CHM 696-11: Week 4-B

Instructor: Alexander Wei

Encoded Self-Assembly, cont’d:

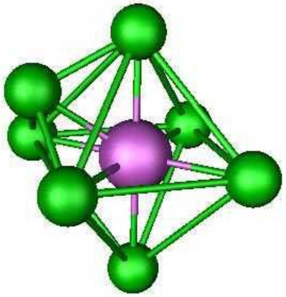
Metal–Ligand Coordination Complexes

Some basic coordination chemistry

Coordination number	Coordination geometry	Selected examples with transition metals (TM)
2	linear	
3	trigonal planar	
4	tetrahedral, square planar	

charge = +1/0/–1, depending on L

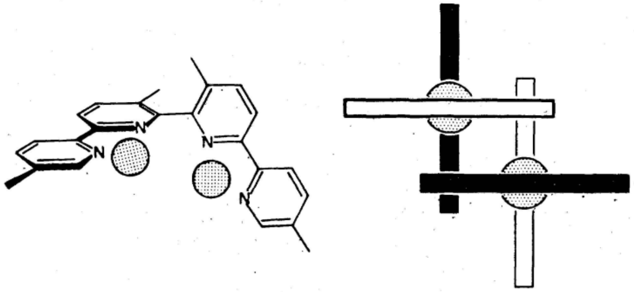
Some basic coordination chemistry

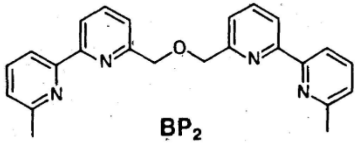
Coordination number	Coordination geometry	Selected examples with transition metals (TM)
5	trigonal bipyramidal, square pyramidal	
6	octahedral, trigonal prismatic	
7	Pentagonal bipyramidal, capped octahedral	

Supramolecular Helicates

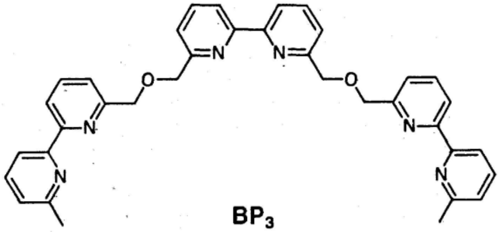
Homomeric helicates [M_nL_2]

Cooperative formation of chiral superstructures



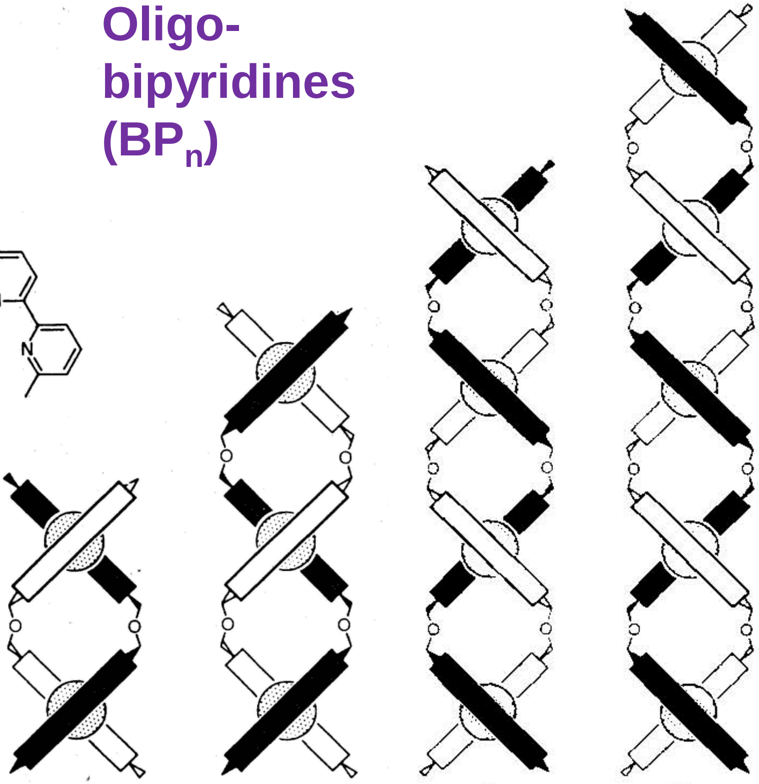


BP_2



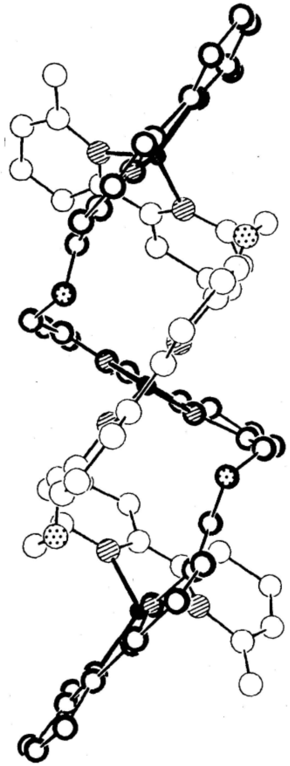
BP_3

Oligo-bipyridines (BP_n)



