Supramolecular Chemistry of Nanomaterials

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Lecture 3 – Self-assembly (2nd Part)

Self-assembly (part 2)

- Self-assembly using the coordination bond
  - Macrocycles
  - Cages
  - Catenanes

- Self assembly of metal-containing species
  - Metal nanoparticles

Metal complexes in the self-assembly process

Why metals?

- The coordination bond is usually more labile than covalent bonds making it very valuable in the assembly process (i.e. bonds can break and form easily to yield complex structures; thermodynamic control not kinetic).

- Wide-range of geometries can be obtained

- Metals have unique optical, magnetic and catalytic properties which make them very attractive

Design Principles

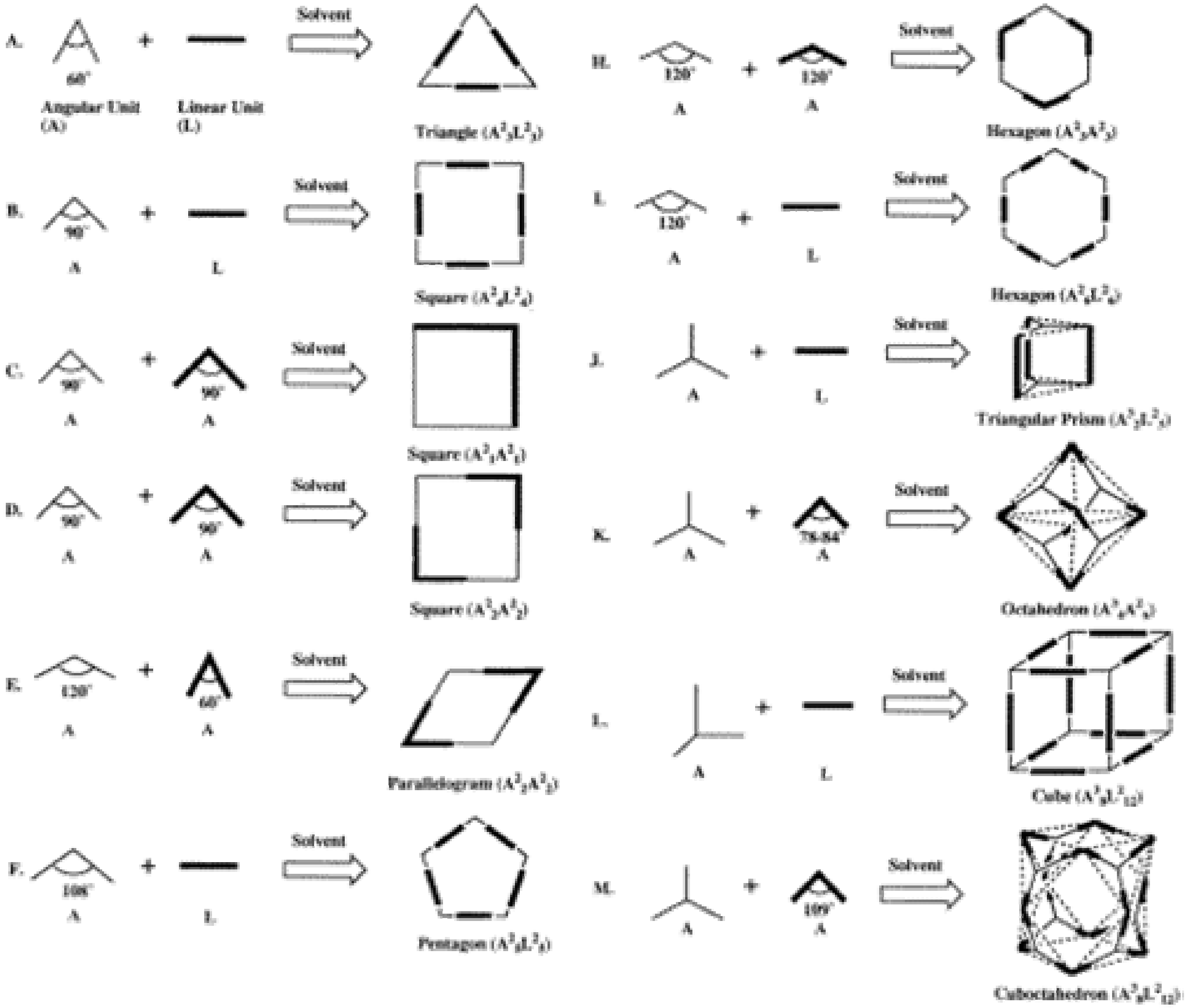
The design of self-assembling supramolecular assemblies based on any kind of directional interaction (such as Hydrogen-bonding or the coordination bond) can be broadly divided in two categories:

-Those that form polymeric materials
-Those that form discrete aggregates

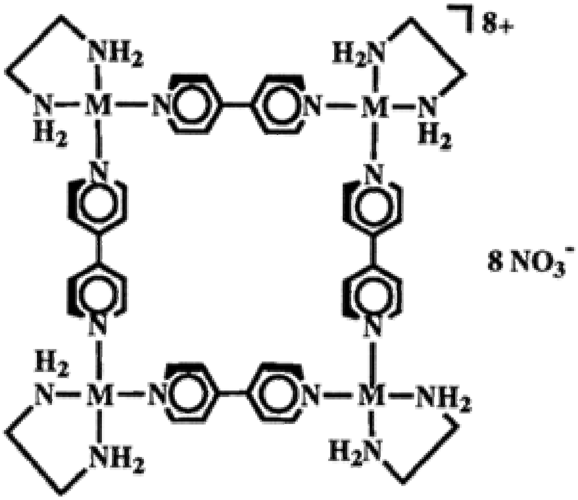
Which one will be formed (and which geometry will it have) depends on the nature of the ligands and the geometry around the metal center. Building blocks can have divergent or convergent binding sites; this, together with the geometry of the metal centers, will largely determine the polymeric/discrete nature of the supramolecular assemblies.

In some occasions, the use of templates to direct the assembly process is essential.

