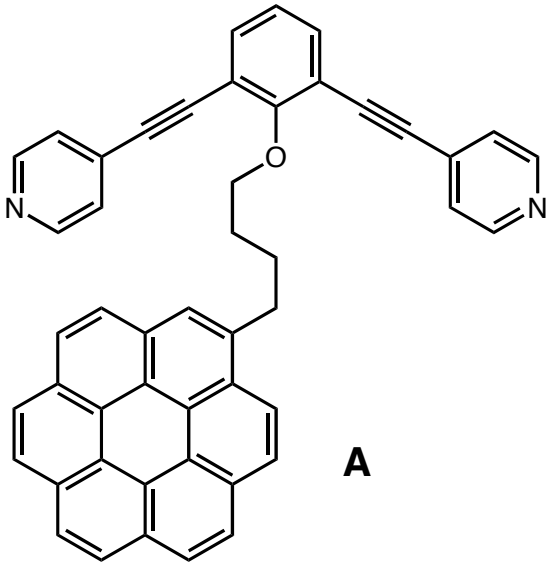
Modification of Molecular Spheres

- Sturcture modification of ligands can result inner or outer modified molecular spheres.



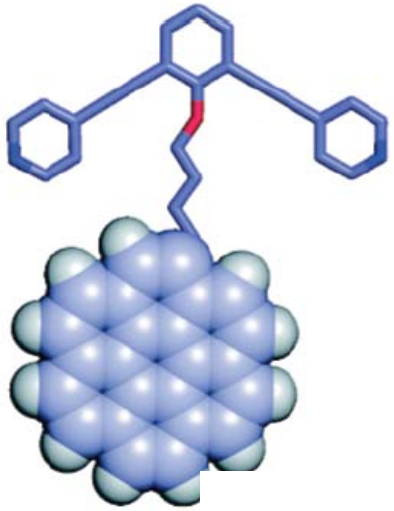
Molecular Sphere as C_{60} Container

- Coronene substituted ligand forms 4.6 nm nanoball

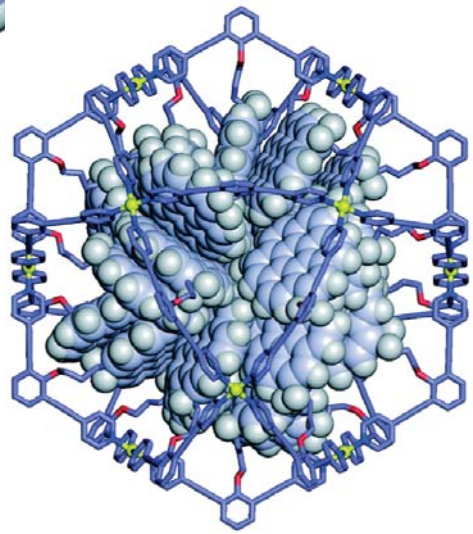


A

≡



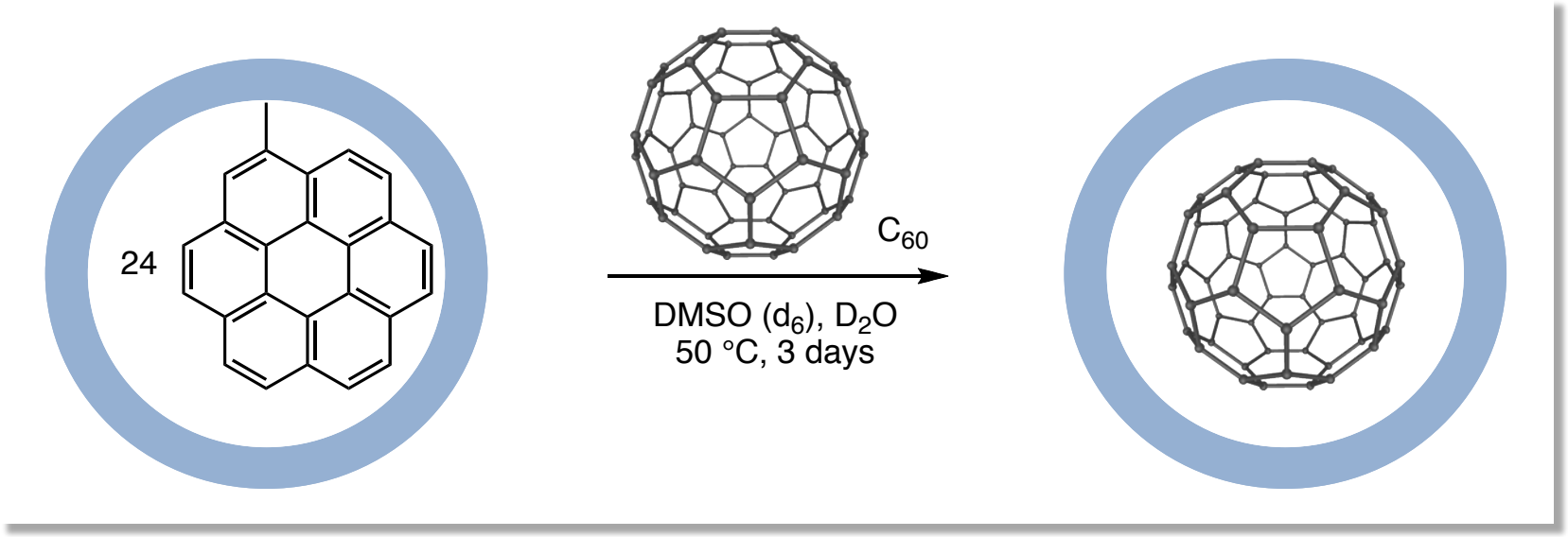
24 **A** + 12 $Pd(NO_3)_2$ ⟶



Suzuki, K.; Takao, K.; Sato, S.; Fujita, M. *J. Am. Chem. Soc.* **2010**, *132*, 2544.

Molecular Sphere – Host of C_{60}

- Molecular sphere increases the solubility of C_{60}

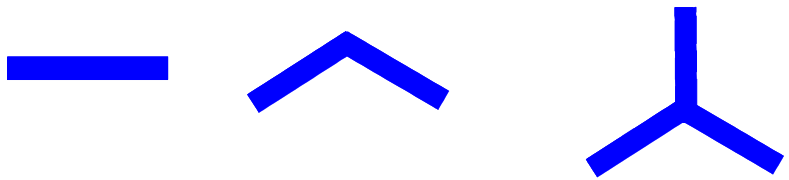


Solvent:	benzene	toluene	1-chloronaphthlene	Molecular Sphere in DMSO
Solubility of C_{60}:	2.4 mM	3.9 mM	70 mM	128 mM

Suzuki, K.; Takao, K.; Sato, S.; Fujita, M. *J. Am. Chem. Soc.* **2010**, *132*, 2544.

Formation of Molecular Cage

- Combination of triangle ligand with palladium created a octahedron complex



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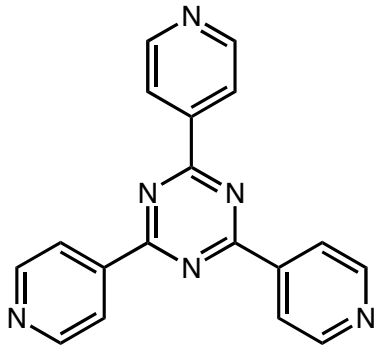


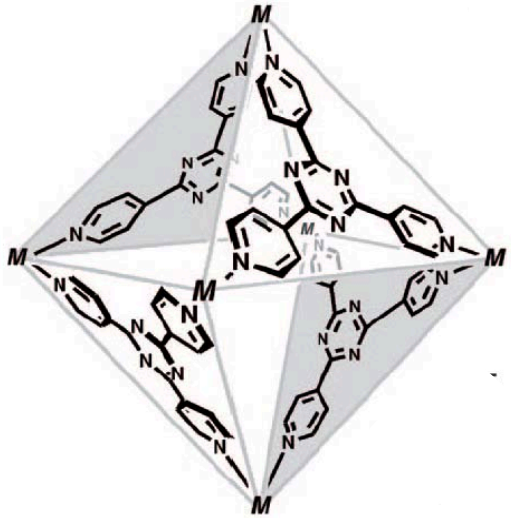
A

4 **A**

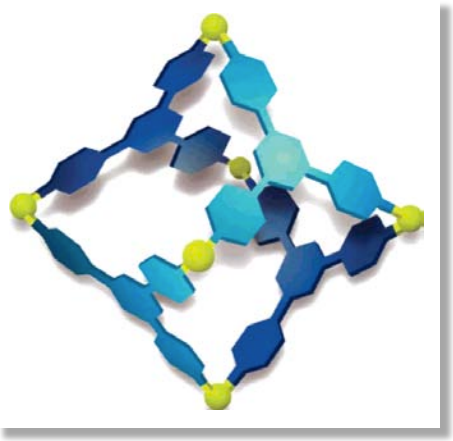
+

6 (en)Pd$(NO_3)_2$

D_2O →



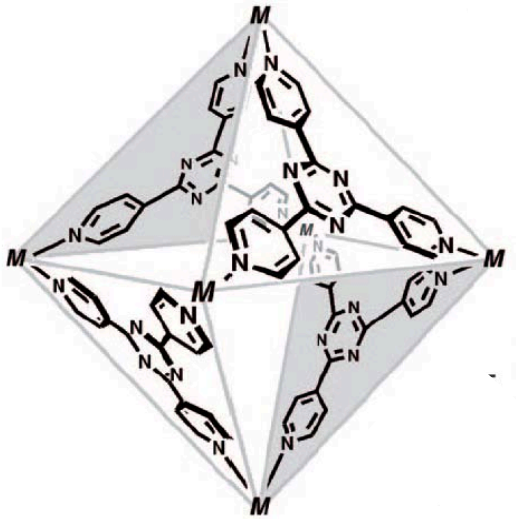
M = Pd^{2+}(en)



Fujita, M.; Oguro, D.; Miyazawa, M.; Oka, H.; Yamaguchi, K.; Ogura, K. *Nature* **1995**, *378*, 469.

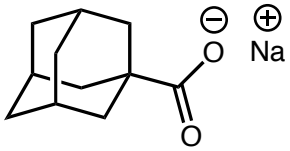
Features of the Molecular Cage

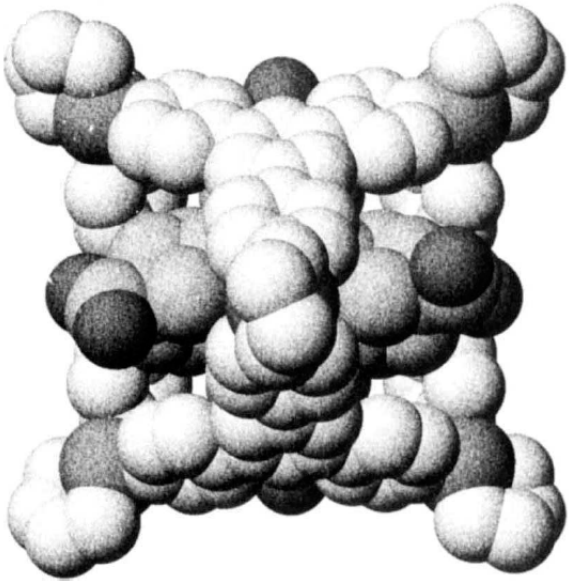
- With 12 pisitive charge, the cage is soluble in water
- Hydrophobic core can recognize organic molecules
- Special properties and activities of organic molecules inside the cage



M = Pd^{2+}(en)