M = Cu^I (ClO_4 salt) or **Ag^I**

Chiral [n]helicates



X-ray crystal structure of [3]helicate: $[Cu_3(BP_3)_2]^{3+}$

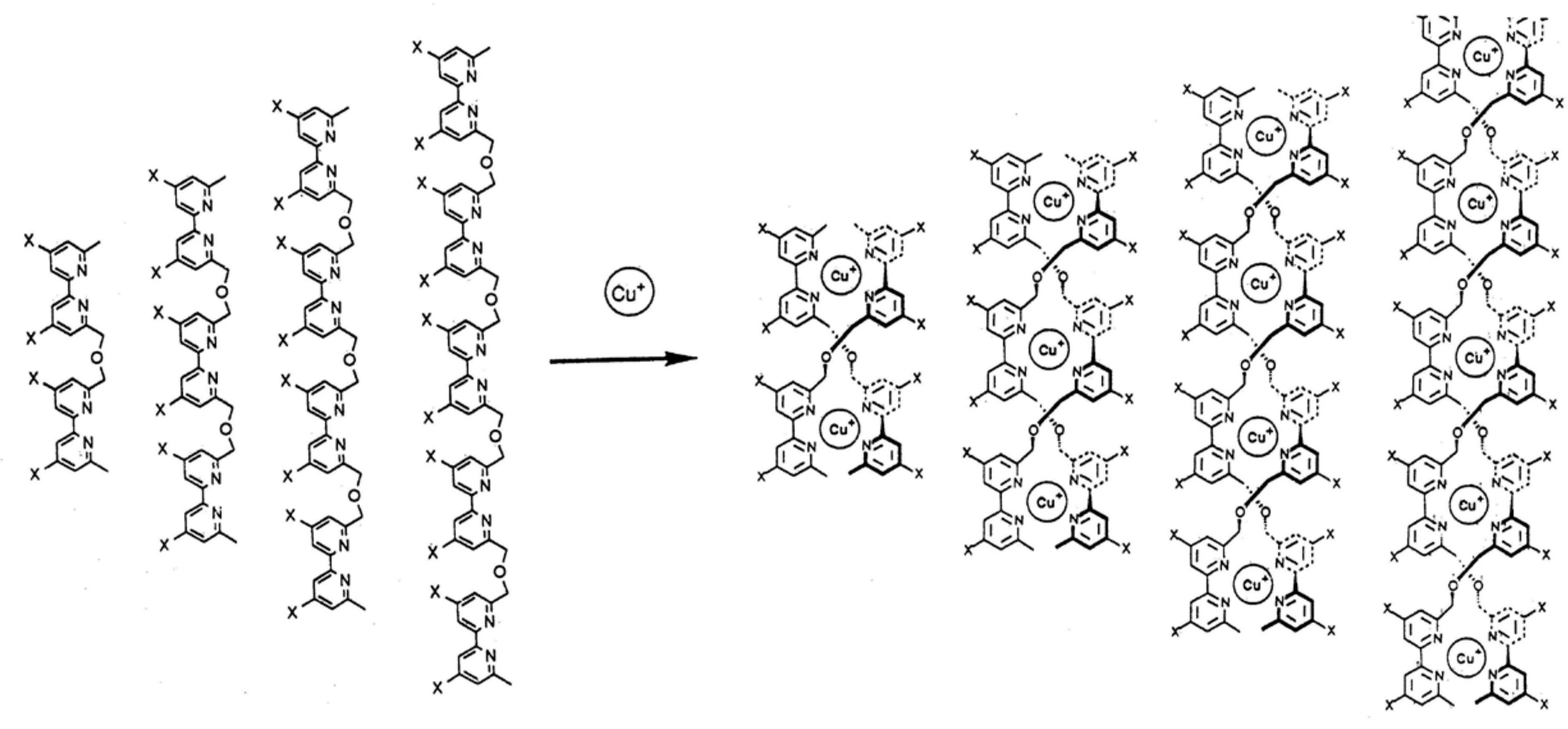
Lehn et al., *Proc. Natl. Acad. Sci. USA*, **1987**, *84*, 2565.
Lehn and Rigault, *Angew. Chem. Int. Ed.*, **1988**, *27*, 1095.

Supramolecular Helicates

Self-sorting helicates [M_nL_2]

Selectivities driven by maximum bonding enthalpies

M = Cu^{I}($CH_3CN)_4$
(BF_4 salt)



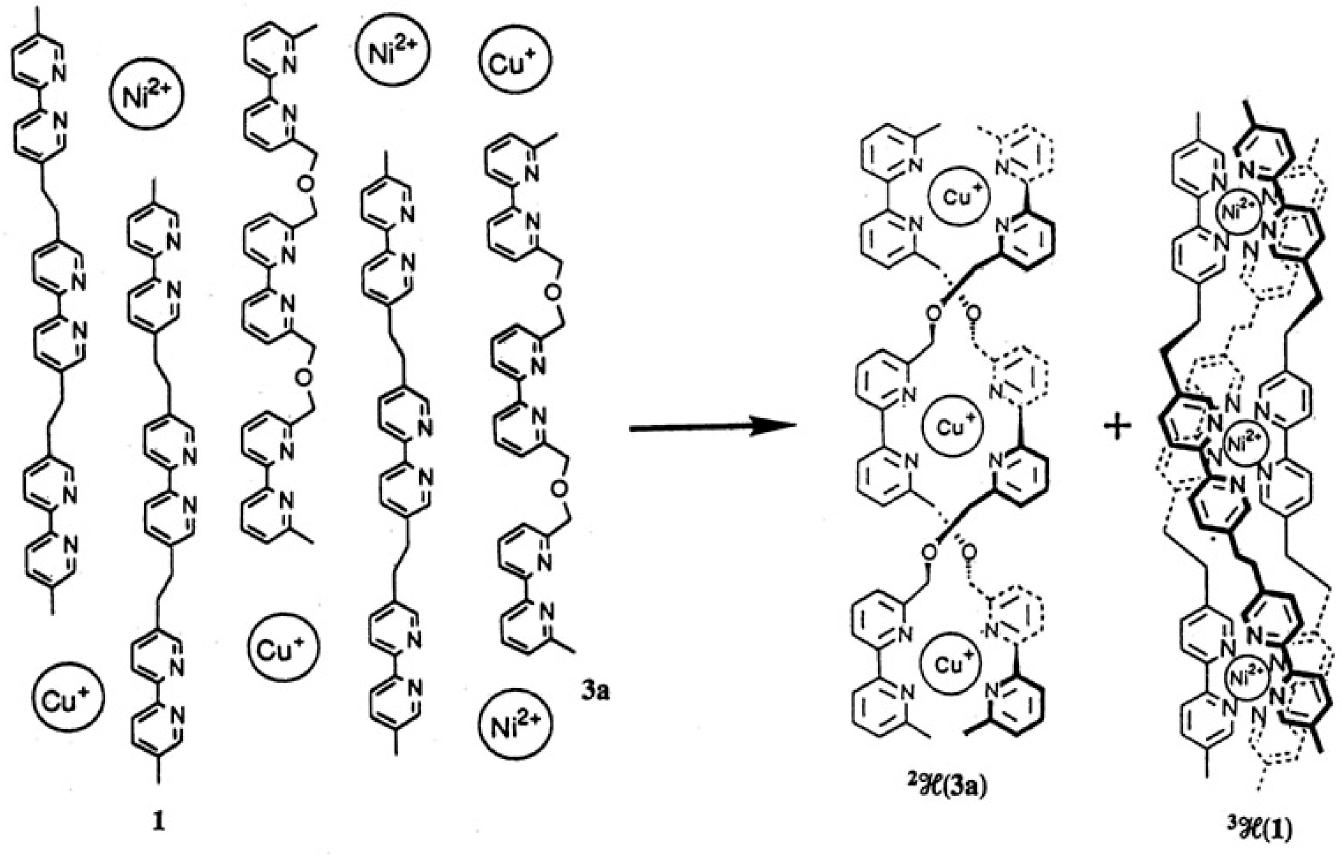
2 3 4 5 $^2\mathcal{H}(2)$ $^2\mathcal{H}(3)$ $^2\mathcal{H}(4)$ $^2\mathcal{H}(5)$