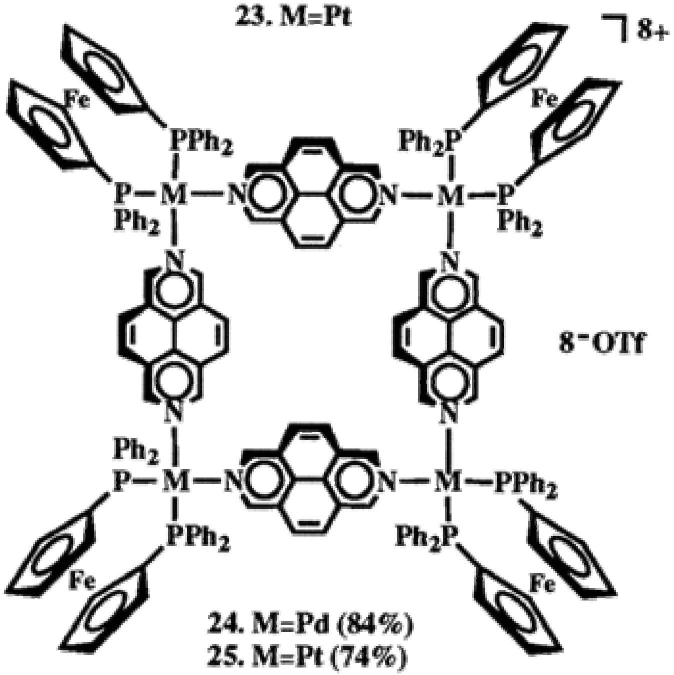
Metalla-macrocycles



Stang*, Acc. Chem. Res.*, **30** (12), 502 -518, 1997



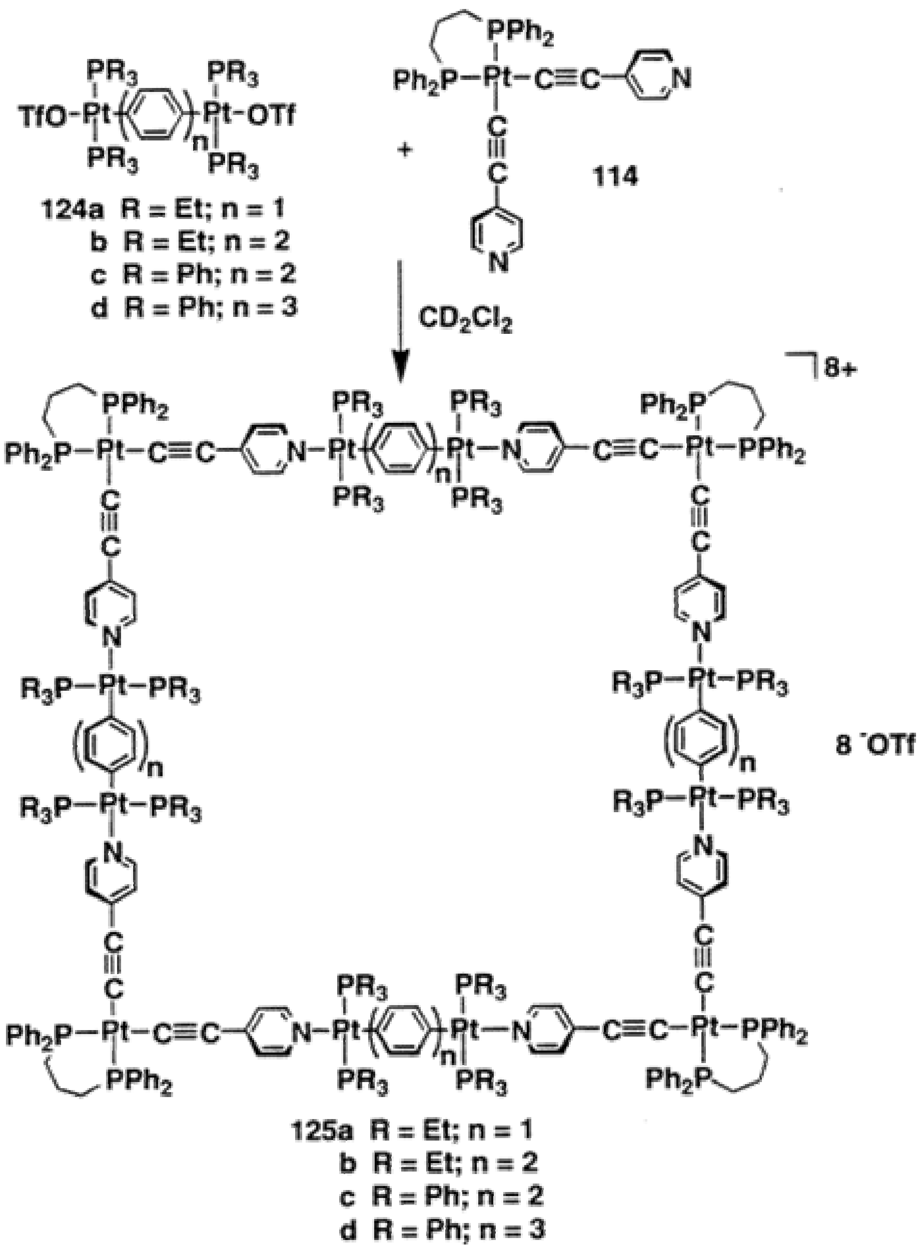
22. M=Pd
23. M=Pt



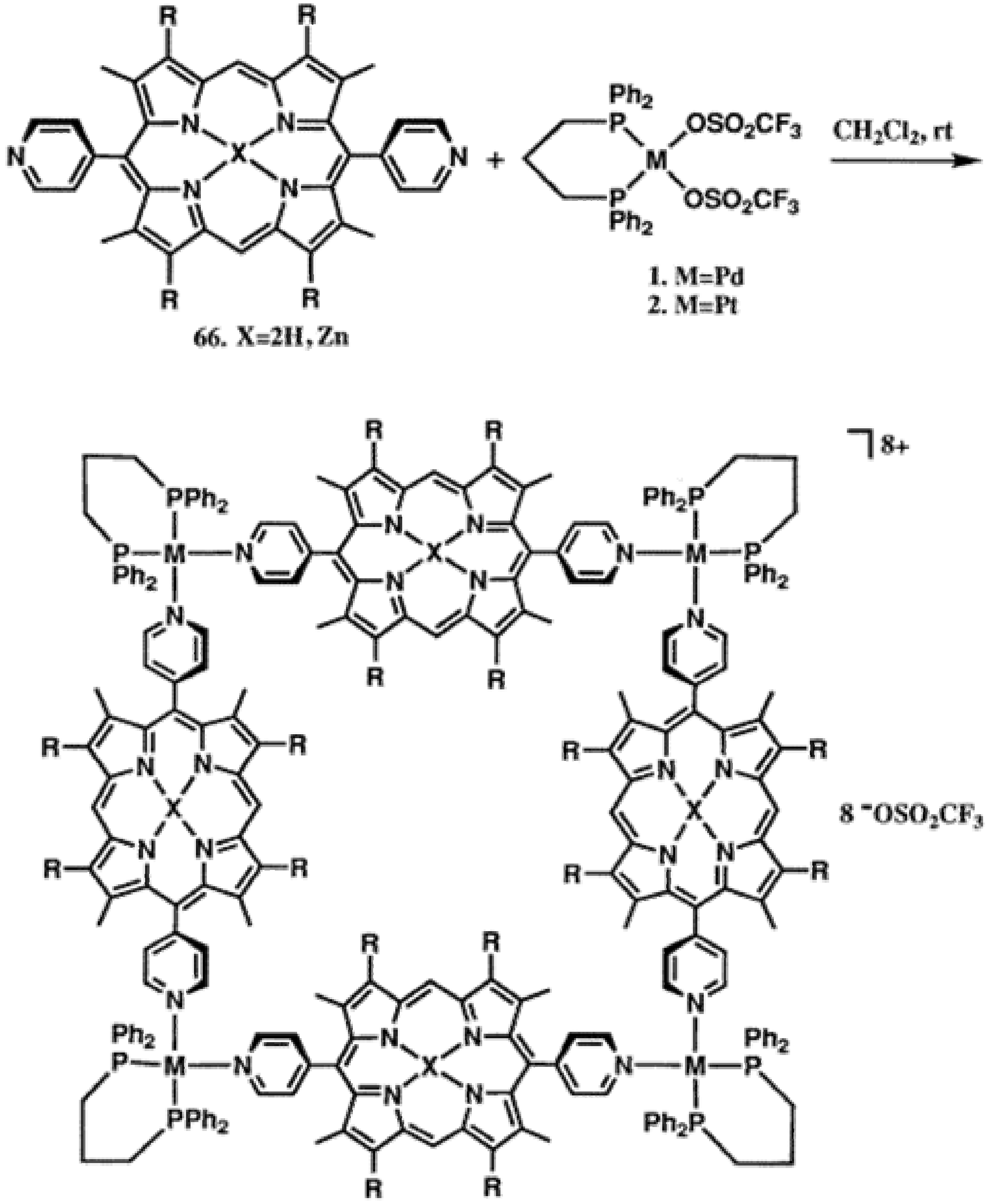
24. M=Pd (84%)
25. M=Pt (74%)

This type of metalla-squares was first prepared by Fujita in 1991. It is a good host for aromatic guests (forces that come into play: hydrophobic effect and pi-pi interactions.

Also in the early 1990s, Stang started to develop a large collection of metalla-cycles. In this case, the ancillary ligands are usually phosphines.



This approach can be applied to prepare metalla-assemblies with larger cavities (nanoscale containers). This can be achieved by choosing the appropriate bridging ligands.