+ 4



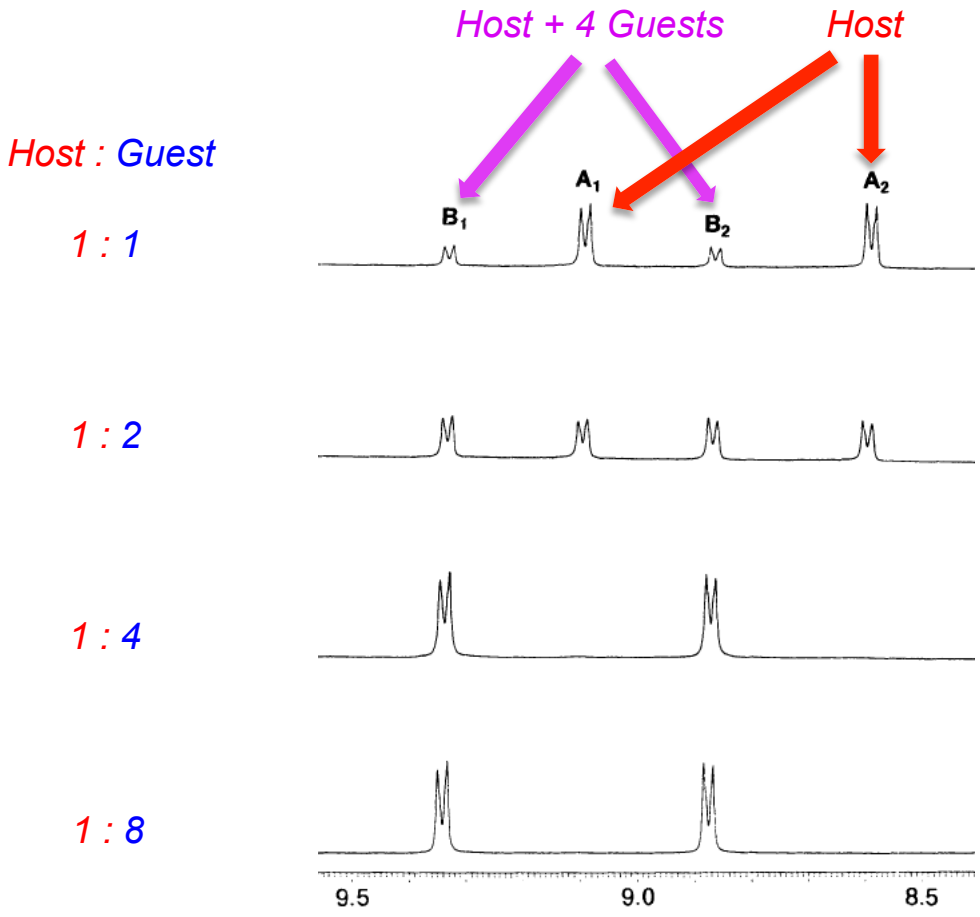


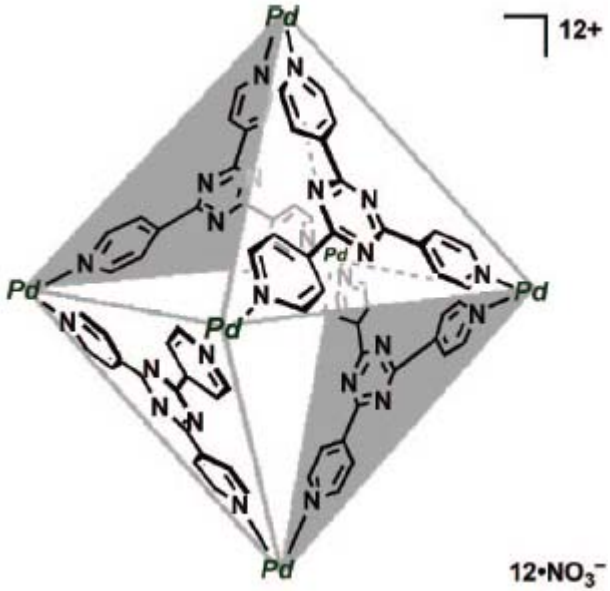
- Molecular cage co-crystallized with four molecular of adamantyl carboxylate ion

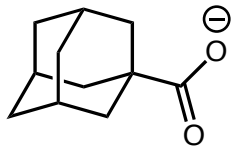
Fujita, M.; Oguro, D.; Miyazawa, M.; Oka, H.; Yamaguchi, K.; Ogura, K. *Nature* **1995**, *378*, 469.

NMR Analysis of the Complex

- Intermediates with less than four guests are not observed



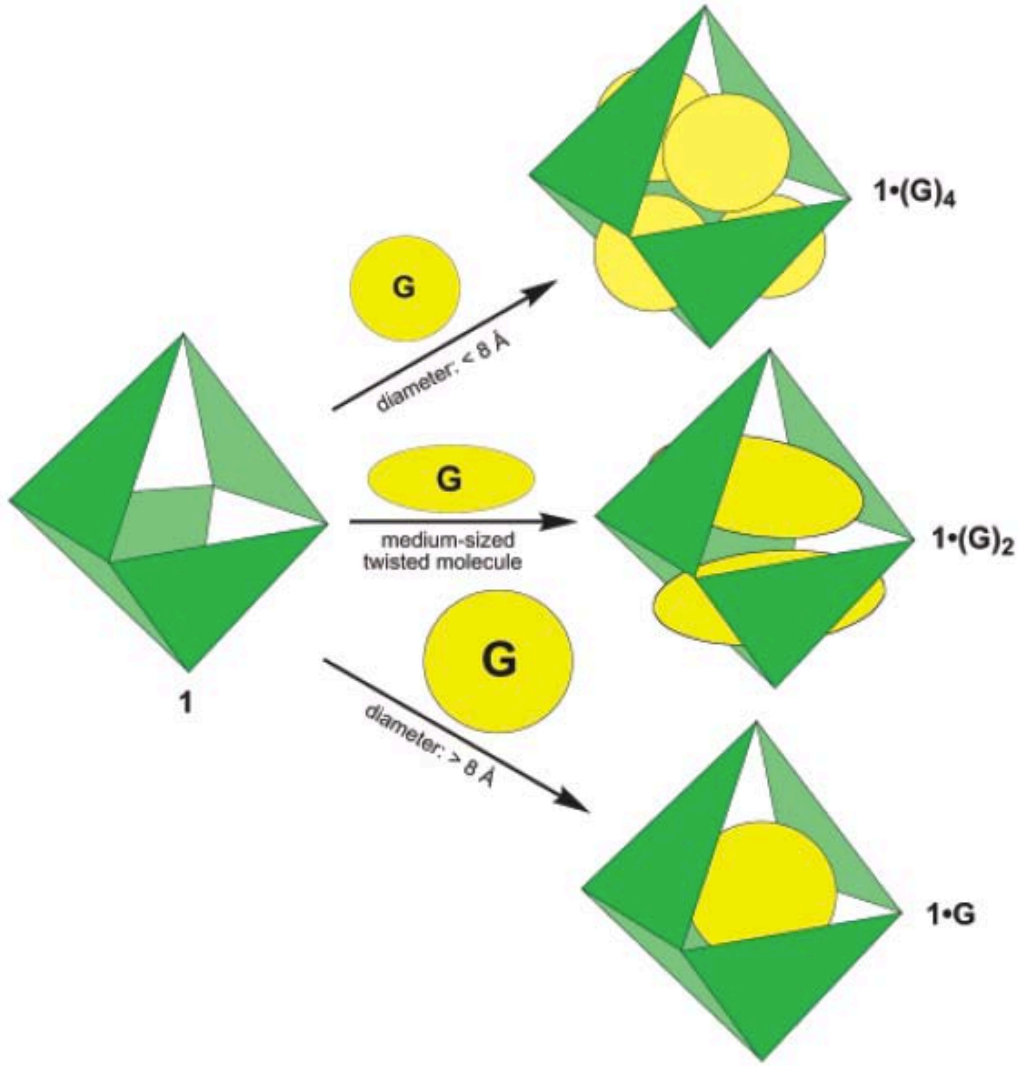


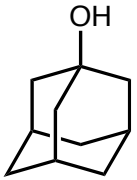


Fujita, M.; Oguro, D.; Miyazawa, M.; Oka, H.; Yamaguchi, K.; Ogura, K. *Nature* **1995**, *378*, 469.

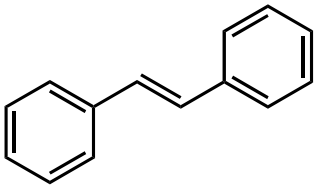
Shape and Size Dependend Binding Pattern

- Three-types of inclusion geometries, depending upon shape/size of the guest

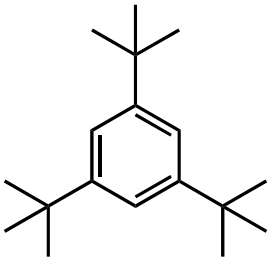




< 8 Å



(medium size, bending)

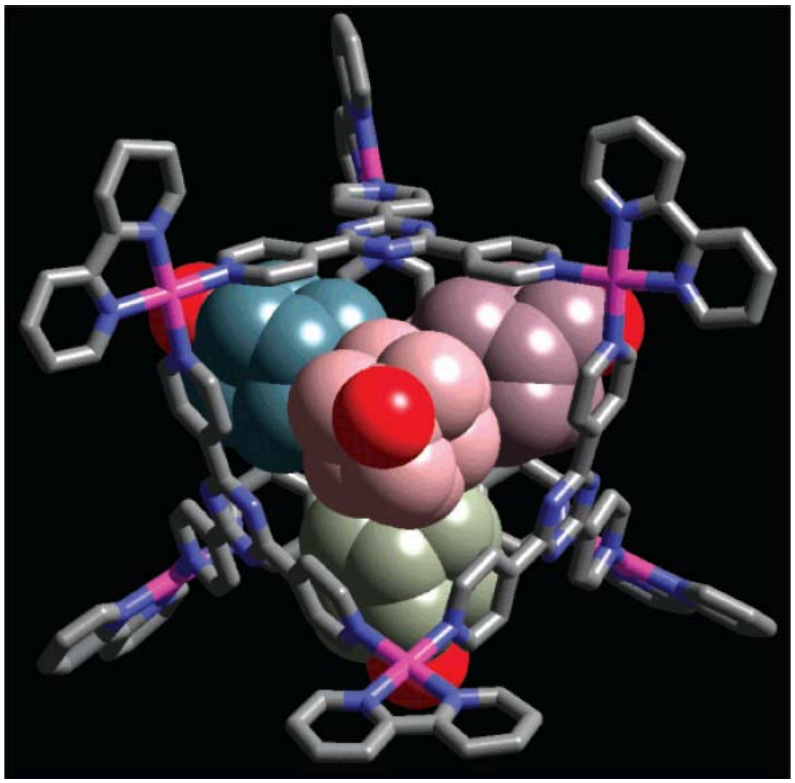


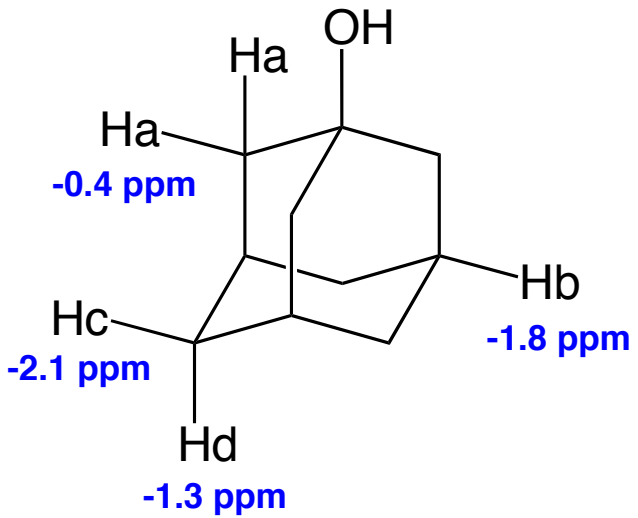
> 8 Å

Kusukawa, T.; Fujita, M. *J. Am. Chem. Soc.* **2002**, *124*, 13576.

X-ray Crystal Structure

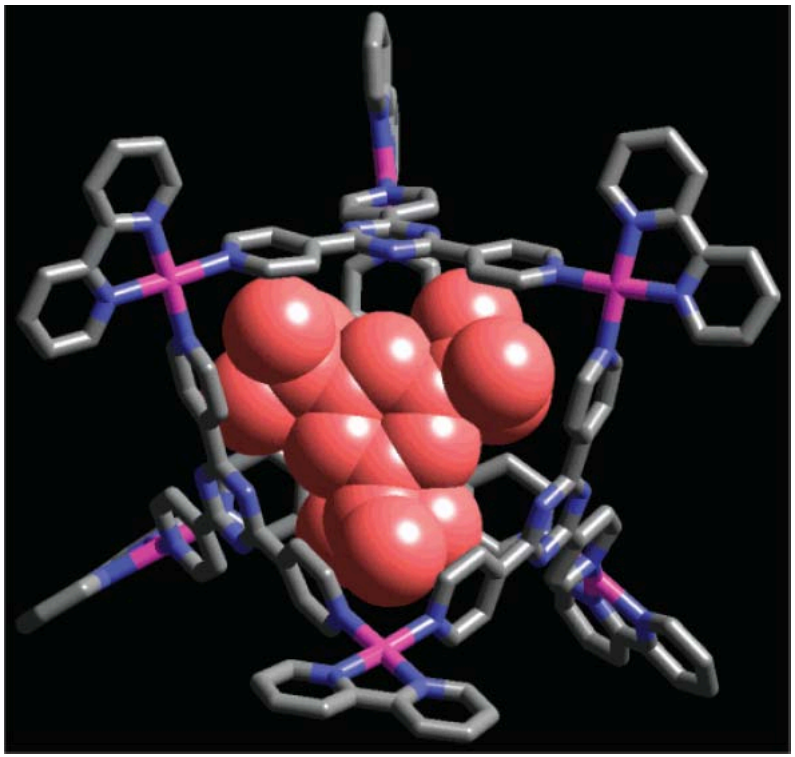
- Using 2,2'-bipyridine as end-cap makes crystallization much easier

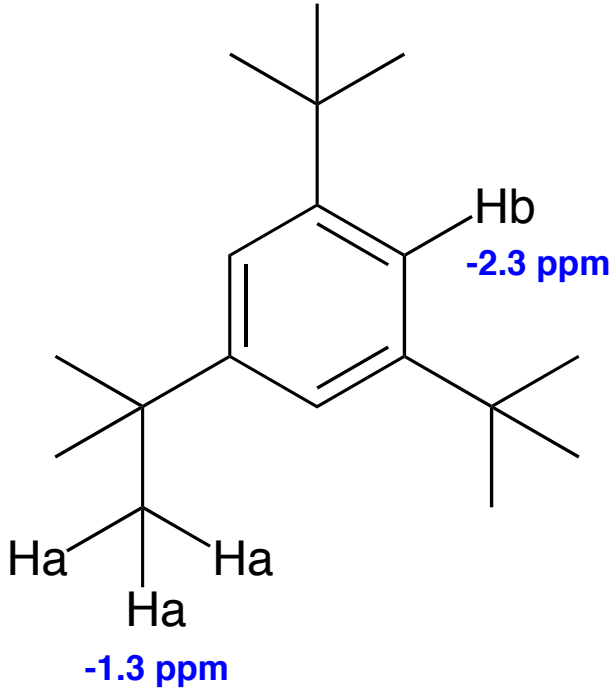




Kusukawa, T.; Fujita, M. *J. Am. Chem. Soc.* **2002**, *124*, 13576.