Kramer et al., *Proc. Natl. Acad. Sci. USA*, **1993**, *90*, 5394

Supramolecular Helicates

Self-sorting helicates [M_nL_2, M_nL_3]

Metal-encoded self-assembly, driven entirely by metal–ligand coordination enthalpies.



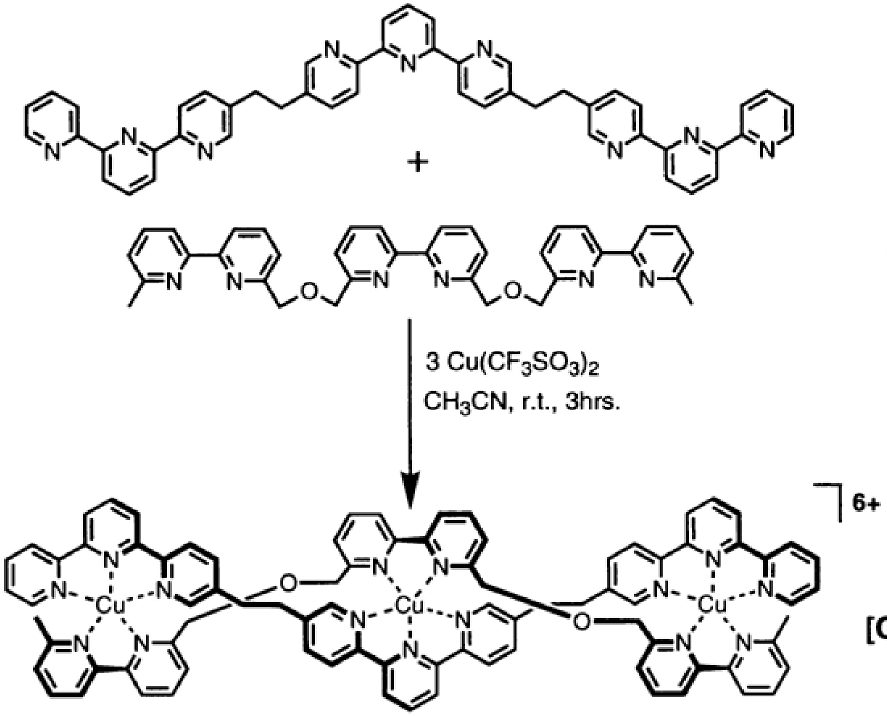
Kramer et al., *Proc. Natl. Acad. Sci. USA*, **1993**, *90*, 5394

Heteromeric Helicates

Heteromeric helicates [**M_n(L,L')**]

Directed by metal-ligand coordination geometry

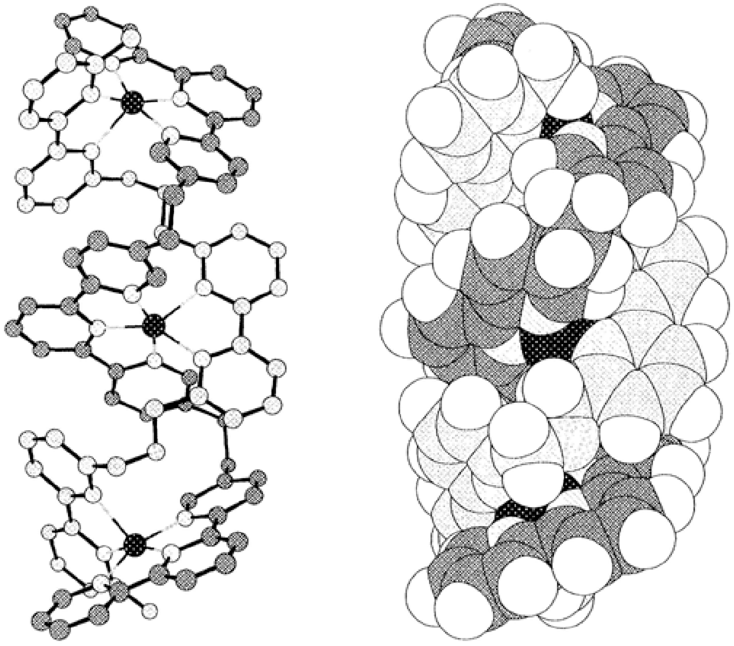
M = Cu^{II} (triflate salt)



T

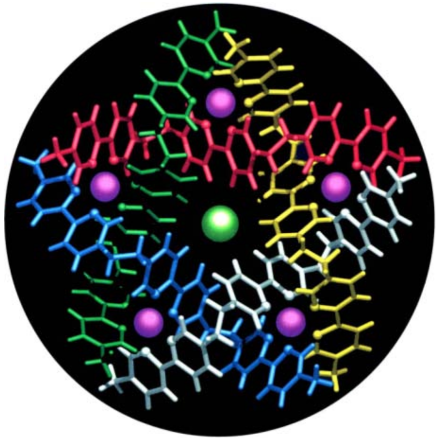
B

$[Cu_3BT]^{6+}$



Hasenknopf et al., *Proc. Natl. Acad. Sci. USA*, **1996**, *93*, 1397.