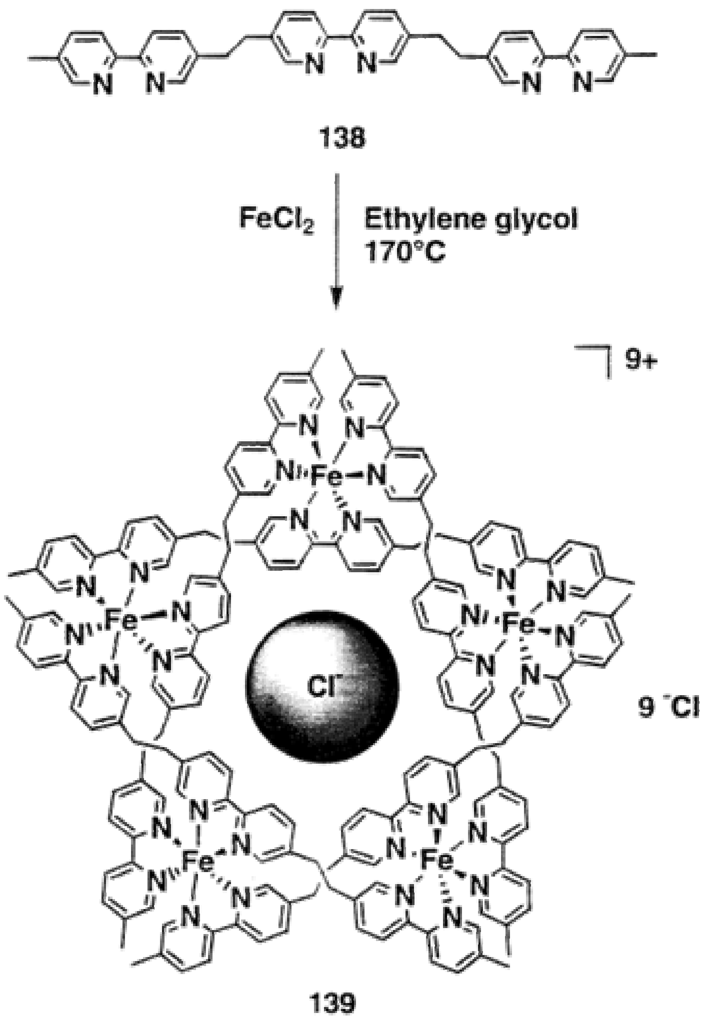
66. X=2H, Zn

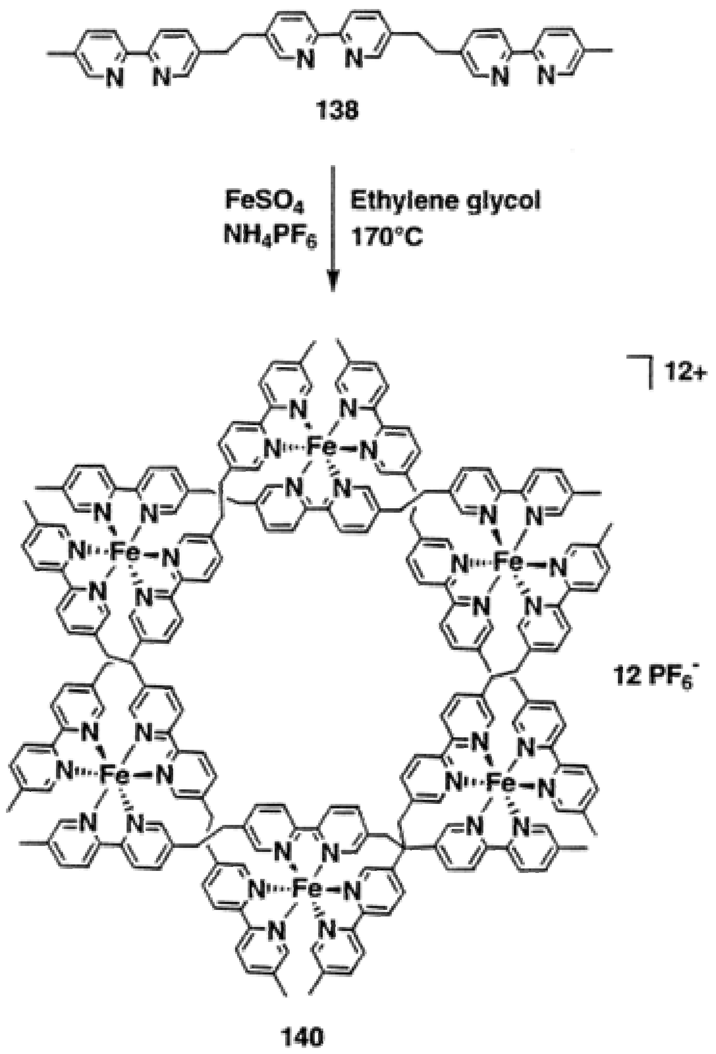
1. M=Pd
2. M=Pt

R=n-C$_6$H$_{13}$

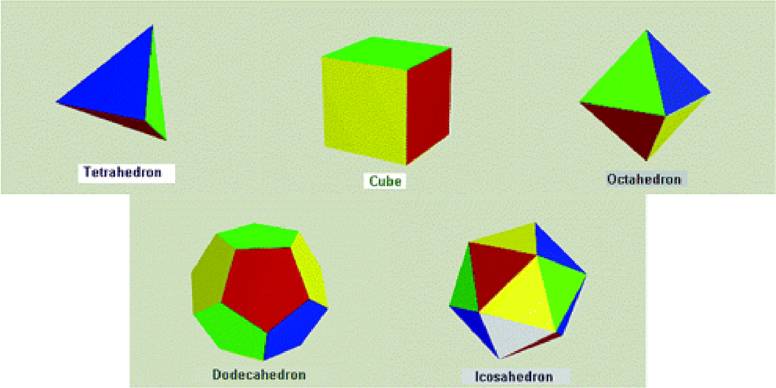
67. M=Pd, X=2H, 96%
68. M=Pt, X=2H, 85%
69. M=Pd, X=Zn, 98%
70. M=Pt, X=Zn, 80%

The presence of a templating agent can direct the formation of a specific Assembly (Lehn, *Angew. Chem. Int. Ed*., 1996, **35**, 1838)

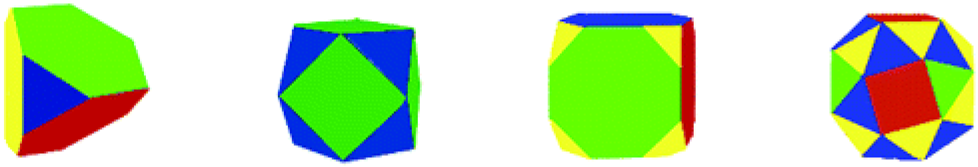




Metalla-cages



Platonic solids

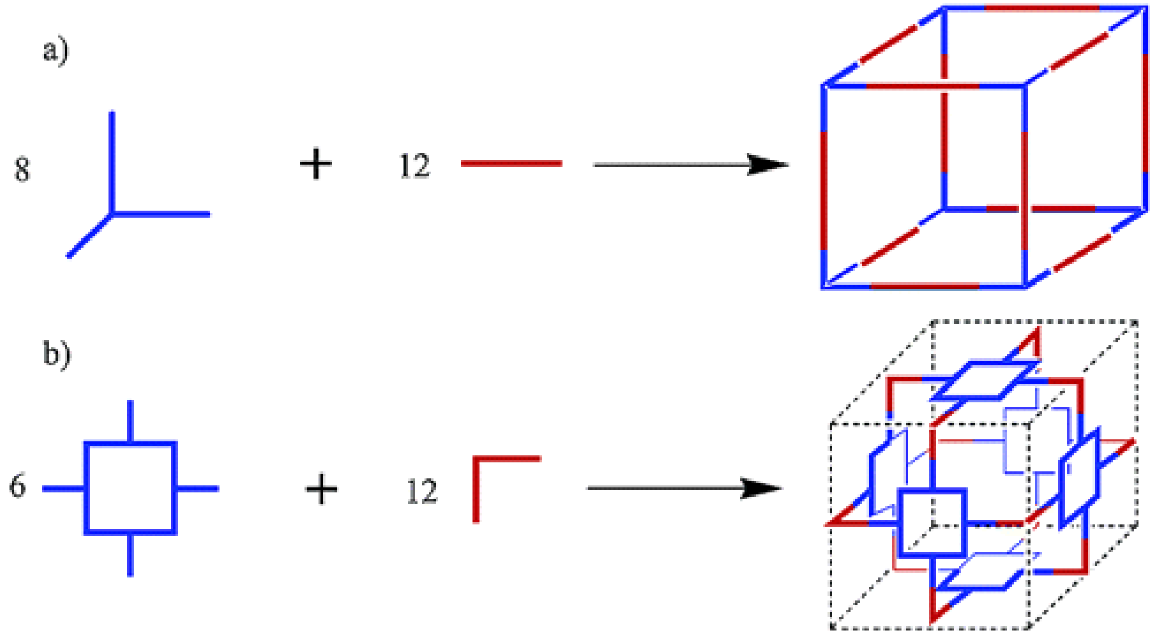


Archimedean Solids: (a) Truncated Tetrahedron, (b) Cuboctahedron, (c) Truncated Cube, and (d) Snub Cube

Stang, *Acc. Chem. Res.*, **2002**, *35*, 972

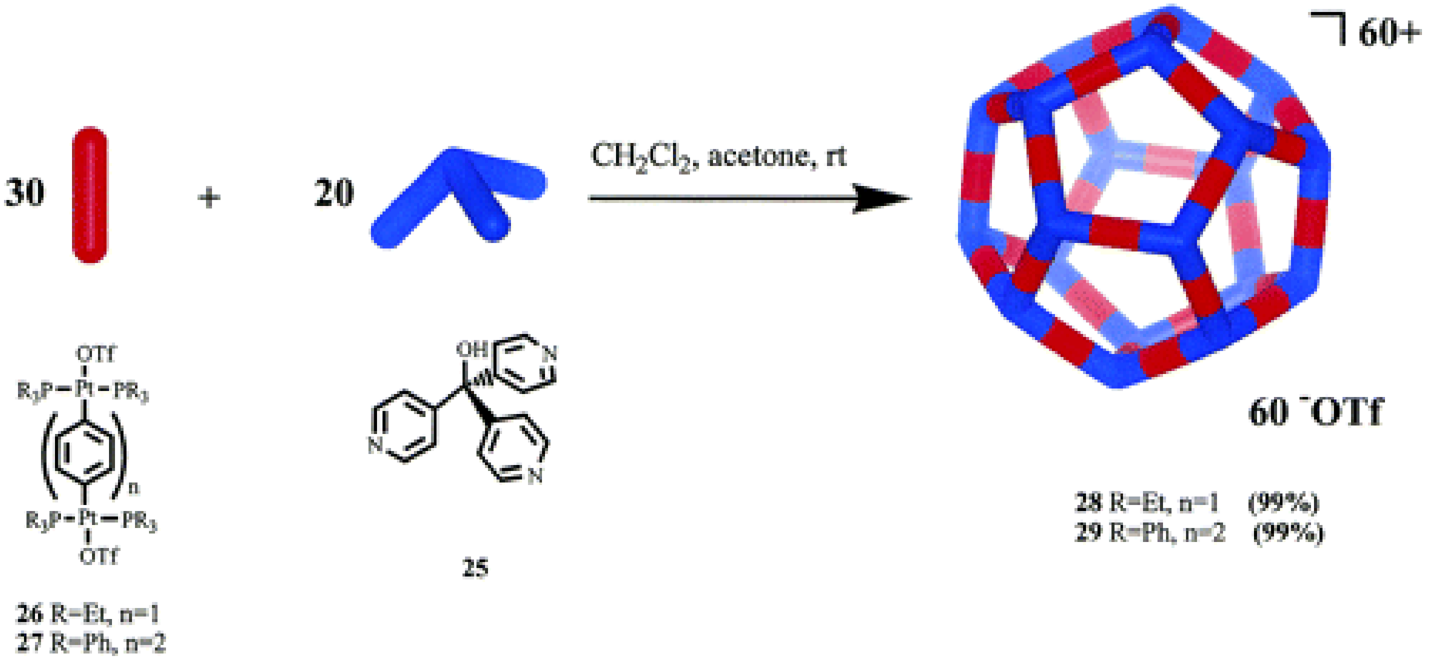
As has been previously proposed by Stang, metalla-cages can be Prepared by using to different approaches: (a) edge-directed self Assembly; (b) face-directed self-assembly.

As for the macrocycles, specific cages can be favoured by the Presence of the appropriate templating agent.