X-ray Crystal Structure

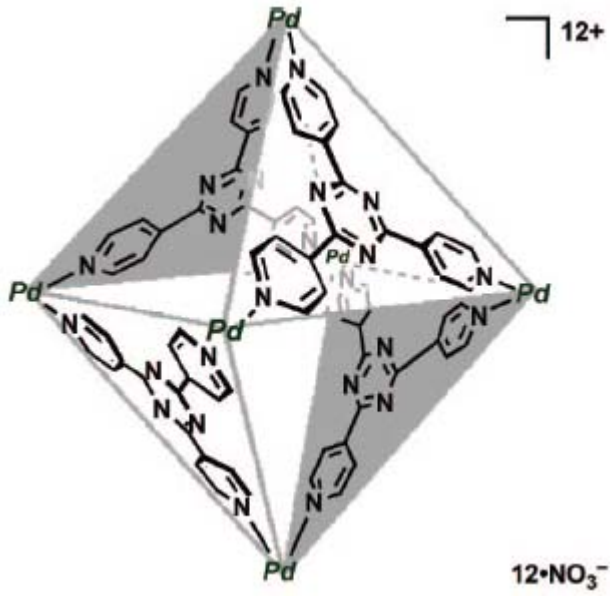




Kusukawa, T.; Fujita, M. *J. Am. Chem. Soc.* **2002**, *124*, 13576.

Sequence Selective Recognition of Peptides

- Molecular cage shows strong and selective affinity to Ac-Trp-Trp-Ala-NH_2



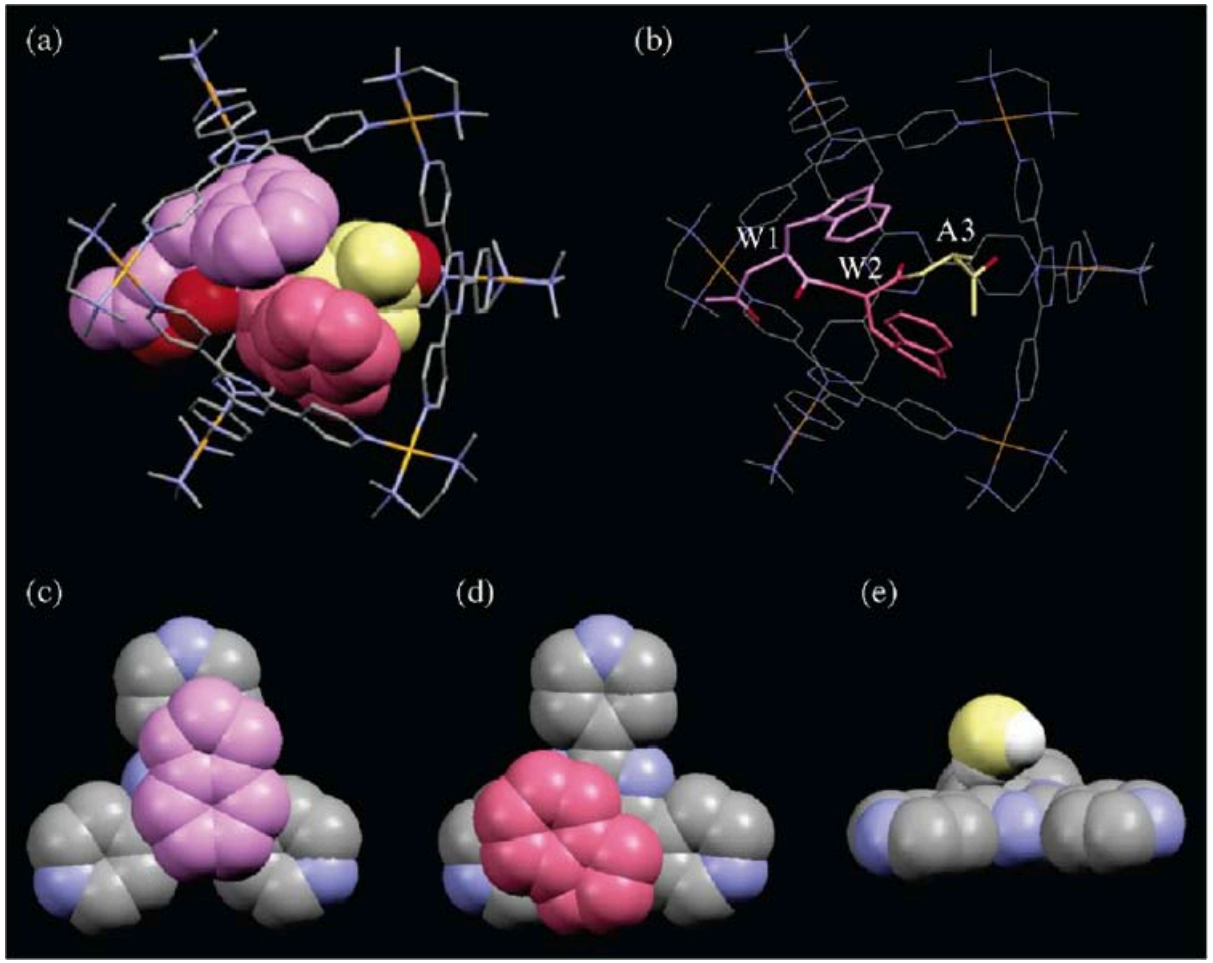
Peptides	K_a (M^{-1})
Ac-Trp-Trp-Ala-NH_2	2.1 x 10^6
Ac-Trp-Ala-Trp-NH_2	2.5 x 10^5
Ac-Ala-Trp-Trp-NH_2	2.1 x 10^4
Ac-Trp-Trp-Gly-NH_2	7.4 x 10^4
Ac-Trp-Tyr-Ala-NH_2	5.3 x 10^4
Ac-Tyr-Tyr-Ala-NH_2	4.7 x 10^3
Ac-Trp-His-Ala-NH_2	no binding
Ac-Ala-Trp-Trp-Ala-NH_2	>10^6
Ac-Ser-Gly-Ala-Trp-Trp-Ala-NH_2	>10^6

K_a was measured by UV-vis titration

Tashiro, S.; Tominaga, M.; Kawano, M.; Therrien, B.; Ozeki, T.; Fujita, M. *J. Am. Chem. Soc.* **2005**, *127*, 4546.

The X-ray Crystal Structure

- π–π Interaction (3.4 – 3.5 Å) between Trp side-chain indoles and triazine ligands
- CH–π Contact (2.5 Å) between Ala side-chain methyl group and ligand



Tashiro, S.; Tominaga, M.; Kawano, M.; Therrien, B.; Ozeki, T.; Fujita, M. *J. Am. Chem. Soc.* **2005**, *127*, 4546.

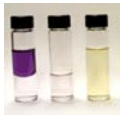
Concept of Functional Molecular Flask

- Molecules inside a nano-size molecular flask will behave differently
- New properties and new reaction

enal synthesis

sequence

small scale



optimization

molecular flask

?

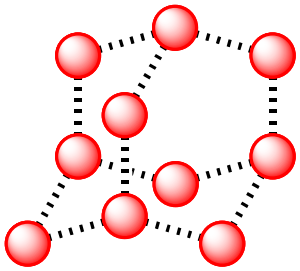
Yoshizawa, M.; Klosterman, J. K.; Fujita, M. *Angew. Chem., Int. Ed.* **2009**, *48*, 3418.

Endohedral Clusterization of Ten Water Molecules

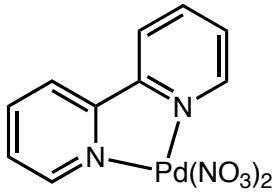
- Water can be "hydrophobic"
- Long pair (cluster) – π electron (triazine of ligand) interaction is crucial

10 H_2O

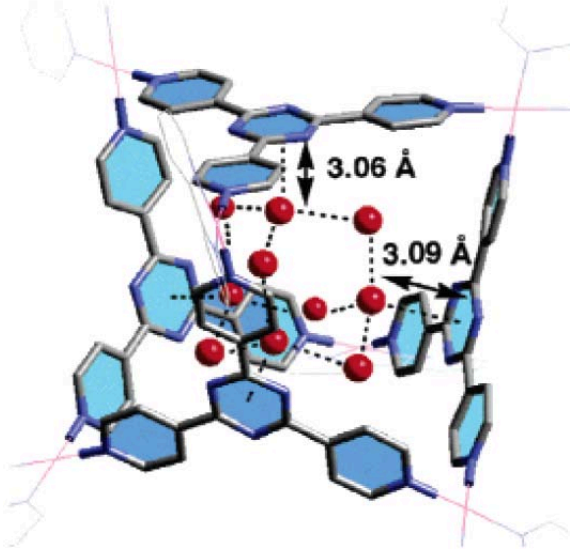
molecular cage



adamantanoid cluster
"Molecular Ice"



is used for crystallization

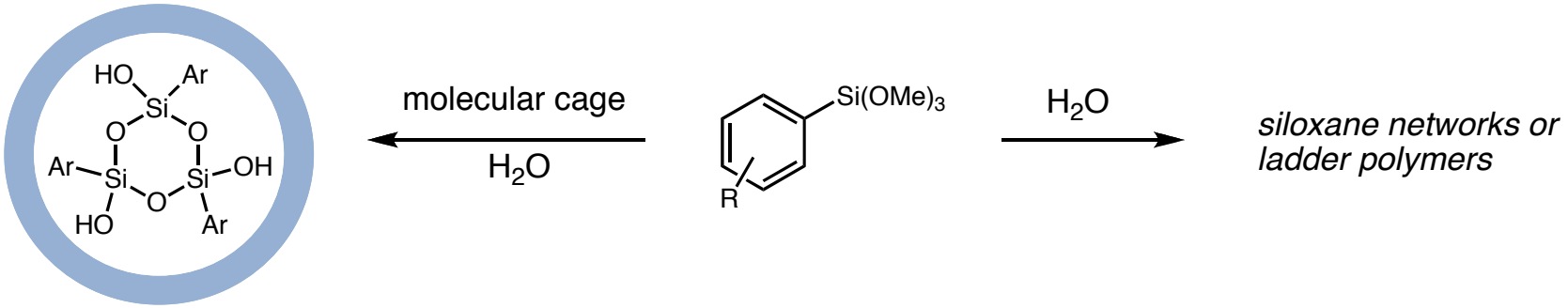


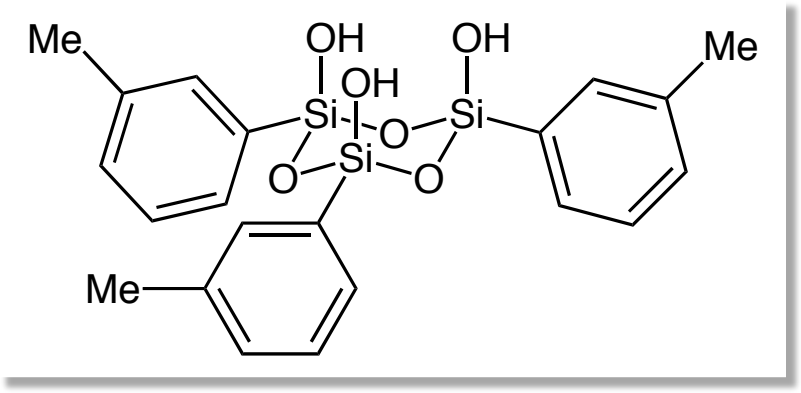
- The molecular ice does not melt even at room temperature.

Yoshizawa, M.; Kusukawa, T.; Kawano, M.; Ohhara, T.; Tanaka, I.; Kurihara, K.; Niimura, N.; Fujita, M. *J. Am. Chem. Soc.* **2005**, *127*, 2798.