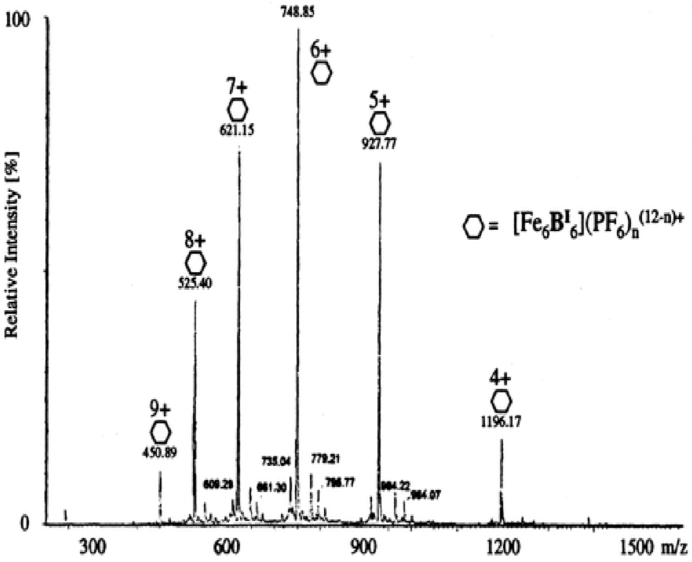
Circular Helicates

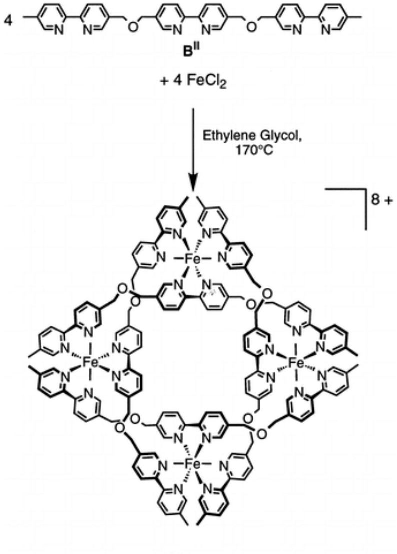


Circular helicates $[M_nL_n]$

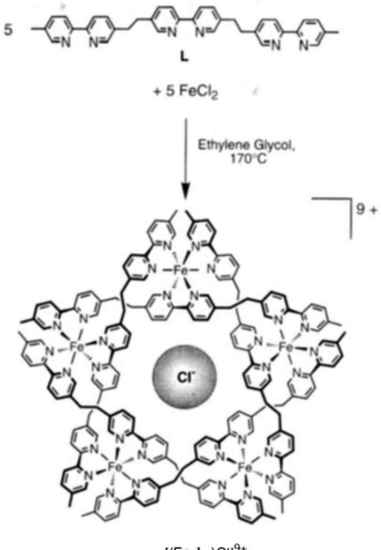
Alternate arrangements for metal-ligand coordination

Hasenknopf et al., *Angew. Chem. Int. Ed.*, **1996**, *35*, 1838
Hasenknopf et al., *J. Am. Chem. Soc.*, **1997**, *119*, 10956

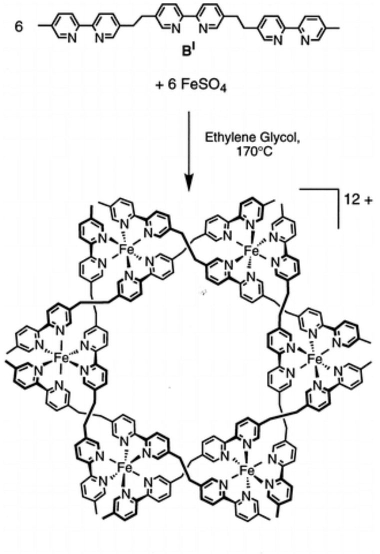




[4]cH



$[(Fe_5L_5)Cl]^{9+}$



[6]cH

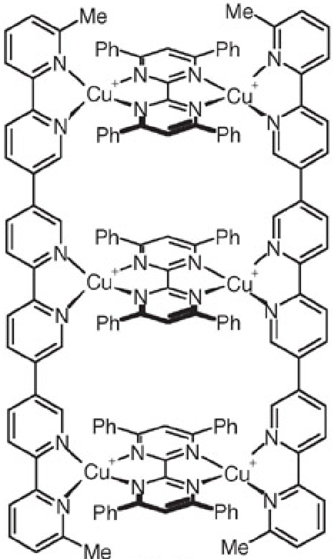
- ESI-MS indicates a statistical mixture of helicates
- Circular assembly appears to be templated by counteranion (only Cl^- is tightly bound)
- X-ray crystal structures of complex assemblies are sometimes not very well resolved (relatively large R values)

Supramolecular Racks, Ladders, and Grids

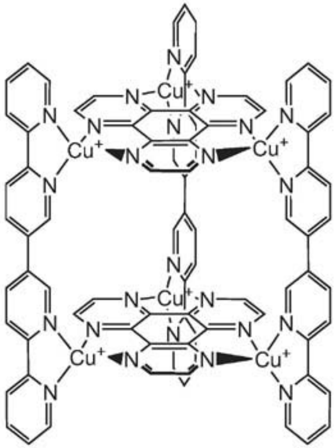
Development of multicomponent assemblies as molecular data storage devices