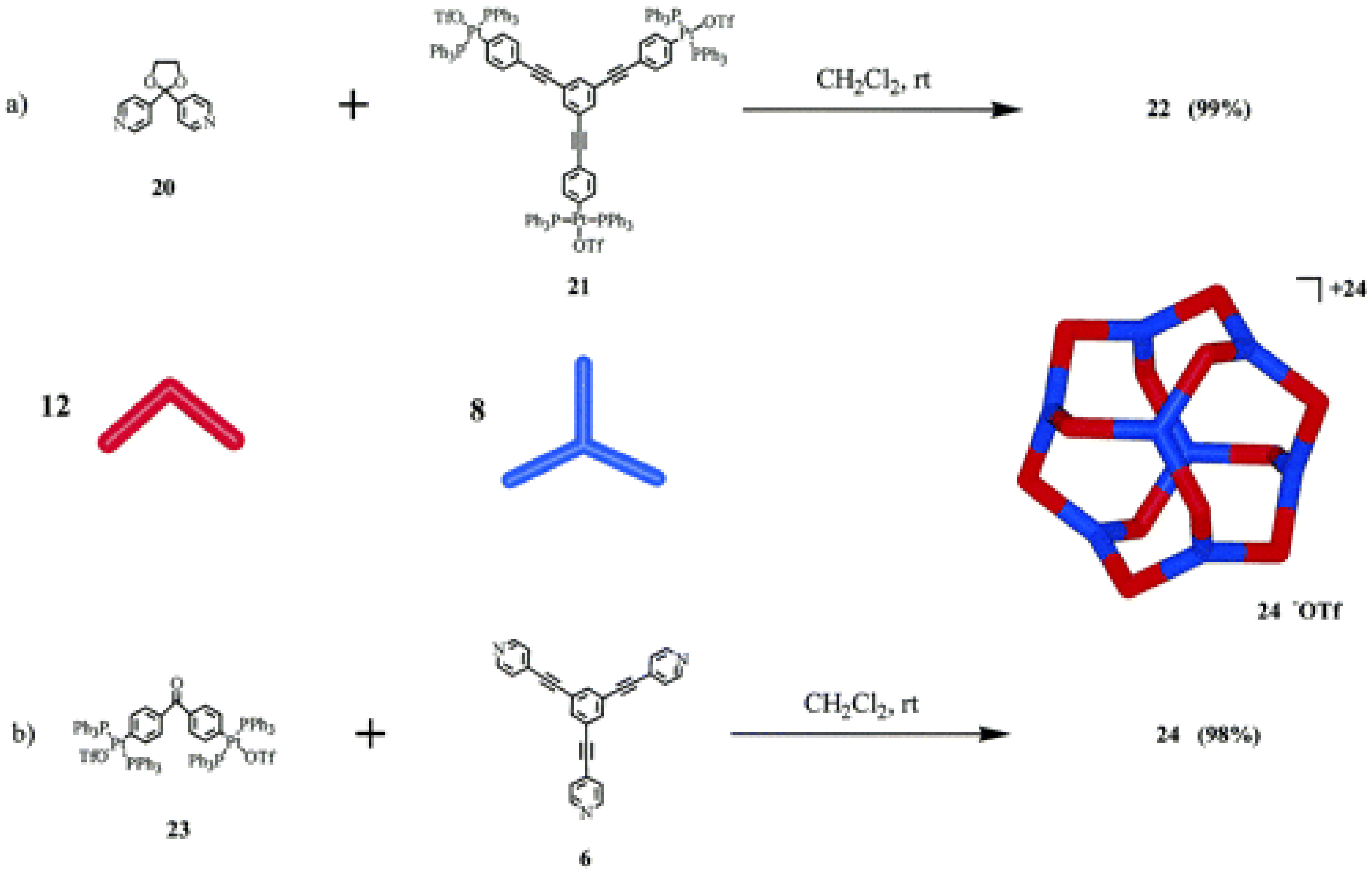
Stang, *Acc. Chem. Res.*, **2002**, *35*, 972

The dodecahedron, consisting of 12 regular pentagonal faces, represents the second largest of the Platonic solids. Using an edge-directed approach, Stang has prepared such cage.



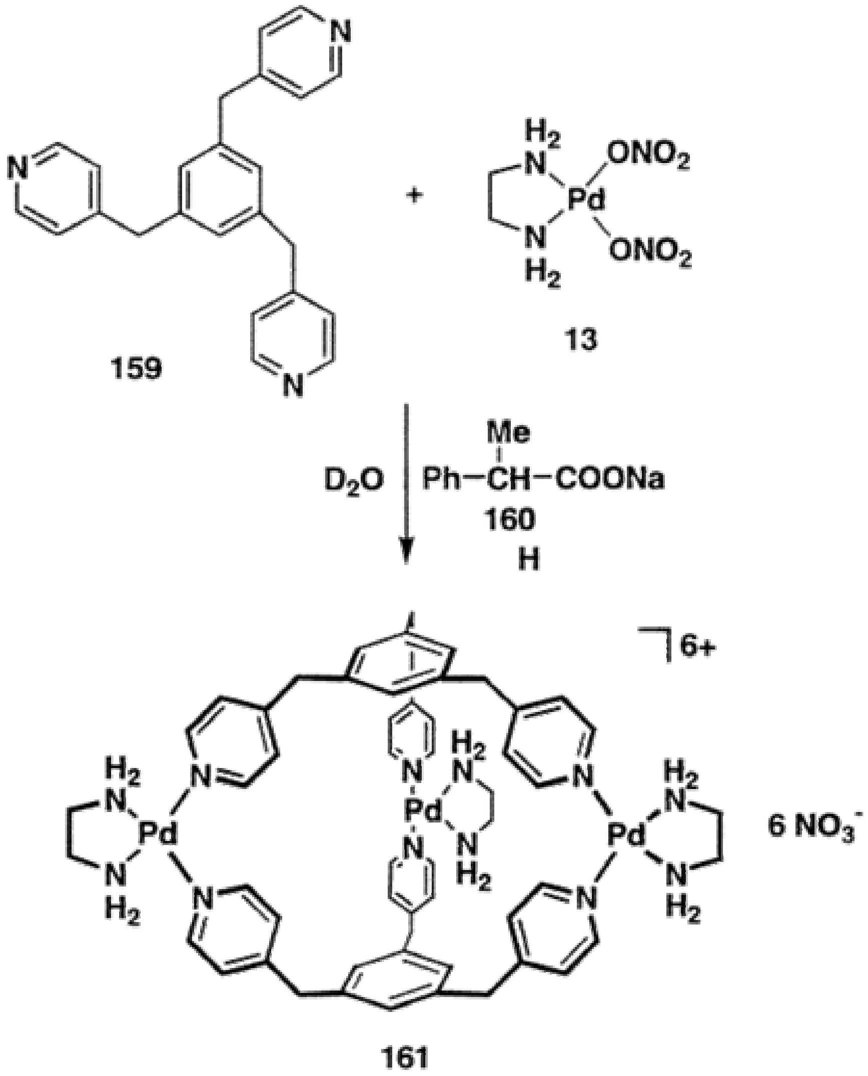
Stang, *J. Am. Chem. Soc.* 1999, **121**, 10434

The cuboctahedron is made up of six square faces and eight equilateral triangular faces, and thereby possesses features of both the Platonic cube and octahedron. Stang has prepared such structure by using an face-based assembly process:

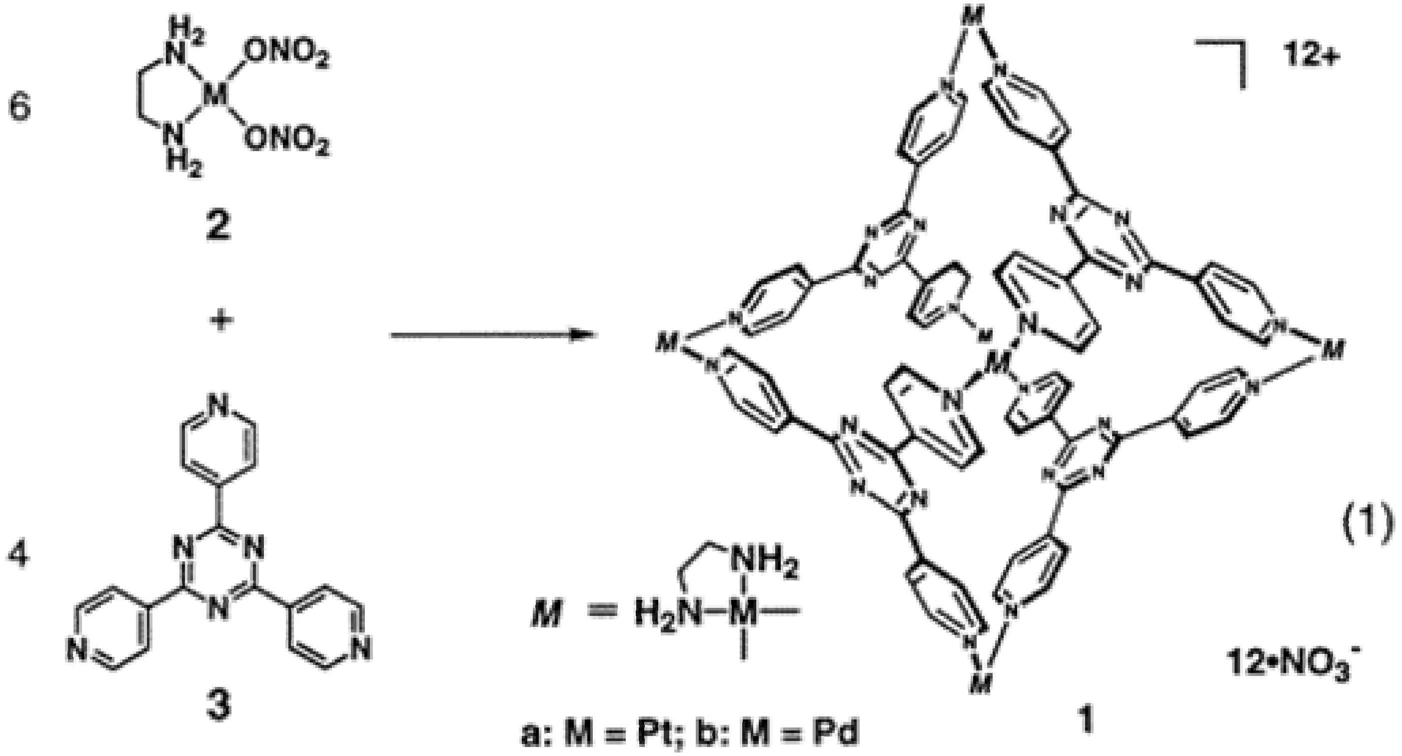


Stang, *Nature* 1999, **398**, 796

The synthesis of specific cages can be achieved by adding the appropriate templating agents. An example reported by Fujita is:

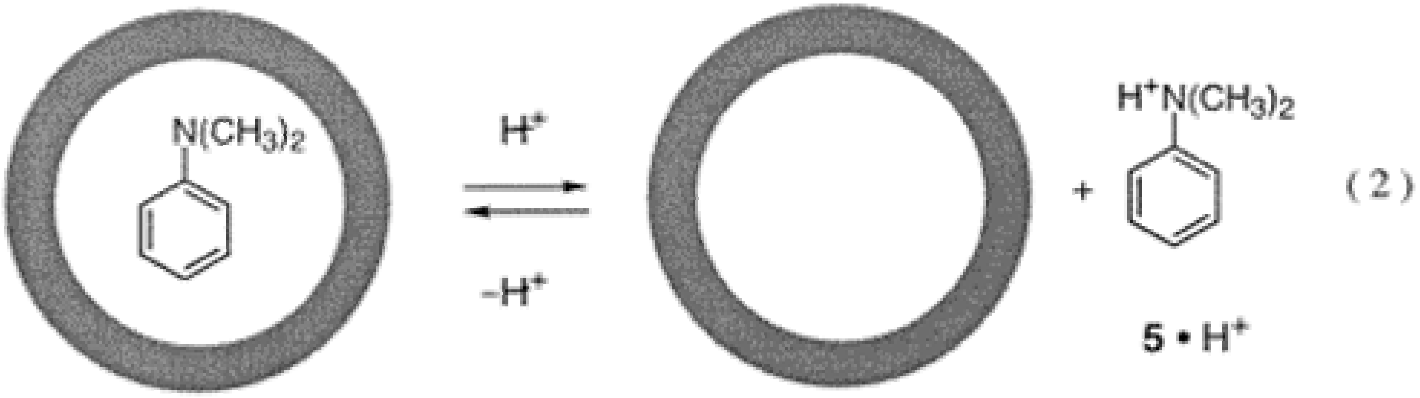


An interesting aspect of the nano-scale cages formed is that the they Can trap specific guests (either once they are formed or in the assembly process):



Fujita, *J. Am. Chem. Soc.,* 1998, **120**, 8561

The internal cavity of the cage is relatively hydrophobic; Consequently, the deprotonated species will be a “better” Guest for this nano-hosts than the protonated one:



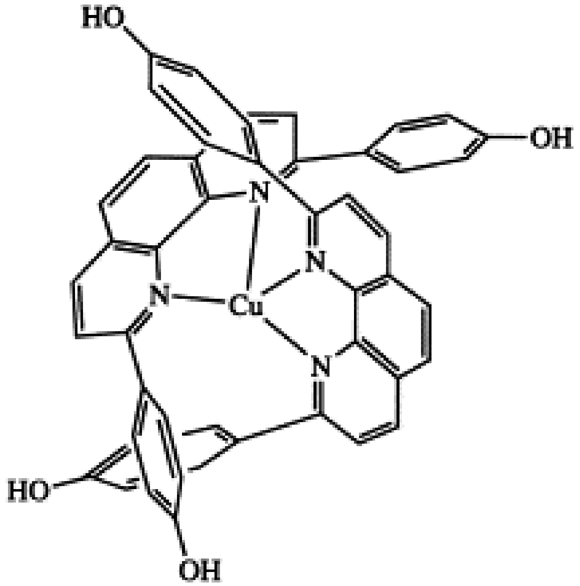
1a • 5 **1a**

Metal-containing catenanes

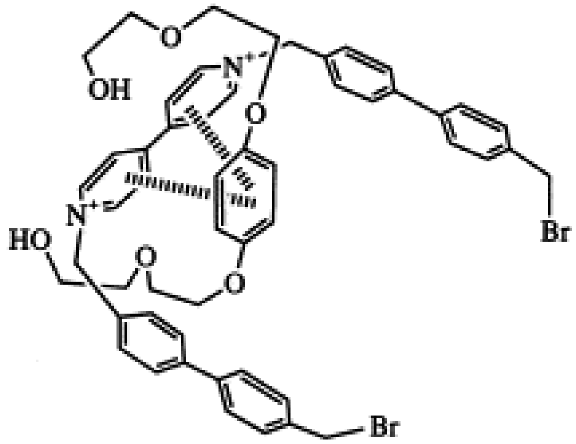
In lecture 2, catenanes were introduced and the main synthetic strategies for their preparation were discussed. One of these strategies is the utilisation of metal centres to direct the components to catenante. in this section we will expand on the topic.

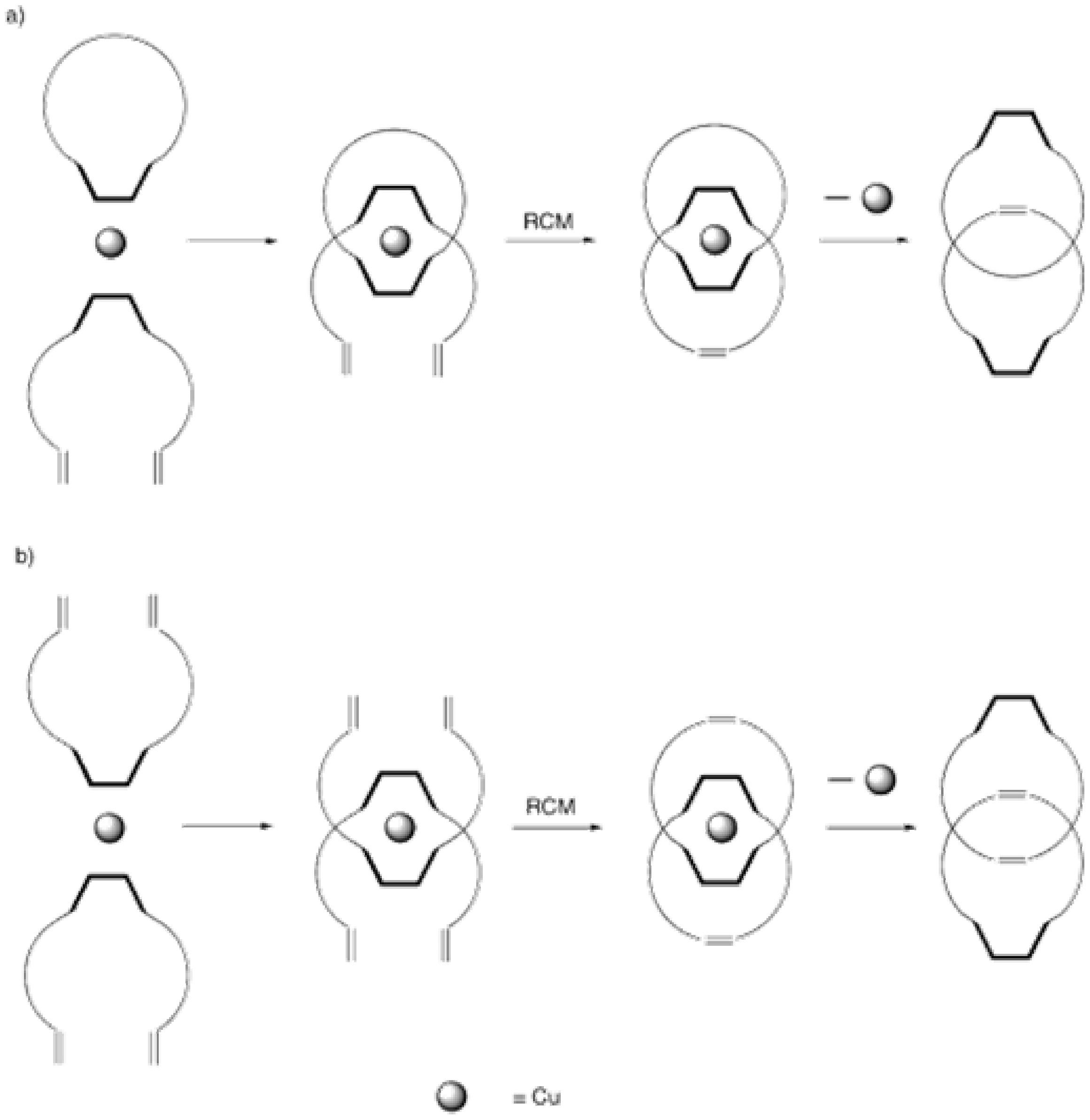
Coord. Chem. Rev. 2000, 200–202, 5–52

a)