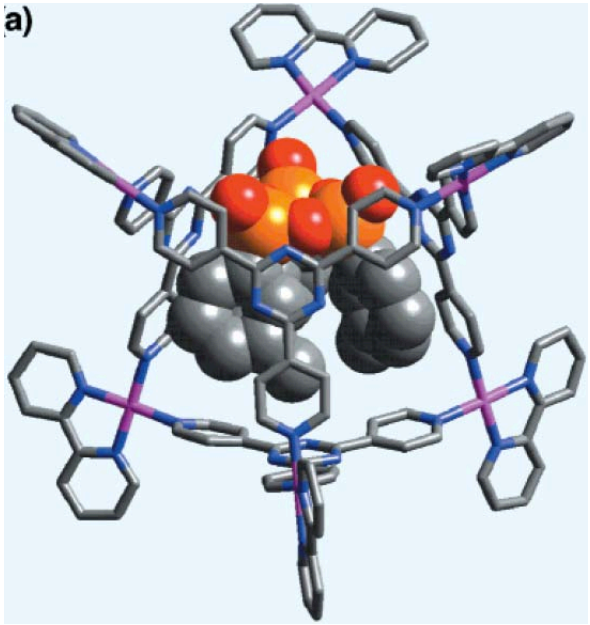
Synthesis of the Labile Cyclic Trimers of Siloxanes

- Molecular cage can trap labile intermediate during polycondensation of trialkoxysilanes





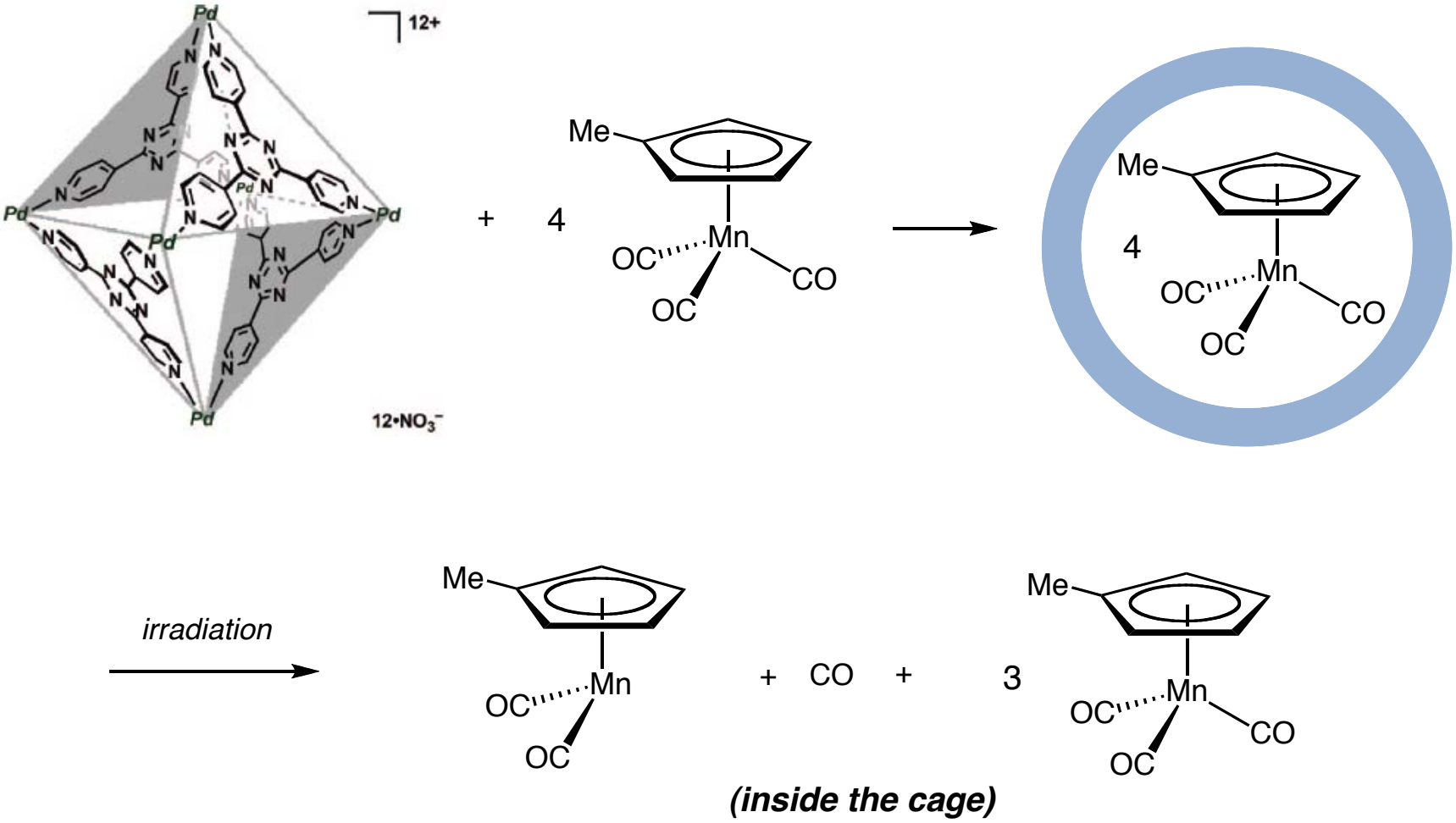
only all-cis isomer formed



Yoshizawa, M.; Kusukawa, T.; Fujita, M.; Yamaguchi. K. *J. Am. Chem. Soc.* **2000**, *122*, 6311.

Stabilization of Coordinatively Unsaturated Transition Metal Complex

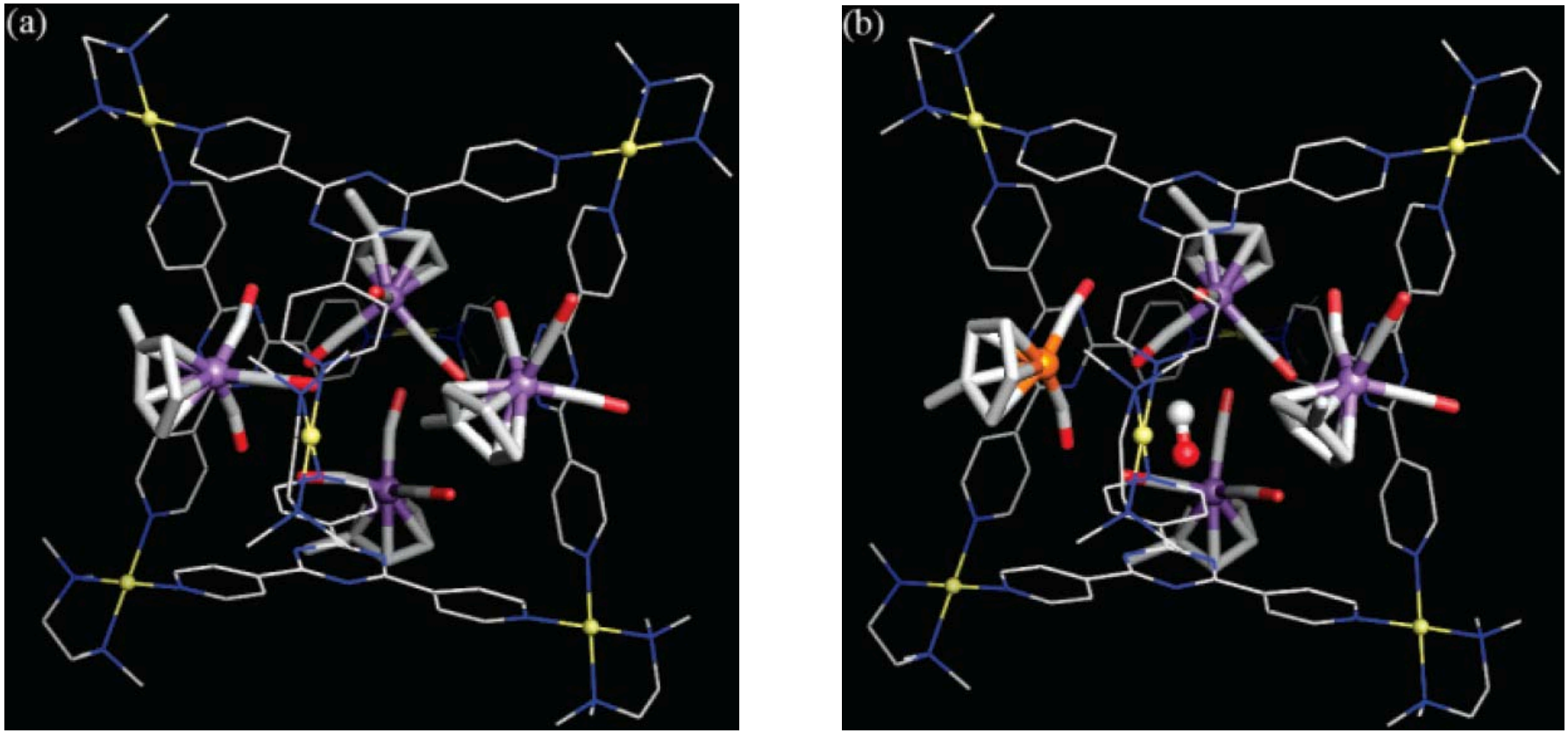
- Molecular cage can stablize the 16 electron Mn complex



Kawano, M.; Kobayashi, Y.; Ozeki, T.; Fujita, M. *J. Am. Chem. Soc.* **2006**, *128*, 6558.

Stabilization of Coordinatively Unsaturated Transition Metal Complex

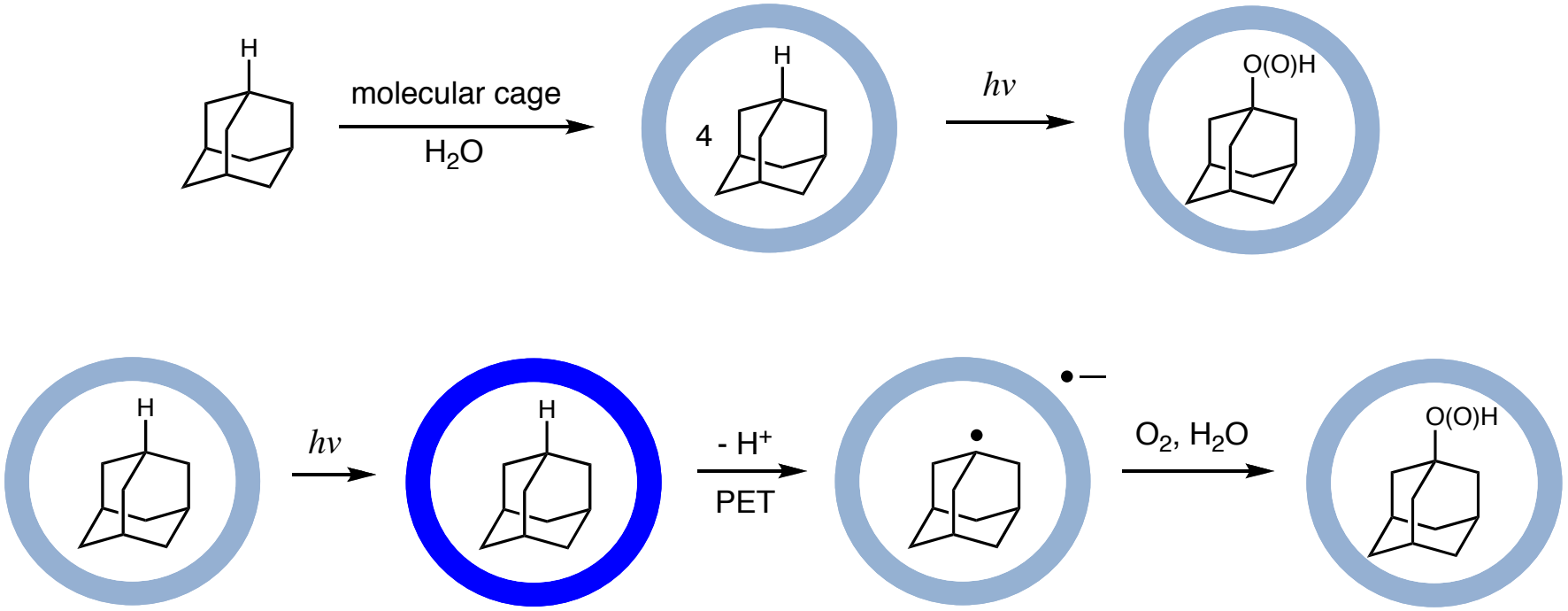
- X-ray crystal structures of before and after irridiation



Kawano, M.; Kobayashi, Y.; Ozeki, T.; Fujita, M. *J. Am. Chem. Soc.* **2006**, *128*, 6558.