Ruben et al., *Angew. Chem. Int. Ed.*, **2004**, *43*, 3644 (review)

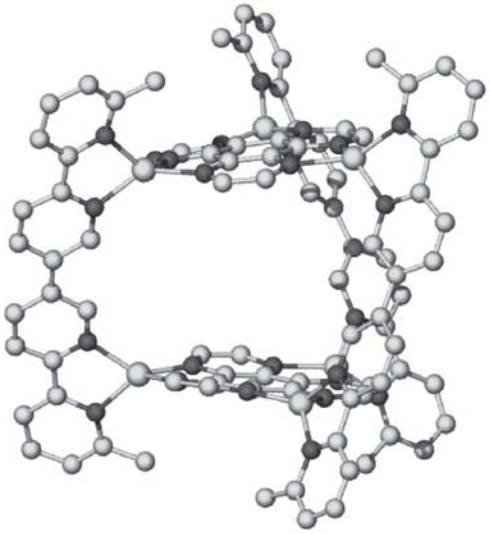
Racks [M_nL_{n+1}]
Ladders [$M_{2n}L_{n+2}$]



10.40

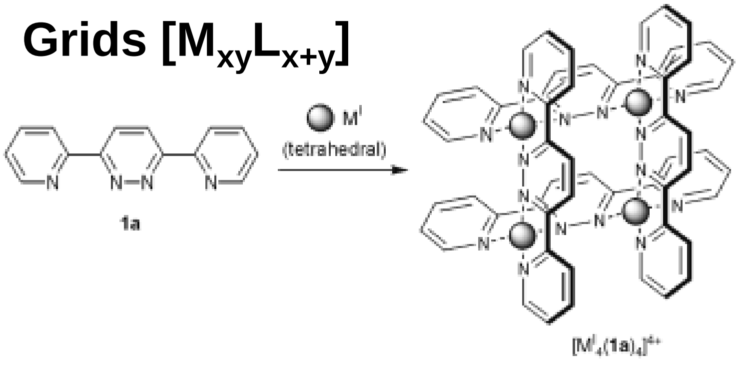


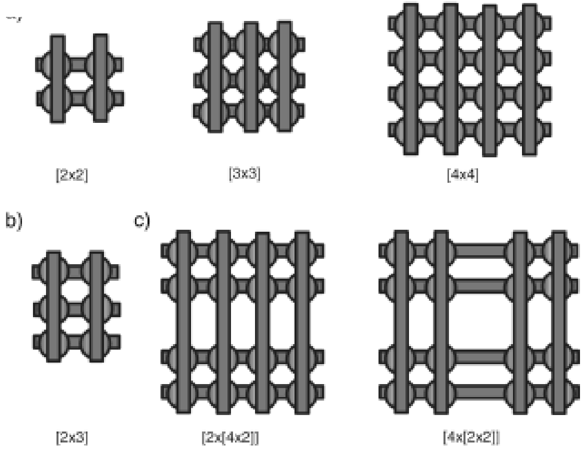
10.46
(substituents omitted for clarity)



HAT Racks
[$M_{3n}L_{n+3}$]

Grids [$M_{xy}L_{x+y}$]

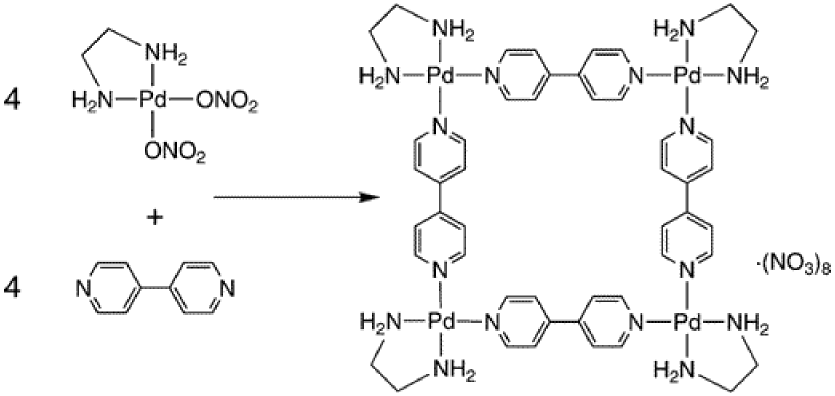




Metal–Ligand Coordination Cages

Reviews: Fujita et al, *Acc. Chem. Res*. **2005**, *38*, 369;
Yoshizawa, Klosterman, Fujita: *Angew. Chem. Int. Ed*., **2009**, *48*, 3418

4 desymmetrized square-planar complexes (corner)
+
4 rigid rods (edges)

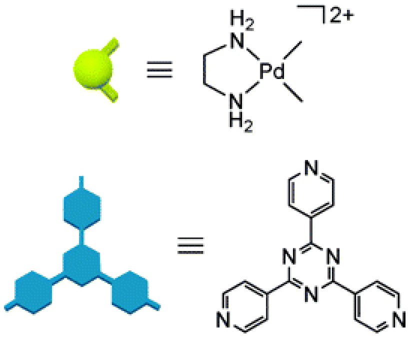


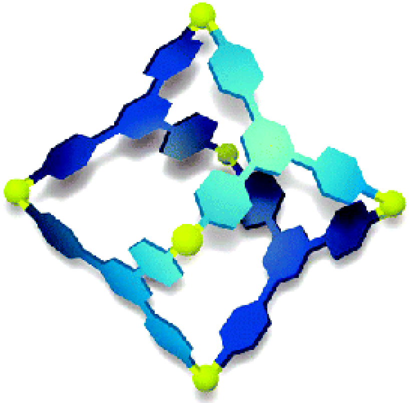
2D square complex

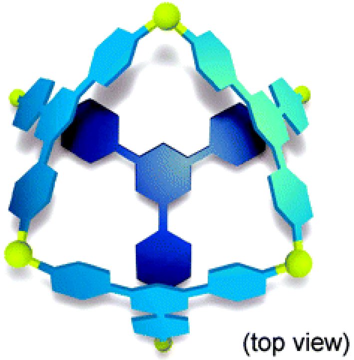
Chem. Commun. **1996**, 1535.