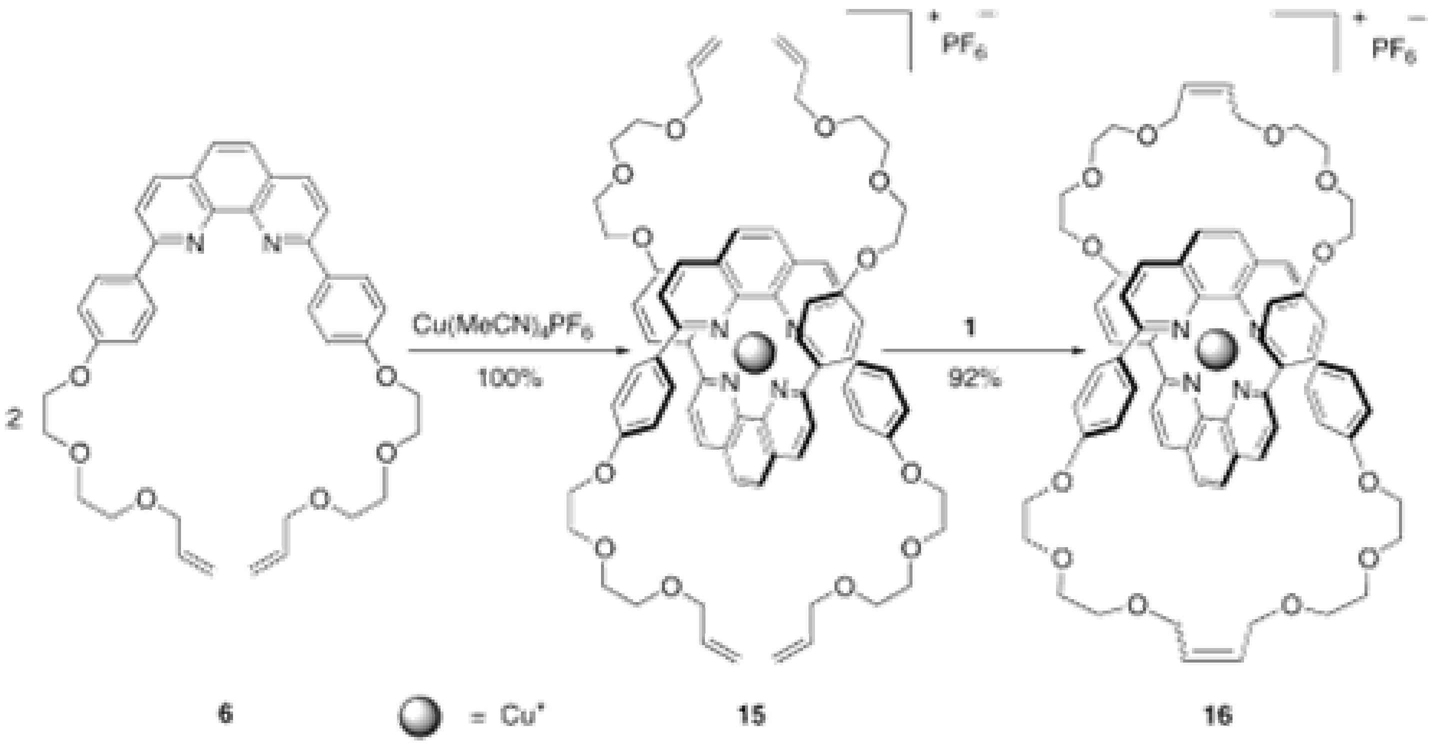


b)

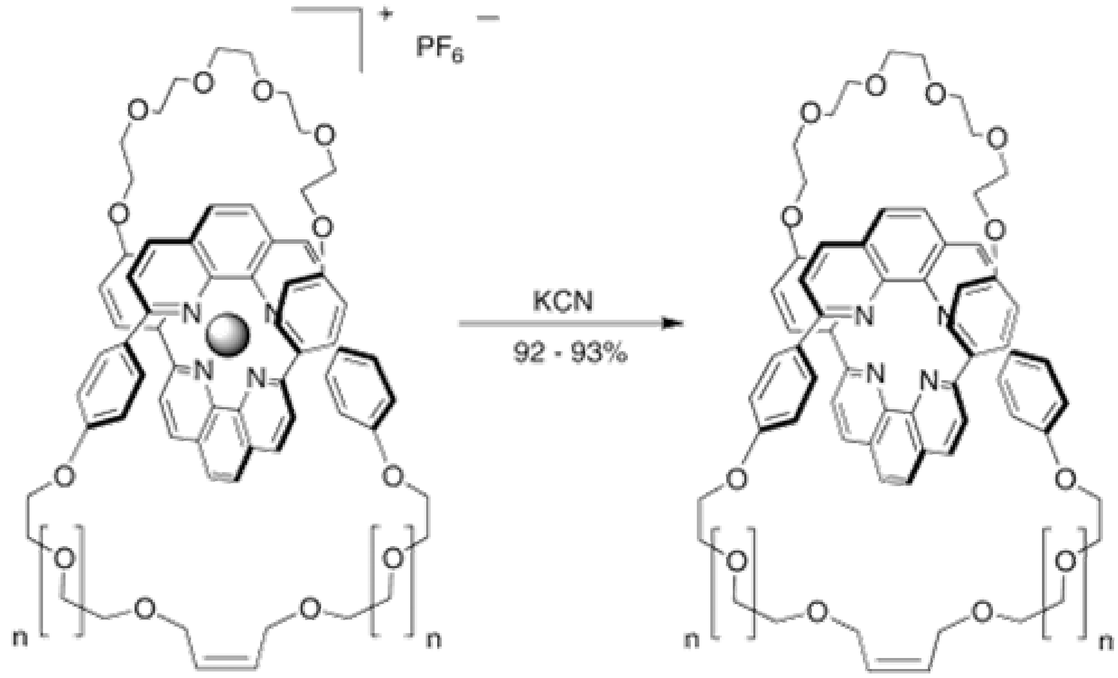




Grubbs y Sauvage, *J.Org.Chem.*, 1999, **64**, 5463



Grubbs y Sauvage, *J.Org.Chem.*, 1999, **64**, 5463



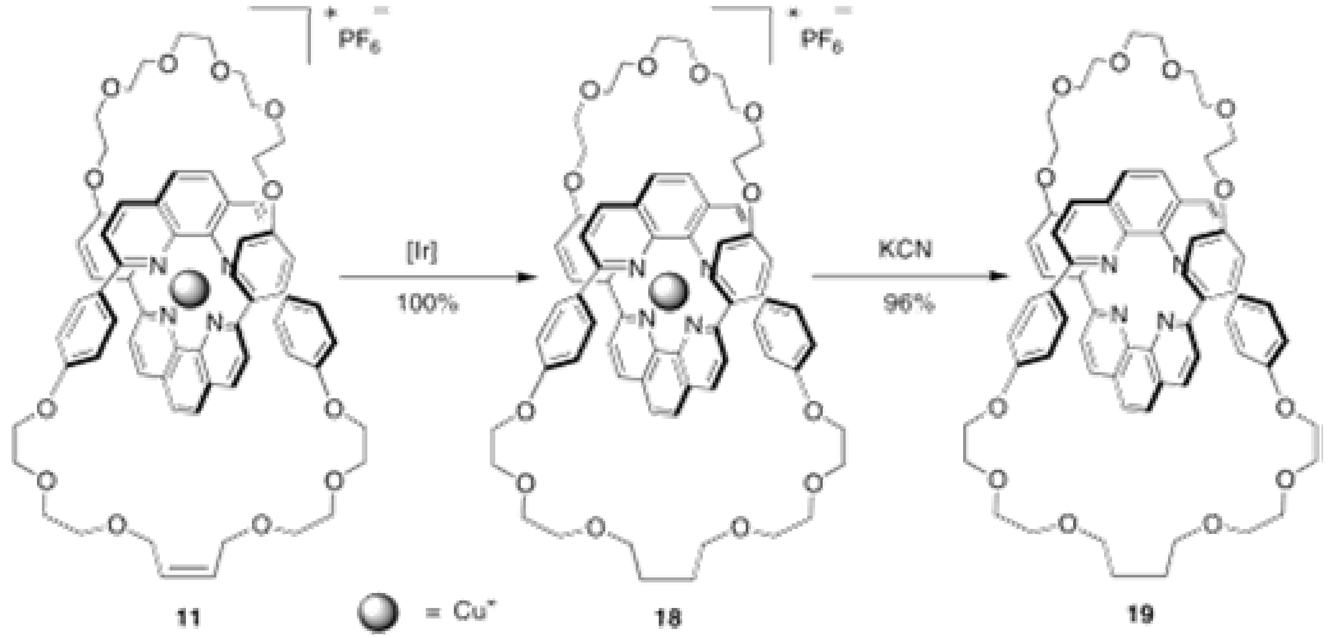
11 (n=1)

12 (n=2)

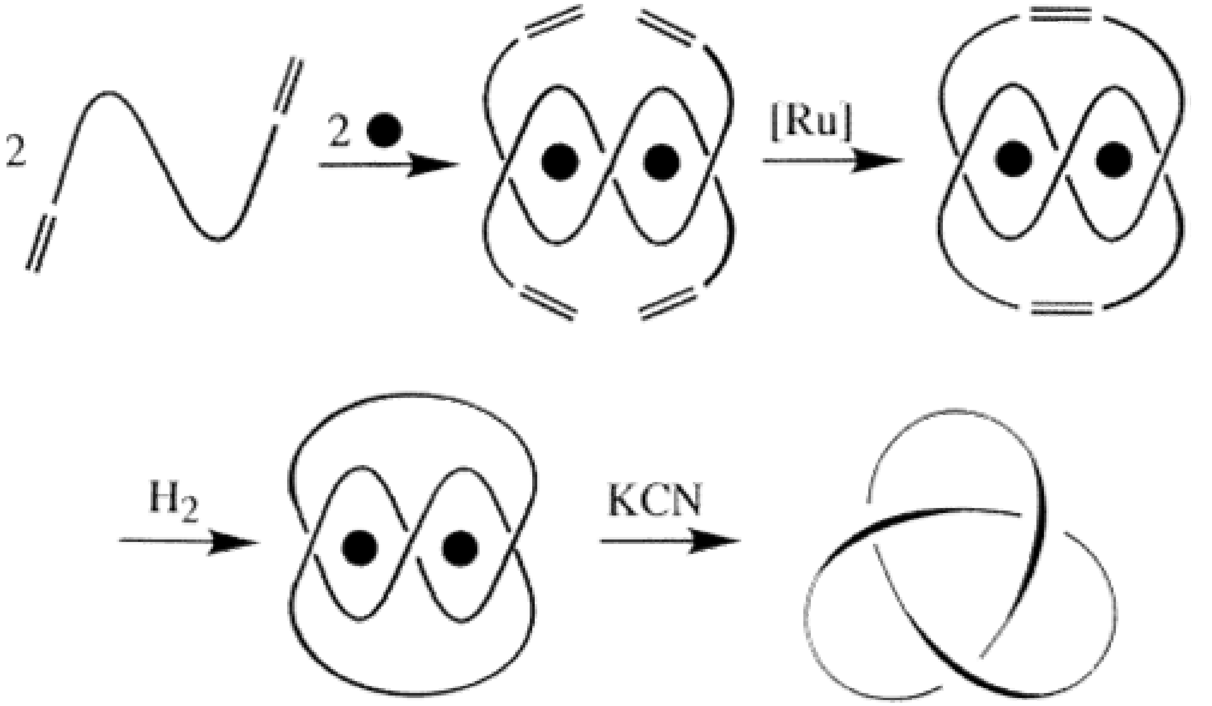
● = Cu^+

13 (n=1)