Alkane Photo-Oxidation via Host-Guest Electron Transfer

- Admantane is not photochemically active, but is oxidized inside the molecular cage
- The yield of 1-adamantyl alcol is 24% (*only one of the four guests is reacted*)
- Aromatic guests (benzene or naphthlene) can not be oxidized

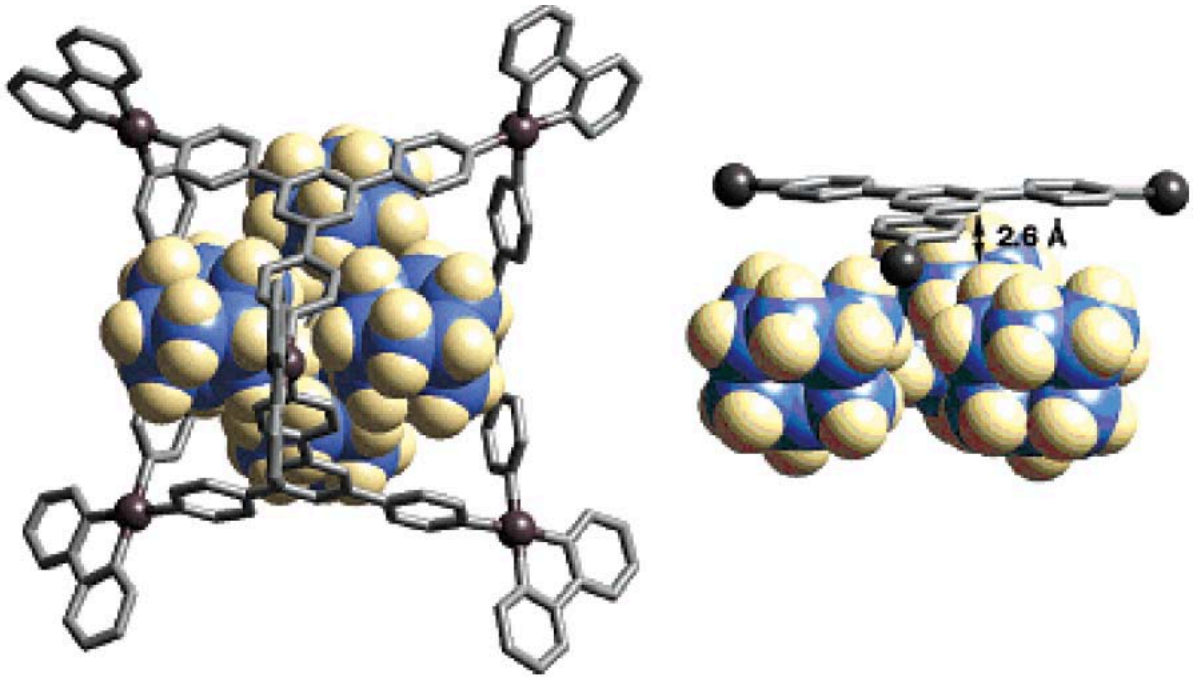


Yoshizawa, M.; Miyagi,S.; Kawano, M.; Ishiguro, K.; Fujita, M. *J. Am. Chem. Soc.* **2004**, *126*, 9172.

Furutani,Y.; Kandori, H.; Kawano, M.; Nakabayashi, K.; Yoshizawa, M.; Fujita, M. *J. Am. Chem. Soc.* **2009**, *131*, 4764.

Alkane Photo-Oxidation via Host-Guest Electron Transfer

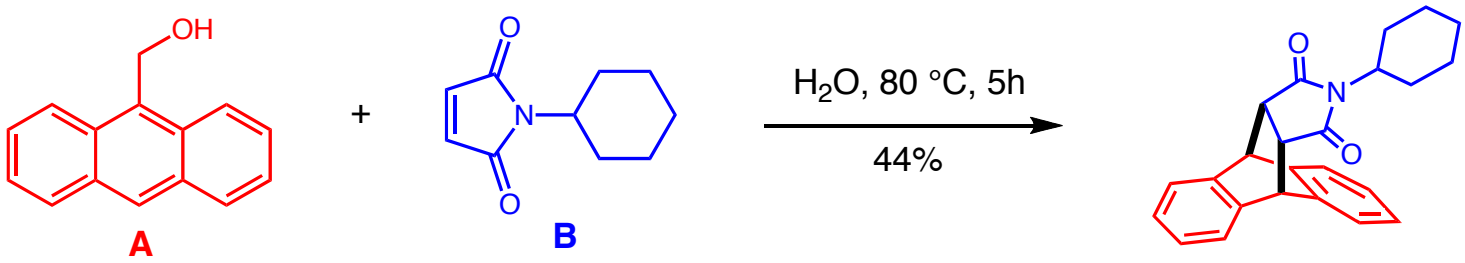
- X-ray analysis shows a short distance between bridgehead C-H and ligand triazine ring
- Cage liand with benzene ring instead of triazine does not have photo-reactivity
- ^{18}O-labeling on O_2 or H_2O resulted in the incorporation of ^{18}O in the oxidized products



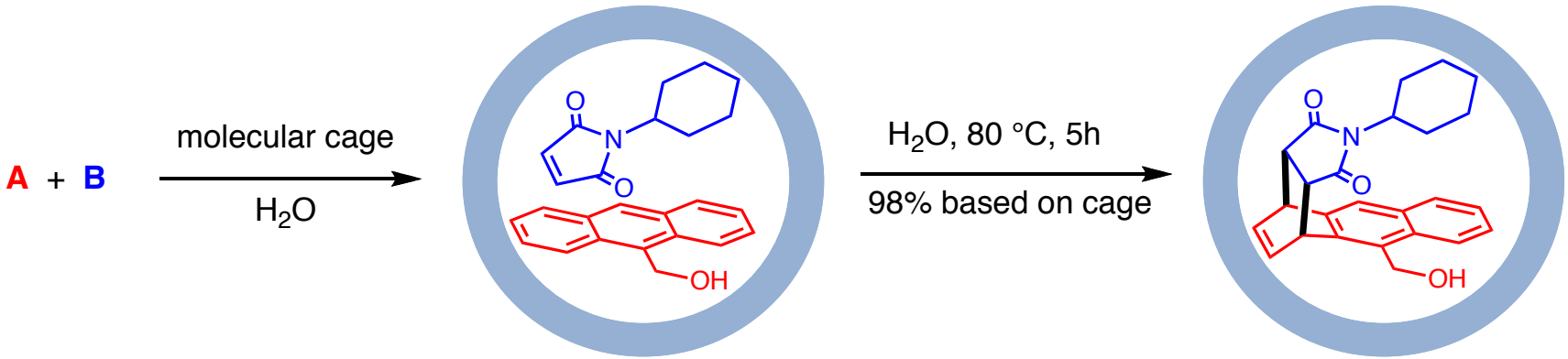
Yoshizawa, M.; Miyagi,S.; Kawano, M.; Ishiguro, K.; Fujita, M. *J. Am. Chem. Soc.* **2004**, *126*, 9172.
Furutani,Y.; Kandori, H.; Kawano, M.; Nakabayashi, K.; Yoshizawa, M.; Fujita, M. *J. Am. Chem. Soc.* **2009**, *131*, 4764.

Unusual Diels-Alder Reaction in Aqueous Molecular Hosts

- 9-hydroxymethylanthrancene (**A**) and N-cyclohexylphthalimide (**B**) forms 9,10-adduct



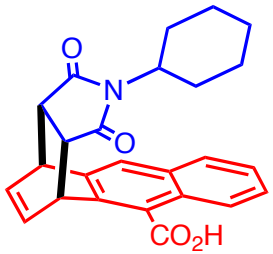
- Only syn-1,4-adduct is formed when molecular cage is present
- Excellent yield and regio/stereo-selectivity



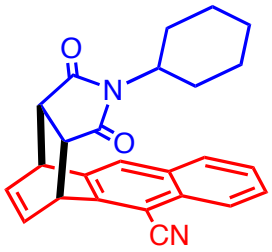
Yoshizawa, M.; Tamura, M.; Fujita, M. *Science* **2006**, *312*, 251.

Unusual Diels-Alder Reaction in Aqueous Molecular Hosts

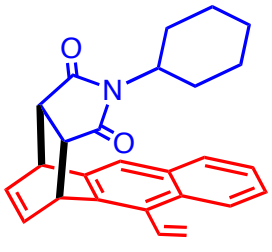
- The 9-substitues with similiar size as hydroxymethyl give similiar yields



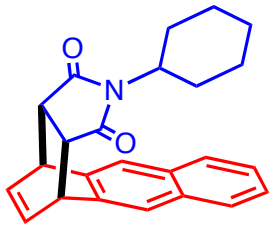
92%



88%

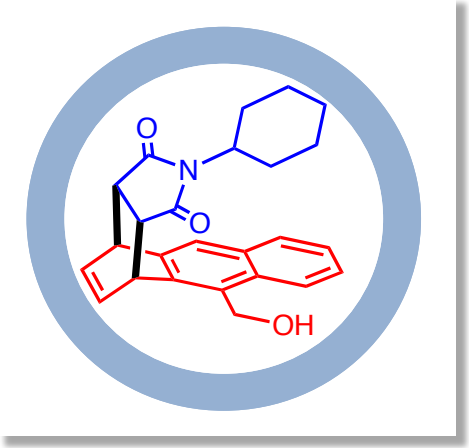


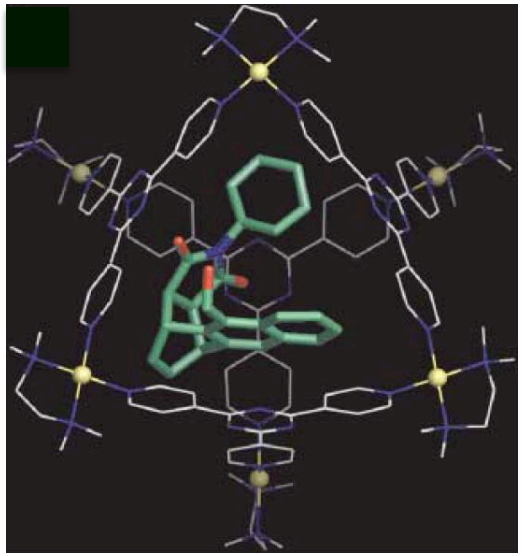
80%



55%

- Structure of product is further confirmed by X-ray analysis

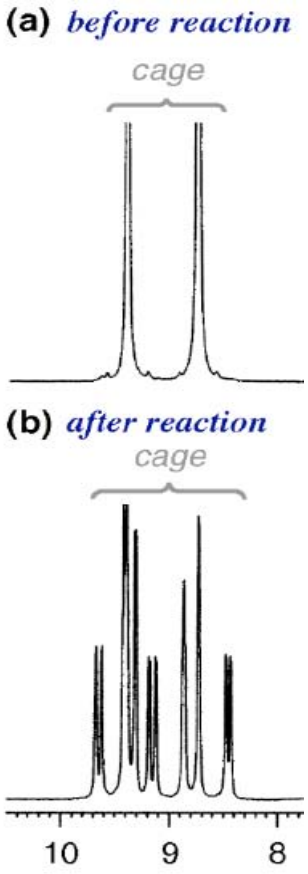


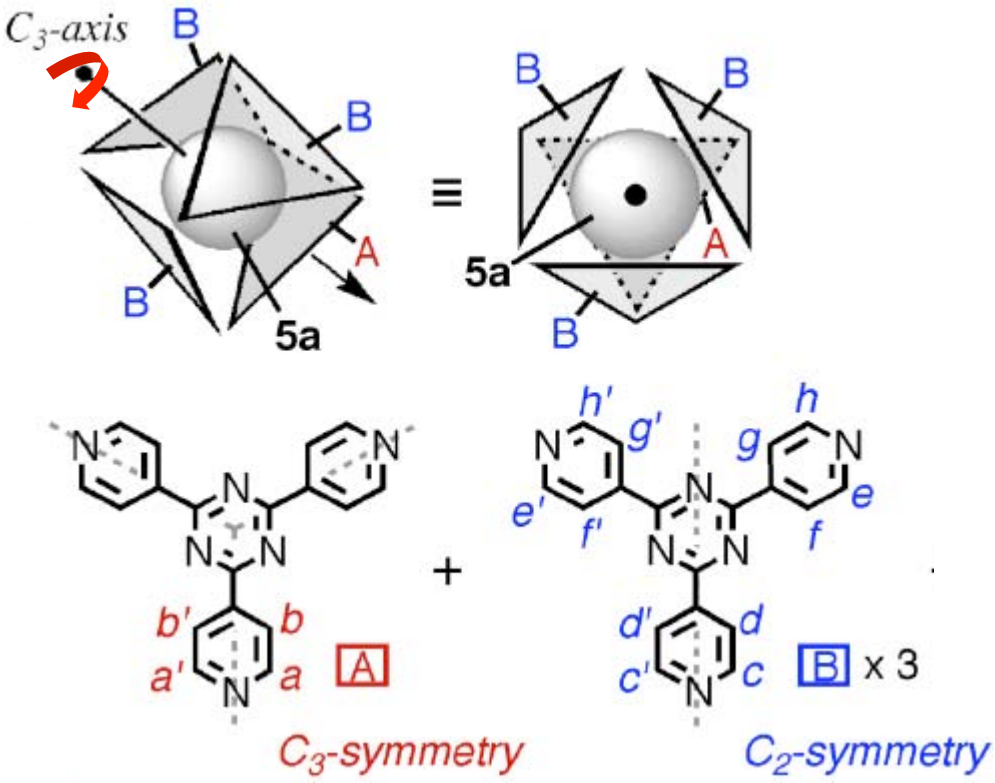


Yoshizawa, M.; Tamura, M.; Fujita, M. *Science* **2006**, *312*, 251.