3D cage complex

6 corners
+
4 trigonal ligands (faces)







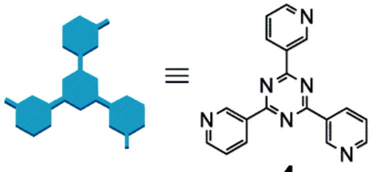
Nature **1995**, *378*, 469.

Nanocages via coordination self-assembly

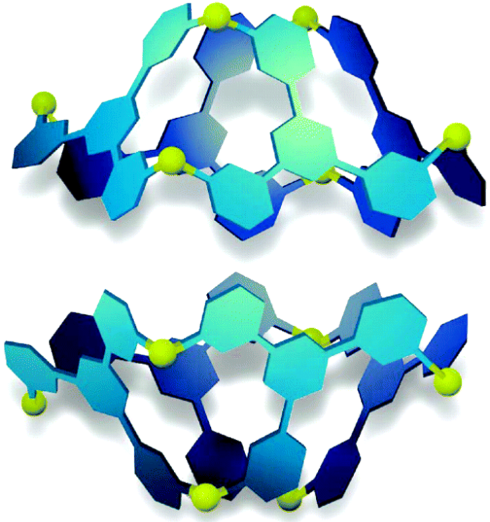
6 corners (M)
+
4 C_{3v}-tridentate ligands (L)

↓

M_6L_4 concave bowl (dimer)



4



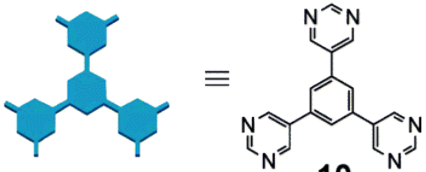
Can accommodate up to 6 organic molecules

J. Am. Chem. Soc. **2000**, *122*, 2665.

18 corners (M)
+
6 hexadentate ligands (L)

↓

$M_{18}L_6$ trigonal-bipyramidal (hexahedral) structure:



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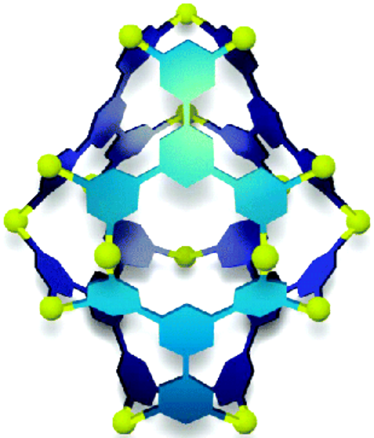
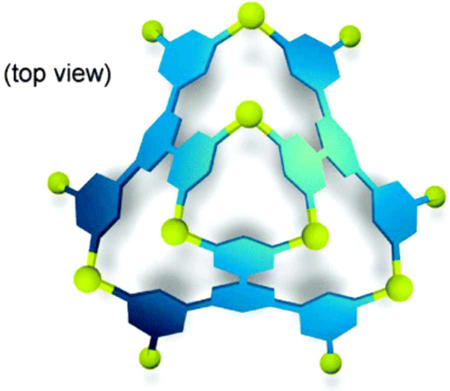




Fully closed-surface cage (vol. 900 Å^3)

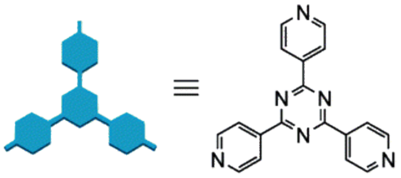
Nature **1999**, *398*, 794.

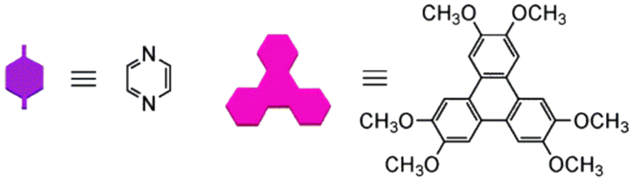
Nanocages via templated self-assembly

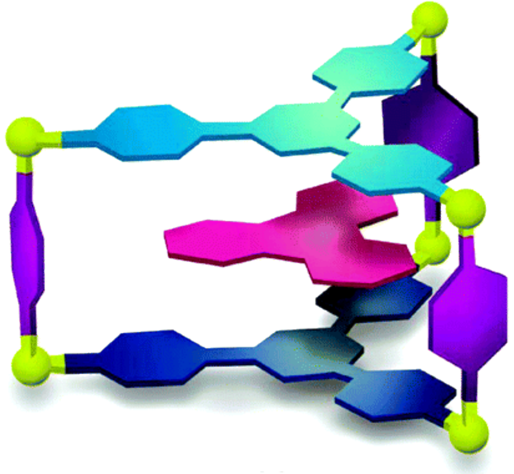
6 corners (M)
+
2 trident. faces (L)
+
3 pyrazines (L')
+
triphenylene (template)