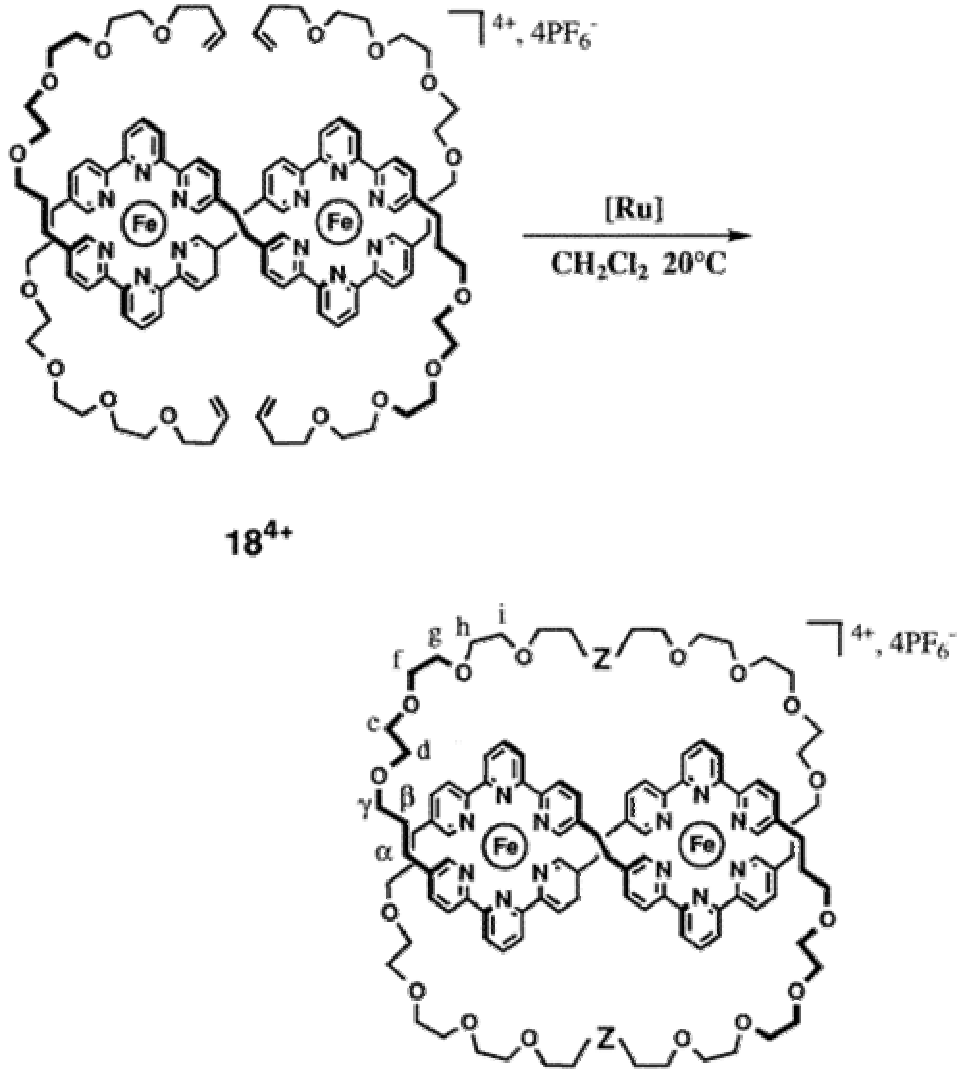
14 (n=2)