Unusual Diels-Alder Reaction in Aqueous Molecular Hosts

- NMR of the cage ligand changed after reaction, indicating symmetry change
- Product has restricted motion along the C_3 axis

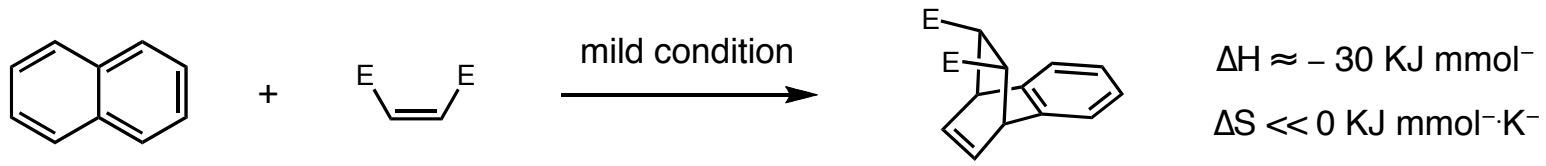




Yoshizawa, M.; Tamura, M.; Fujita, M. *Science* **2006**, *312*, 251.

Diels-Alder Reaction of Naphthlene Derivatives in Molecular Flask

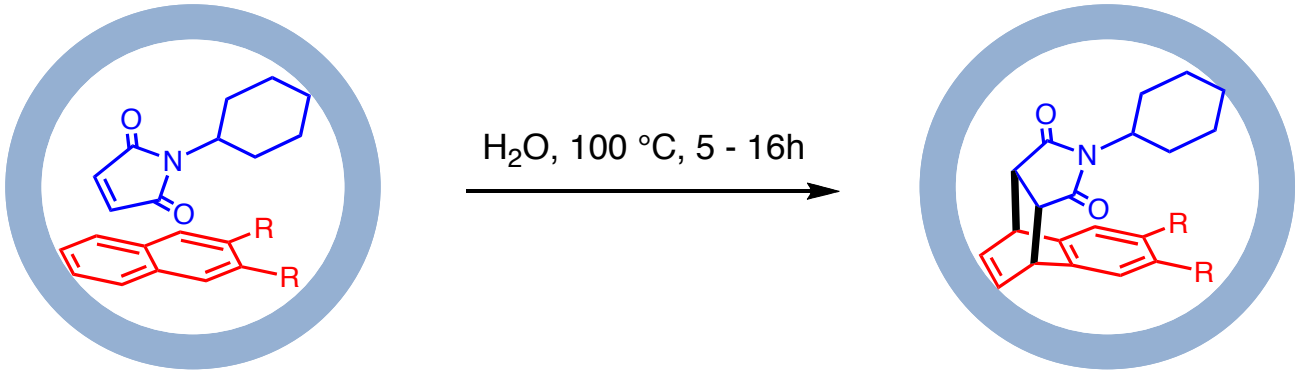
- D-A reaction of naphthlene is very studdorn due to the a large activation entropy.



$\Delta H \approx -30$ KJ mmol^{-}

$\Delta S << 0$ KJ mmol^{-}·K^{-}

- Preorganization of reactants inside the molecular flask circumvented entropy costs.



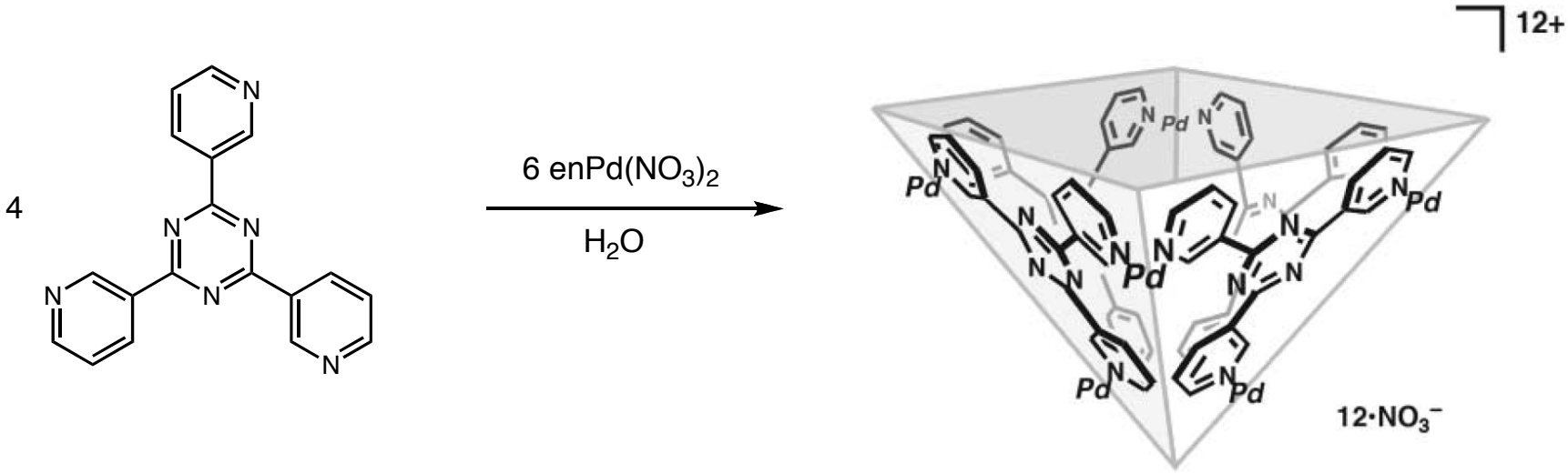
Single Isomer (X-ray)

R	H	Me	Et	*n*-Pr	-$(CH_2)_4$-	-O$(CH_2)_2$O-
Yield	0	8	60	64	62	0
k			4.1	6.2	2.7	

Morase, S.; Hiriuchi, S.; Fujita, M. *J. Am. Chem. Soc.* **2010**, *132*, 2866.

Molecular Flask as a Catalyst for Diels-Alder Reaction

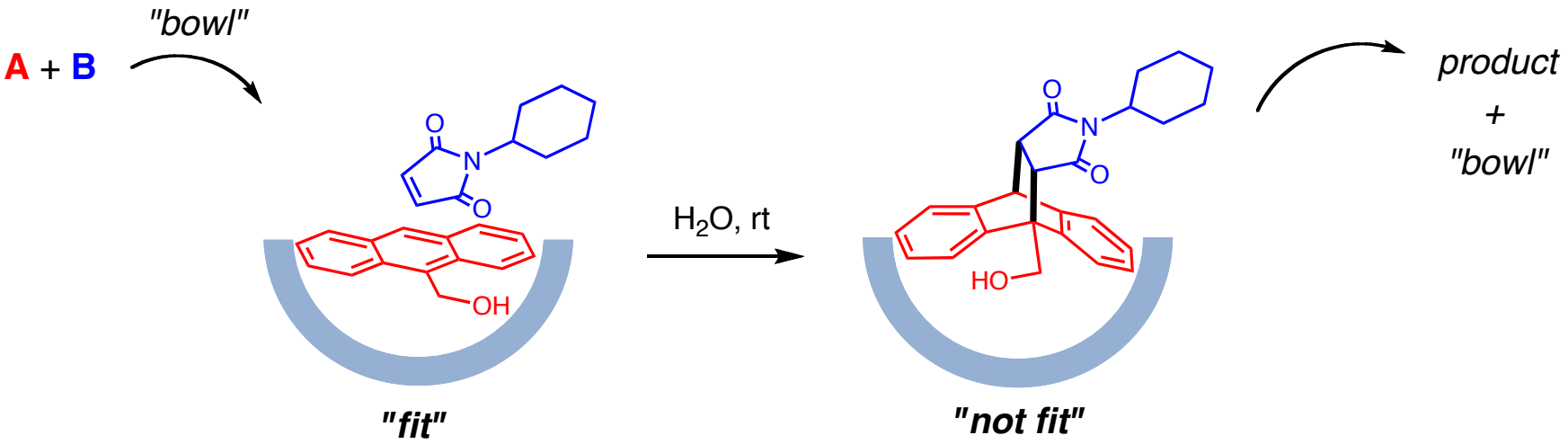
- Bowl-shape molecular flask is synthesized from 3-pyridyl substituted triazine ligand.
- D-A product is releasable due to the bowl-shape cavity



Fujita, M.; Yu, S.-Y.; Kusukawa, T.; Funaki, H.; Ogura, K.; Yamaguchi, K. *Angew. Chem. Int. Ed.* **1998**, *37,* 2082.

Molecular Flask as a Catalyst for Diels-Alder Reaction

- Normal 9,10-regioselectivity is observed.
- Product with a bent framework cut-off aromatic stacking with host and left.
- Similarity with enzymatic behavior



no bowl: 5h, 3% yield

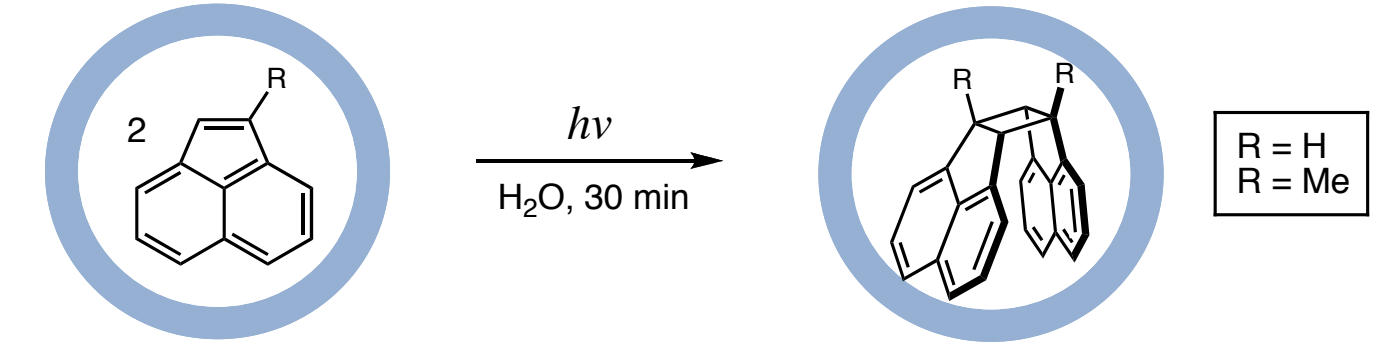
with 10% bowl: 5h, >99% yield

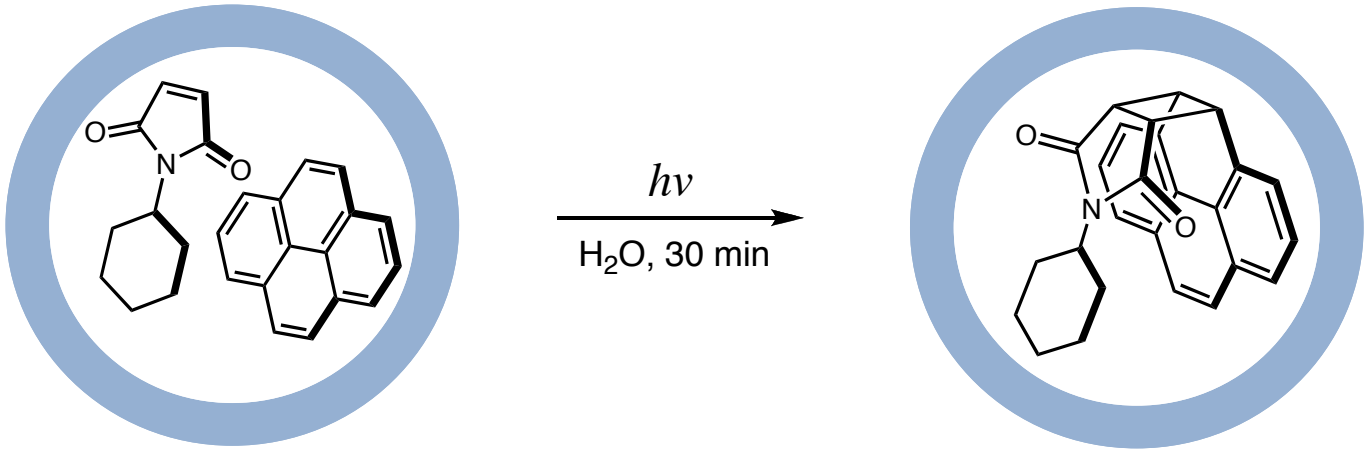
with 1% bowl: 24h, >99% yield

Yoshizawa, M.; Tamura, M.; Fujita, M. *Science* **2006**, *312*, 251.