↓

$M_6L_2L'_3$ cage + guest

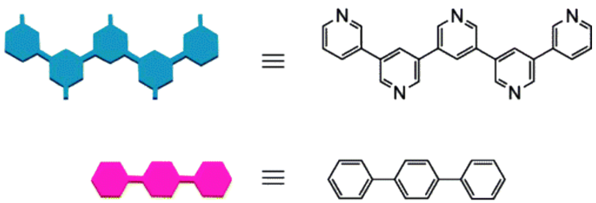


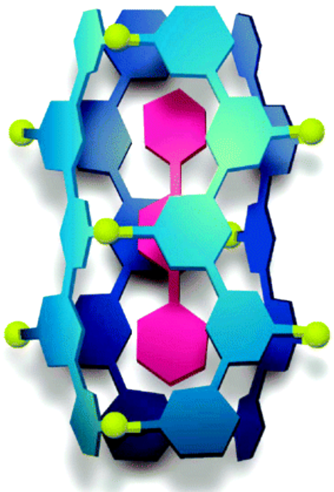




Guest template can be removed or substituted by chemical exchange

Angew. Chem., Int. Ed. **2003**, *42*, 3909



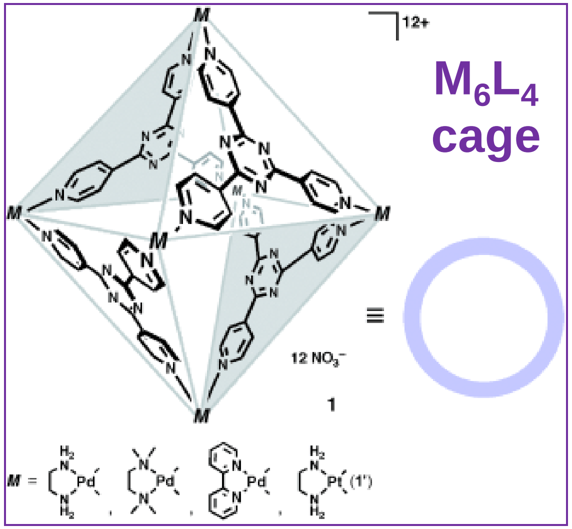


Tubular complex:
$M_{10}L_4$ cage + guest

stabilized by π–π and C-H–π interactions

J. Am. Chem. Soc. **1999**, *121*, 7457;
Chem. Commun. **2002**, 2036.

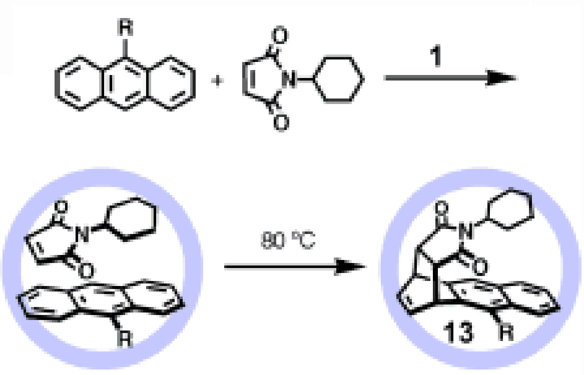
Nanocages as reaction vessels (flasks)

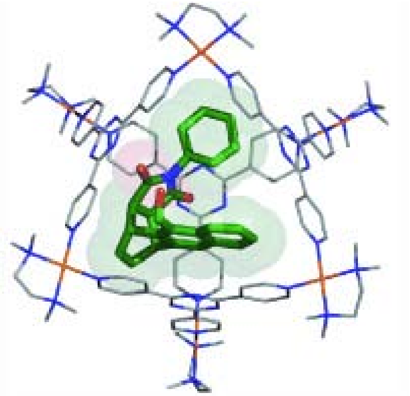


M_6L_4 cage

J. Am. Chem. Soc. **2004**, *126*, 6846.

Kinetically altered Diels-Alder reaction:



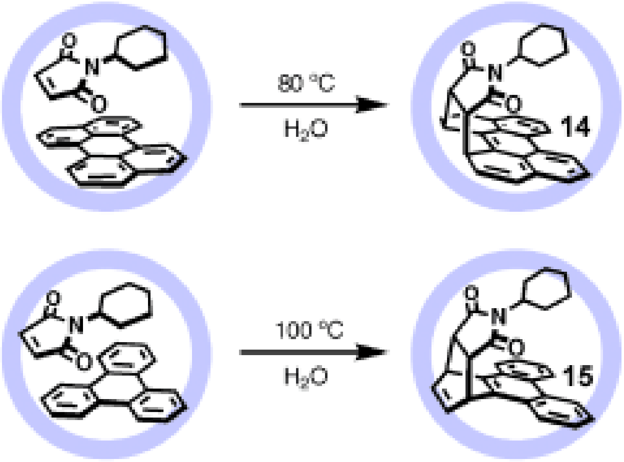


← expected product (uncatalyzed)

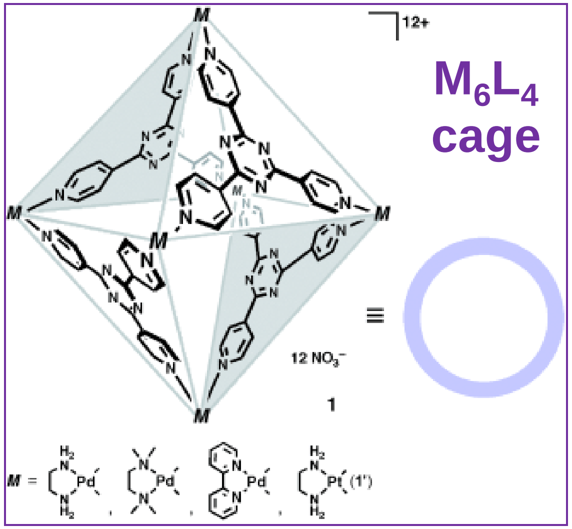
Nanocage-catalyzed Diels-Alder additions of unreactive dienes:

“Nanoflask” effectively increases pressure on encapsulated guest molecules, accelerating reaction rate

J. Am. Chem. Soc. **2007**, *129*, 7000–7001.

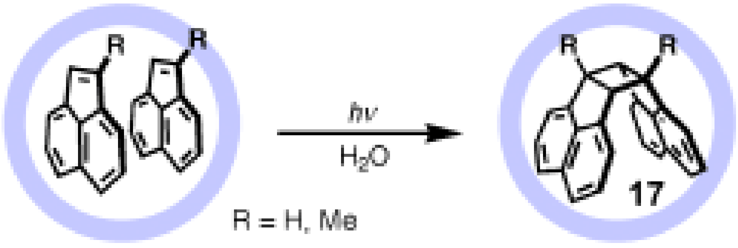


Nanocages as reaction vessels (flasks)