Unusual [2 + 2] Photoadditions

- With the host, quantitative yields and excellent selectivities are usually observed
- Without the host, either no reaction or non-selective low yield reaction



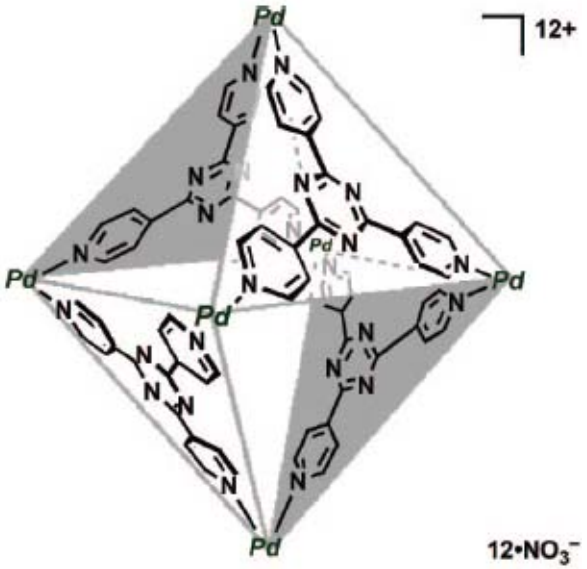


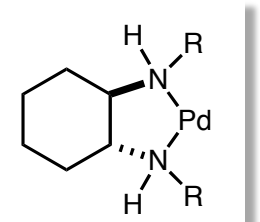
Yoshizawa, M.; Takeyama, Y.; Kusukawa, T.; Fujita, M. *Angew. Chem. Int. Ed.* **2002**, *41*, 1347

Nishioka, Y.; Yamaguchi, T.; Yoshizawa, M.; Fujita, M. *J. Am. Chem. Soc.* **2007**, *129*, 7000

Chiral Cages Formed from Chiral Diamine Ligands

- Asymmetric synthesis in a chiral cavity remains relatively unexplored
- Large chiral cages and capsules are difficult to prepare



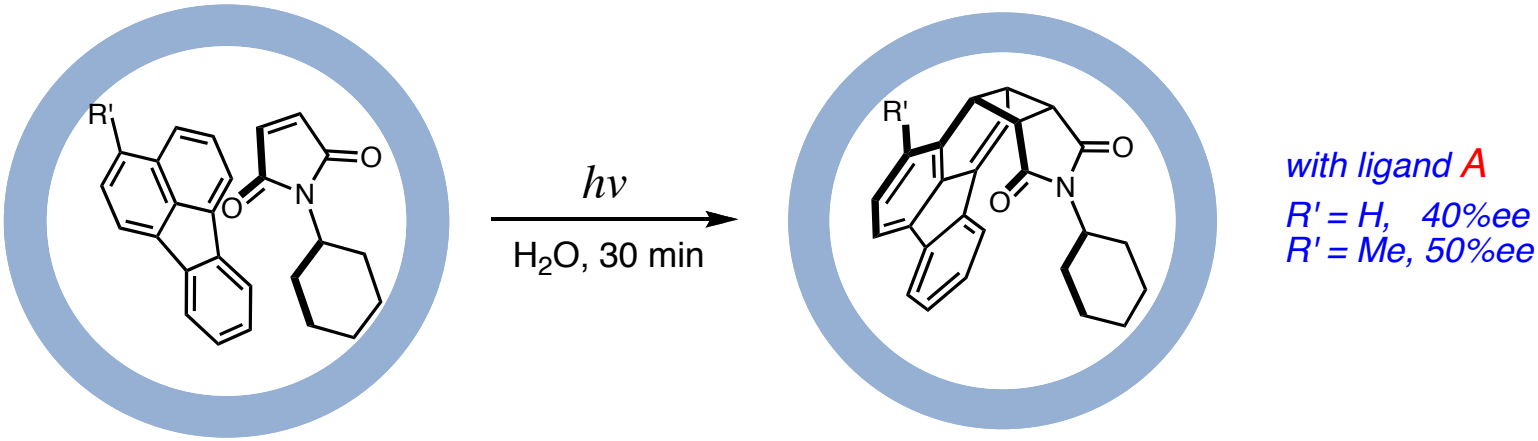


- Indirect cavity-control by remote ligands (enzyme-like)

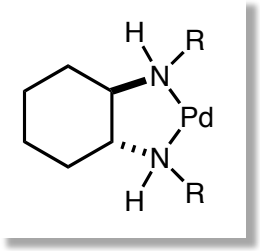
Nishioka, Y.; Yamaguchi, T.; Kawano, M.; Fujita, M. *J. Am. Chem. Soc.* **2008**, *130*, 8160

Chiral Cages Formed from Chiral Diamine Ligands

- Substitute on *N* is crucial for the enantio-control
- The dihedral angel is related to the enantioselectivity



with ligand A
R' = H, 40%ee
R' = Me, 50%ee

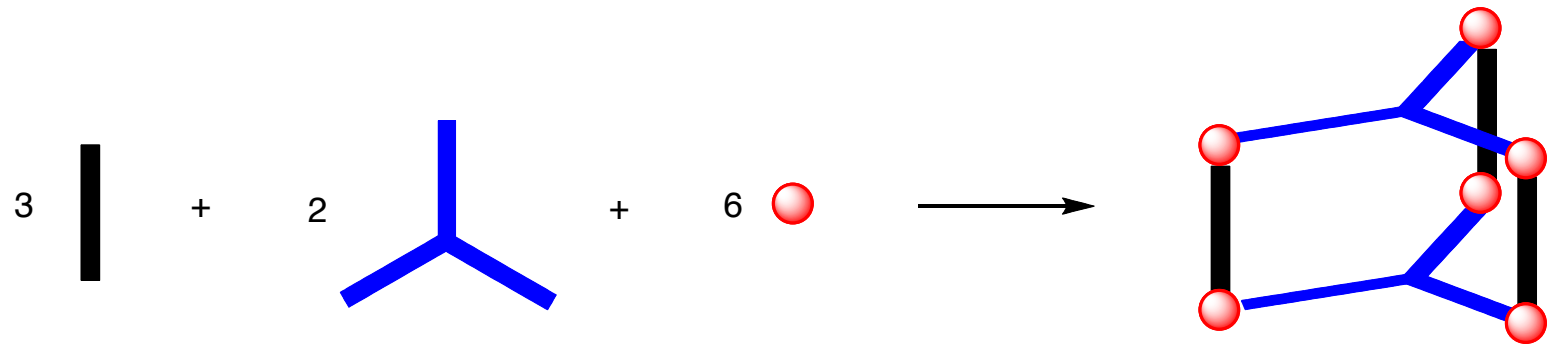


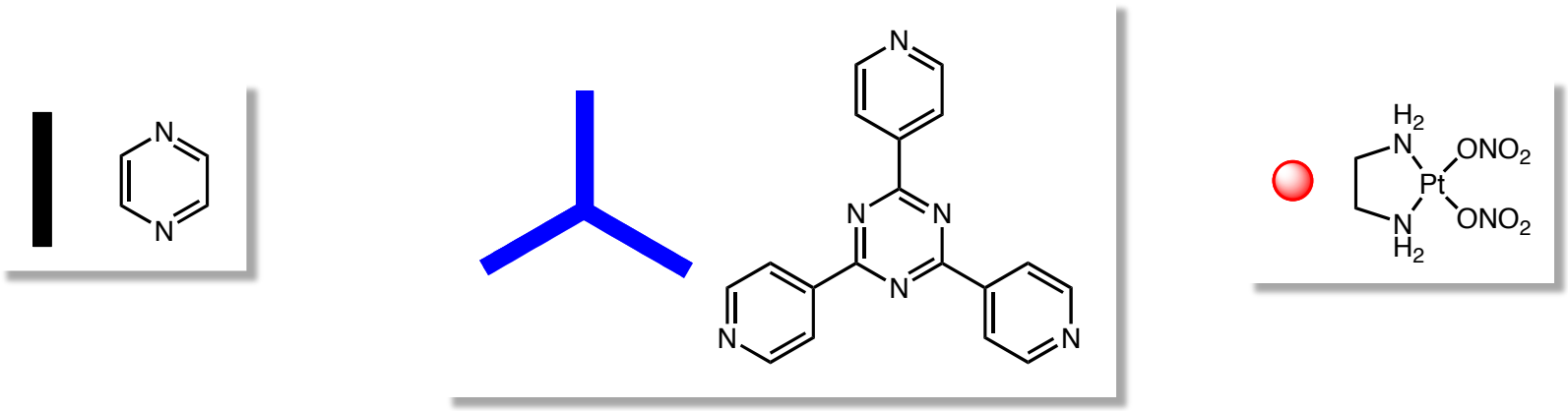
ligand	A	B	C
R	Et	Me	H
dihedral angle	17°	13°	~ 0°
ee	40%	20%	5%

Nishioka, Y.; Yamaguchi, T.; Kawano, M.; Fujita, M. *J. Am. Chem. Soc.* **2008**, *130*, 8160

Formation of Molecular Prisms by Combination of Multiple Ligands

- Combination of two types of ligands can result in formation of molecular prism.
- Aromatic template is crucial for the formation of prism and it is removable afterwards.





Kumazawa, K.; Biradha, K. Kusukawa, T. Okano, T. Fujita, M. *Angew. Chem. Int. Ed.* **2003**, *42*, 3909.

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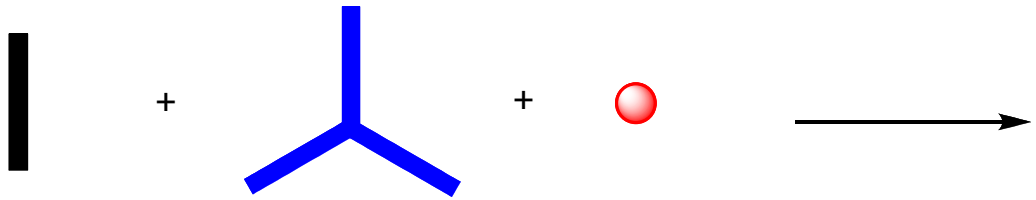

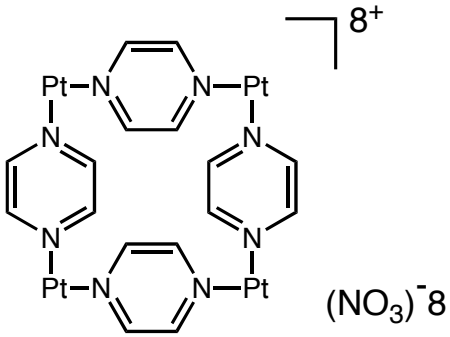

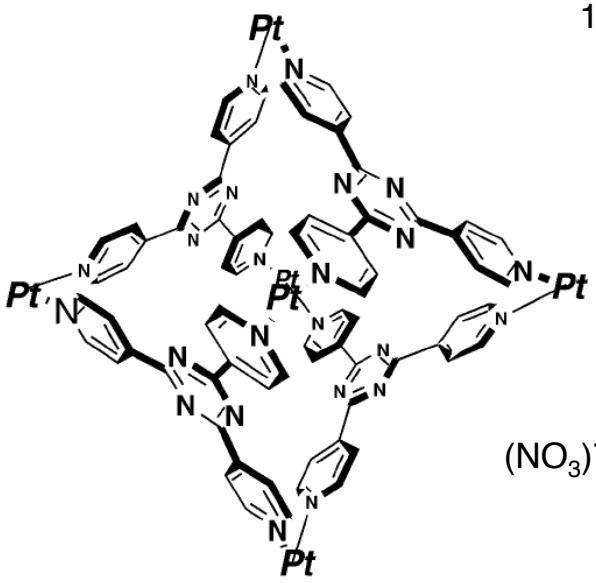

etc.

(messy NMR)

Kumazawa, K.; Biradha, K. Kusukawa, T. Okano, T. Fujita, M. *Angew. Chem. Int. Ed.* **2003**, *42*, 3909.

Formation of Molecular Prisms by Combination of Multiple Ligands

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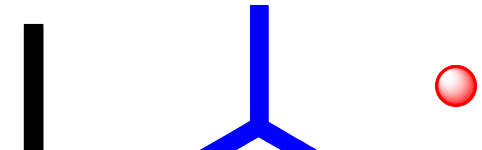
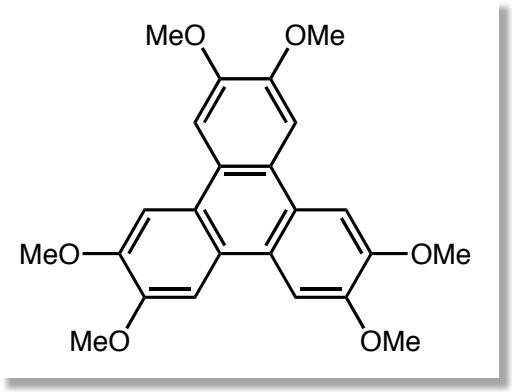
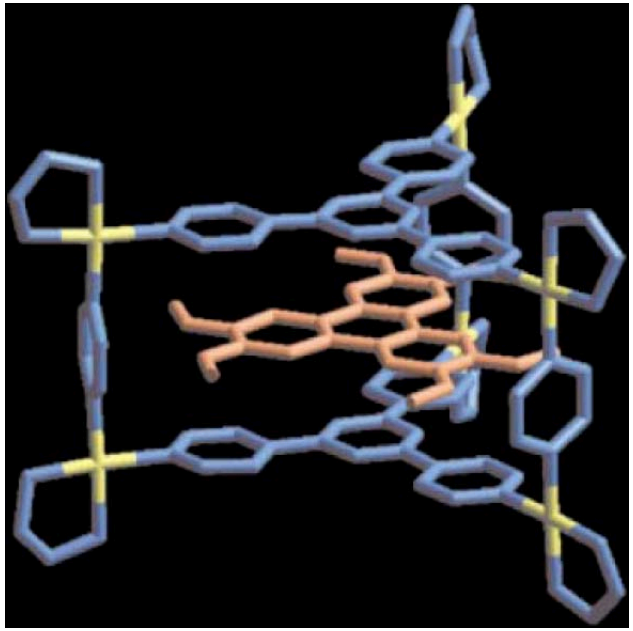




100 °C, 48h

H_2O

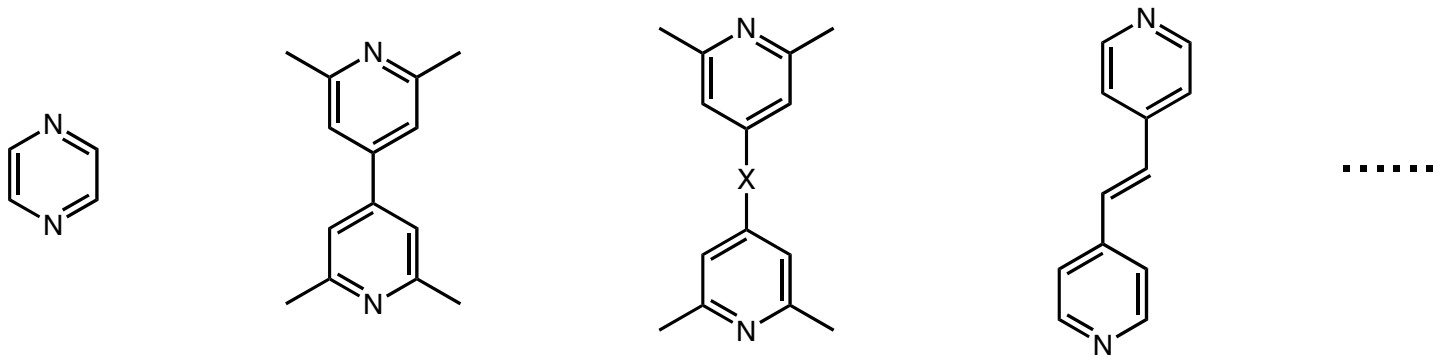


- Host-guest distance is 3.3 Å, suggesting a strong π–π interaction.

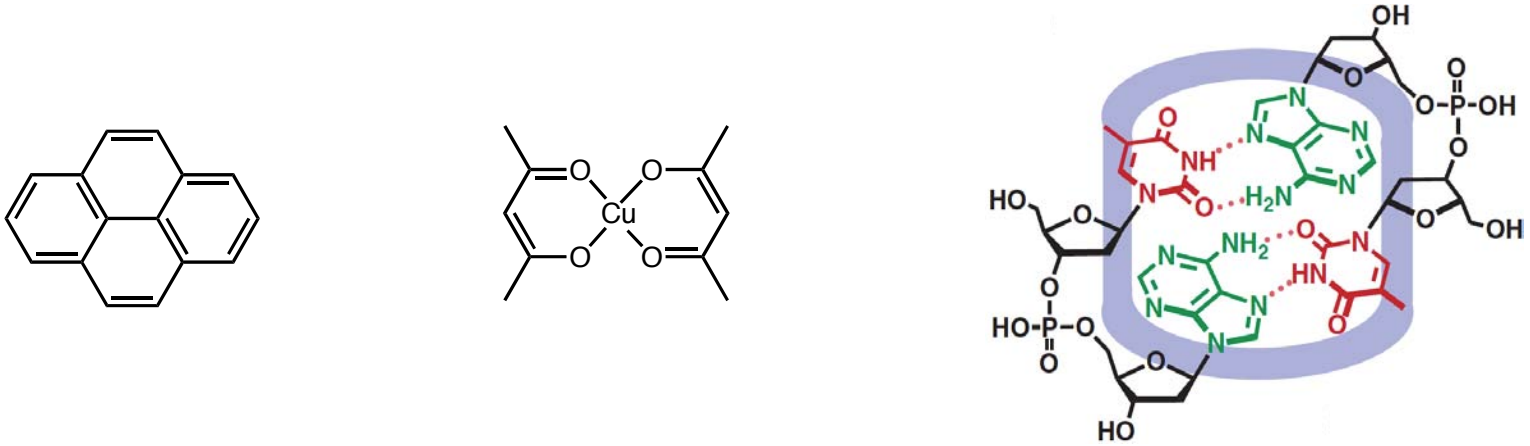
Kumazawa, K.; Biradha, K. Kusukawa, T. Okano, T. Fujita, M. *Angew. Chem. Int. Ed.* **2003**, *42*, 3909.

Formation of Molecular Prisms by Combination of Multiple Ligands

- Molecular prisms with different size and shape could be synthesized



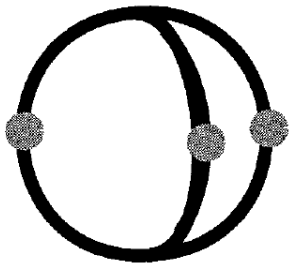
- Many types of "flat" guests (aromatic molecule ; metal complex; nucleotide etc.)

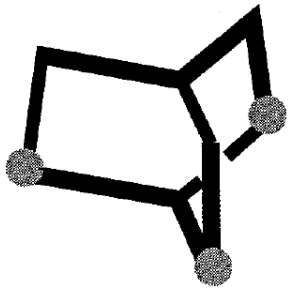


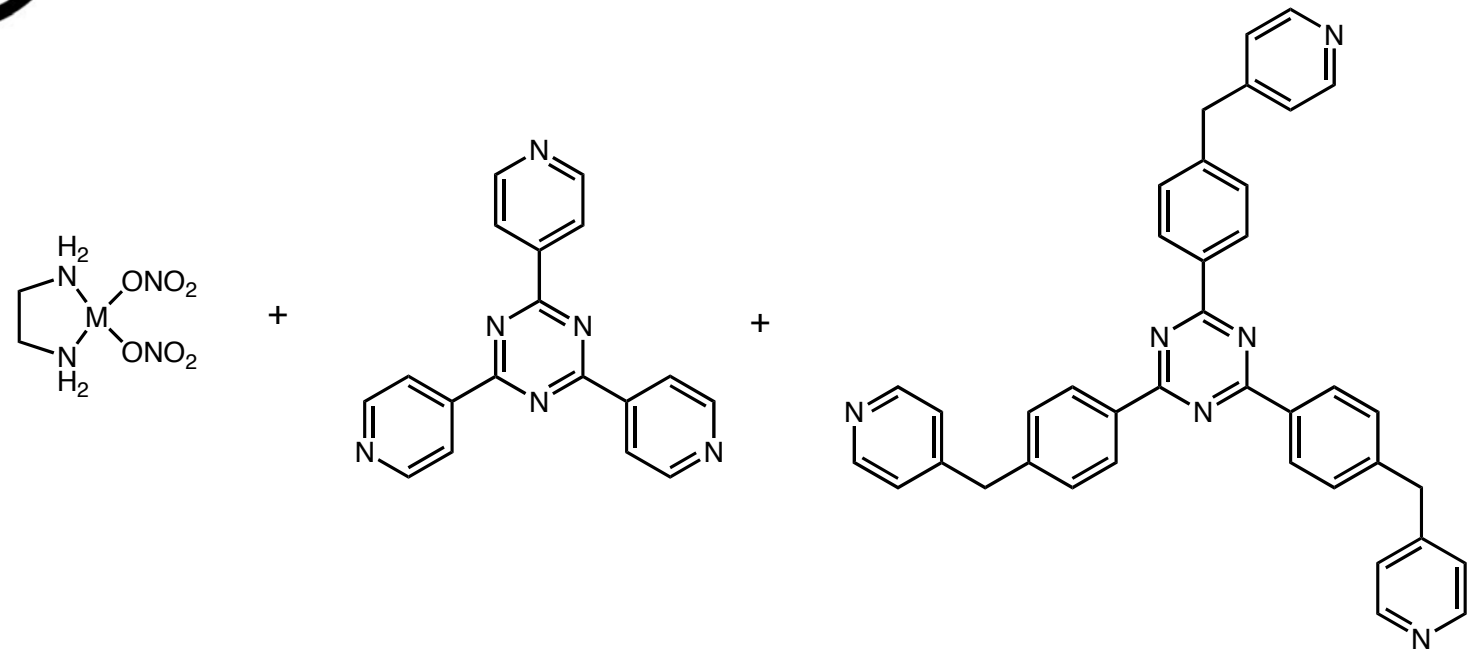
Klosterman, J. K.; Yamauchi, Y.; Fujita, M. *Chem. Soc. Rev.* **2009**, *38,* 1714.

Formation of 3D Interlock by Combination of Multiple Ligands

- A complex 3D interlock is designed and synthesized



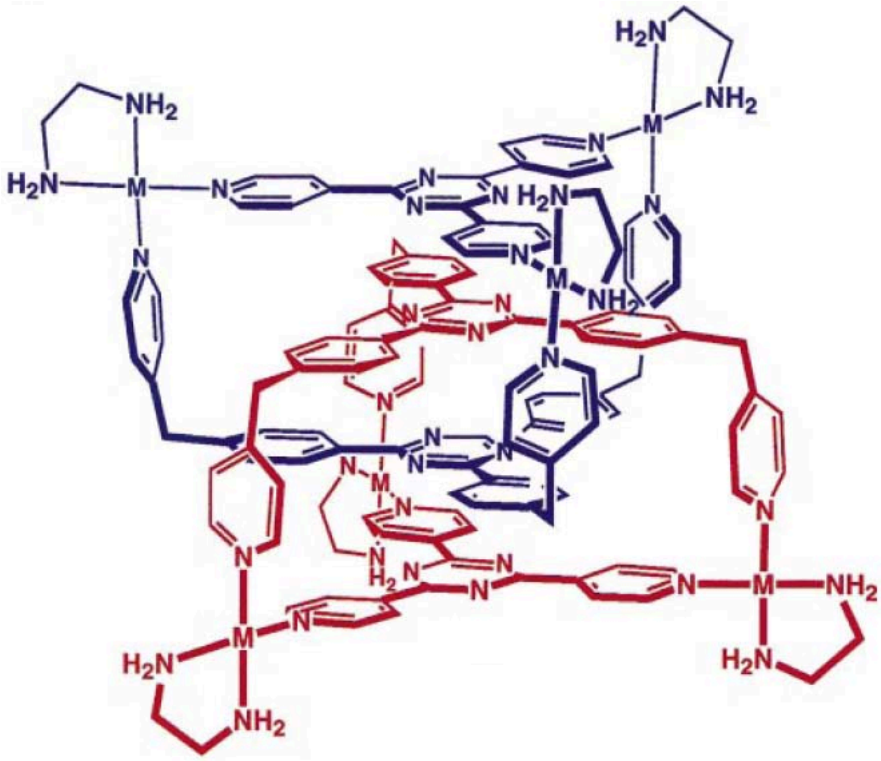


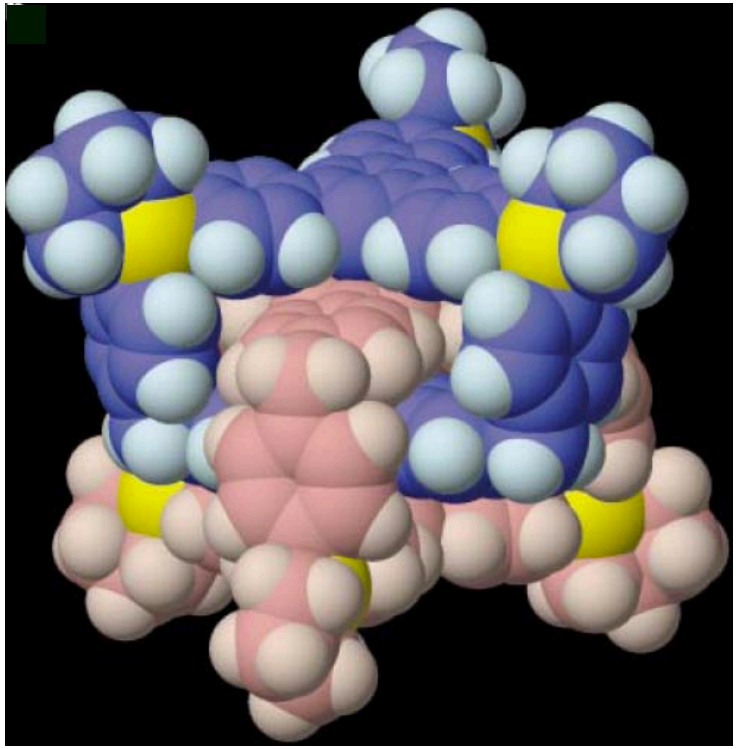


Fujita, M. Fujita, N.; Ogura, K.; Yamaguchi, K. *Nature* **1999**, *400*, 52.

Formation of 3D Interlock by Combination of Multiple Ligands

- The X-ray crystal structure confirmed a beautiful 3D interlock





Fujita, M. Fujita, N.; Ogura, K.; Yamaguchi, K. *Nature* **1999**, *400*, 52.

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Klosterman, J. K.; Yamauchi, Y.; FUjita, M. *Chem. Soc. Rev.* **2009**, *38*, 1714.

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Kumazawa, K.; Biradha, K. Kusukawa, T. Okano, T. Fujita, M. *Angew. Chem. Int. Ed.* **2003**, *42*, 3909.

Fujita, M. Fujita, N.; Ogura, K.; Yamaguchi, K. *Nature* **1999**, *400*, 52.

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