M_6L_4 cage

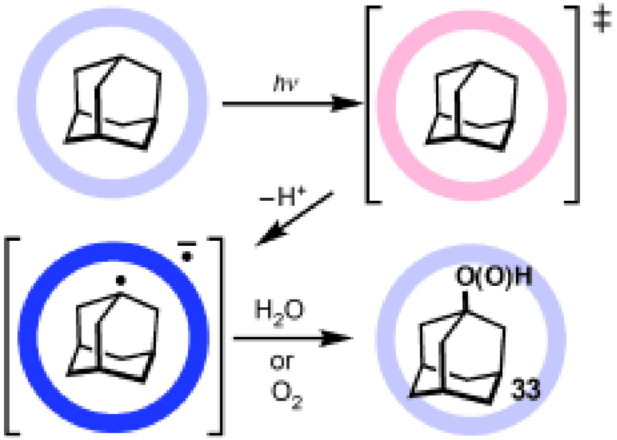
Stereoselective photochemical [2+2] cycloadditions:



Quantitative yield of *syn* adducts

(uncatalyzed version: 1:1 mixture of diastereomers, in fair yield)

Angew. Chem. Int. Ed. **2002**, *41*, 1347.



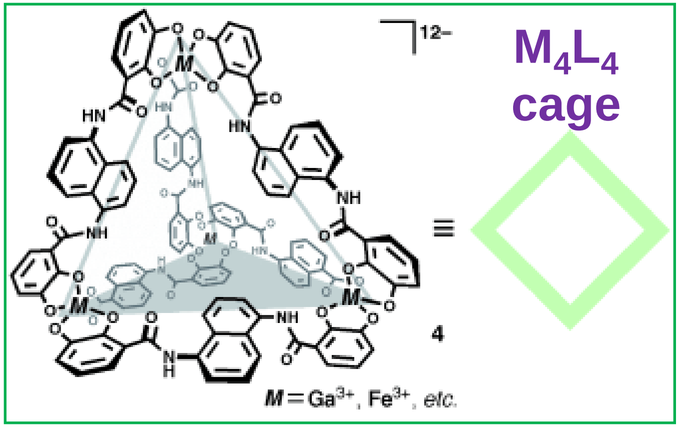
Photochemical oxidation (C–H bond insertion):

Triazine ring of nanocage is photochemically excited, then electron transfer from an encapsulated adamantane leads to an adamantyl radical and radical anion of **1**.

J. Am. Chem. Soc. **2009**, *131*, 4764.

Nanocages as reaction vessels (catalysts)

Raymond and coworkers

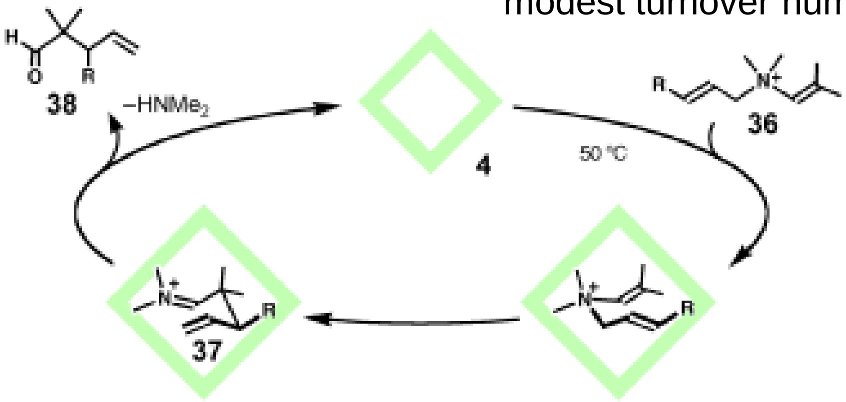


M_4L_4 cage

Anionic & hydrophobic cage:
good host for cationic guests

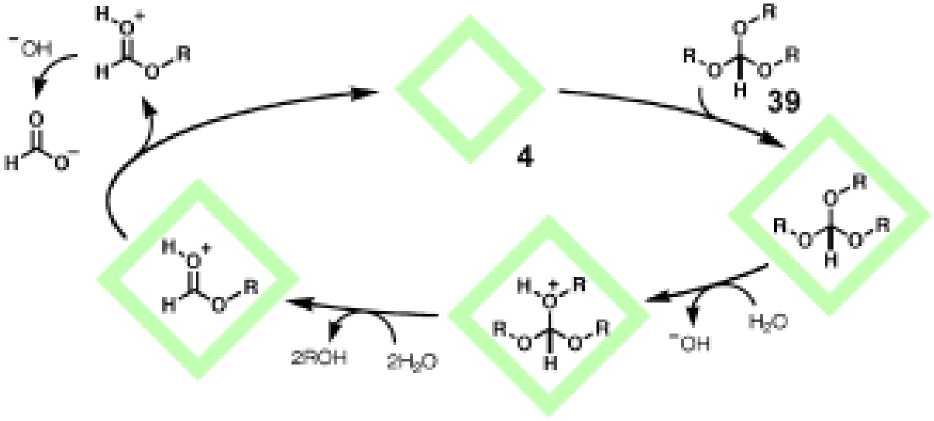
Unimolecular catalysis: cationic aza-Cope rearrangement

850-fold rate acceleration;
modest turnover number (<10)



J. Am. Chem. Soc. **2006**, *128*, 10240.

Accelerated hydrolysis of orthoformates:



Neutral reactant and product,
cationic intermediate

Rate determining step: H^+ transfer

Science **2007**, *316*, 85.
Angew. Chem. Int. Ed. **2007**, *46*, 8587.