+
PF6−
+
PF6−
[Ir]
100%
KCN
96%
N
11
= Cu+
18
19



J.P. Sauvage, *J.Am.Chem.Soc.*, 1999, **121**, 994

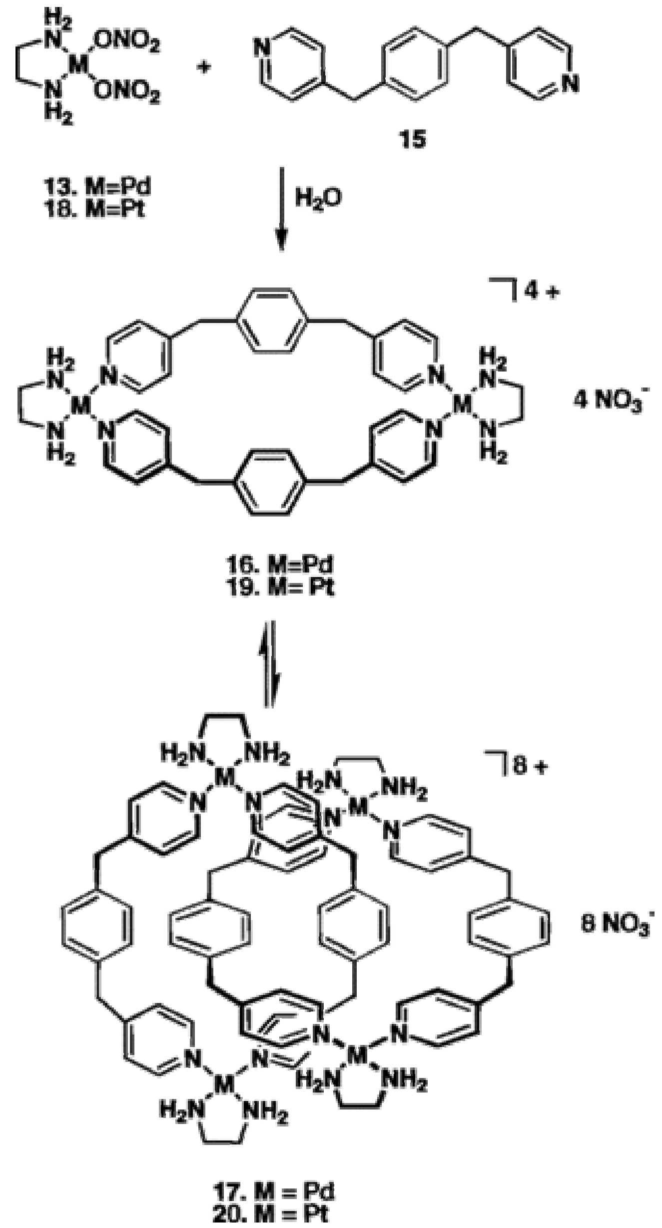


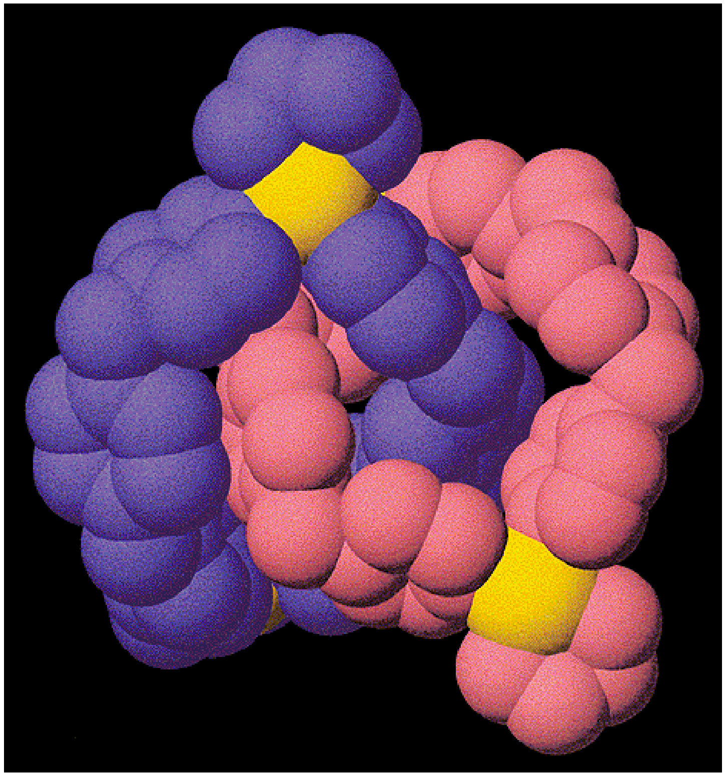
$\mathbf{18}^{4+}$

$\mathbf{19}^{4+}$: $-Z- \;=\; -CH{=}CH-$

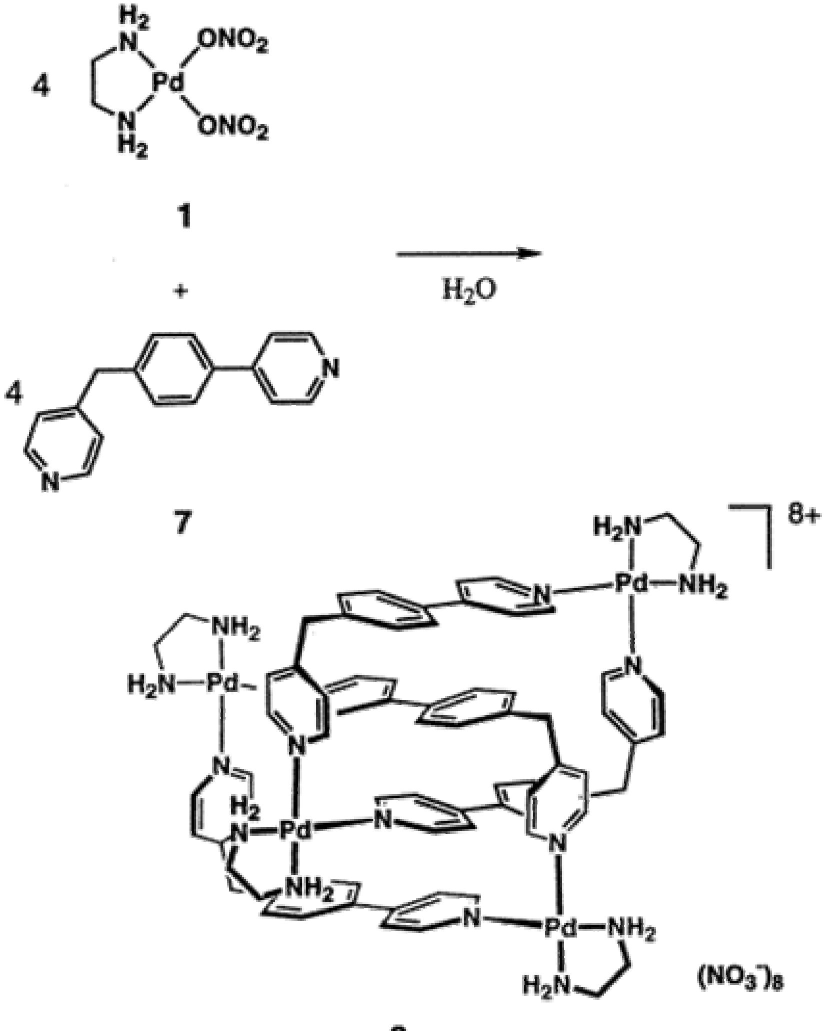
$\mathbf{20}^{4+}$: $-Z- \;=\; -CH_2-CH_2-$

H_2 Pd/C





M. Fujita, *Acc.Chem.Res.*, **1999**, *32*, 53

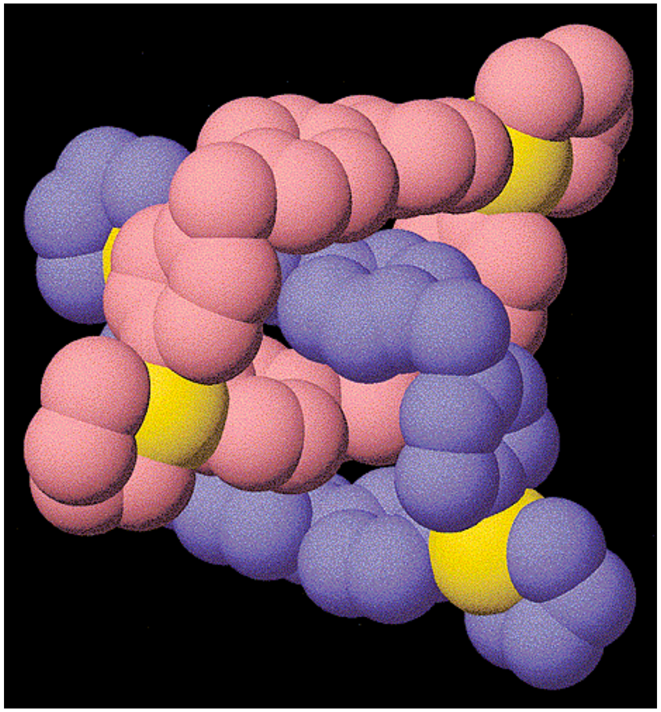


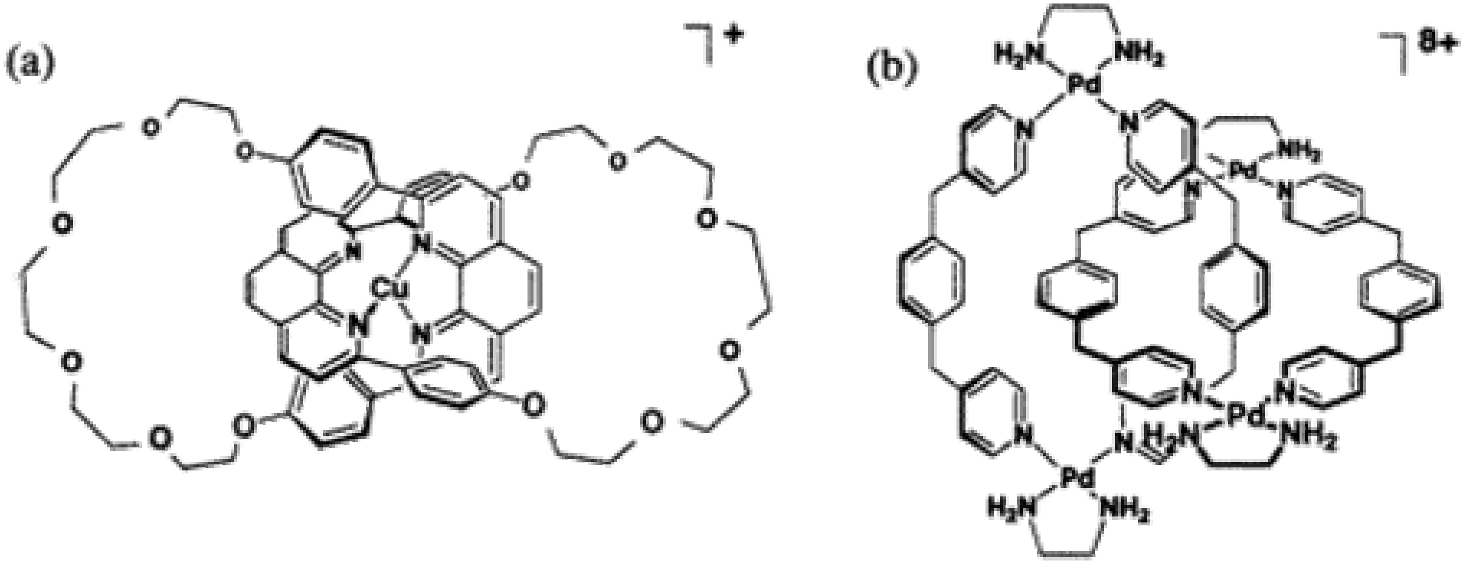
1

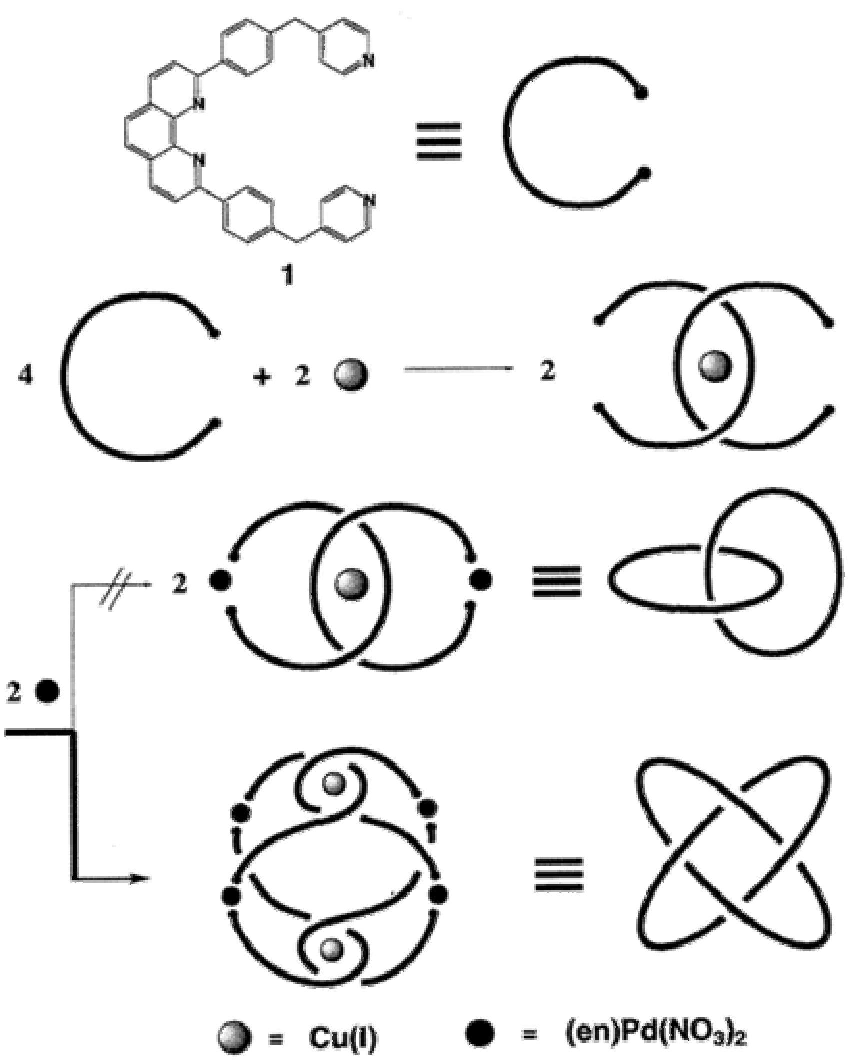
7

8

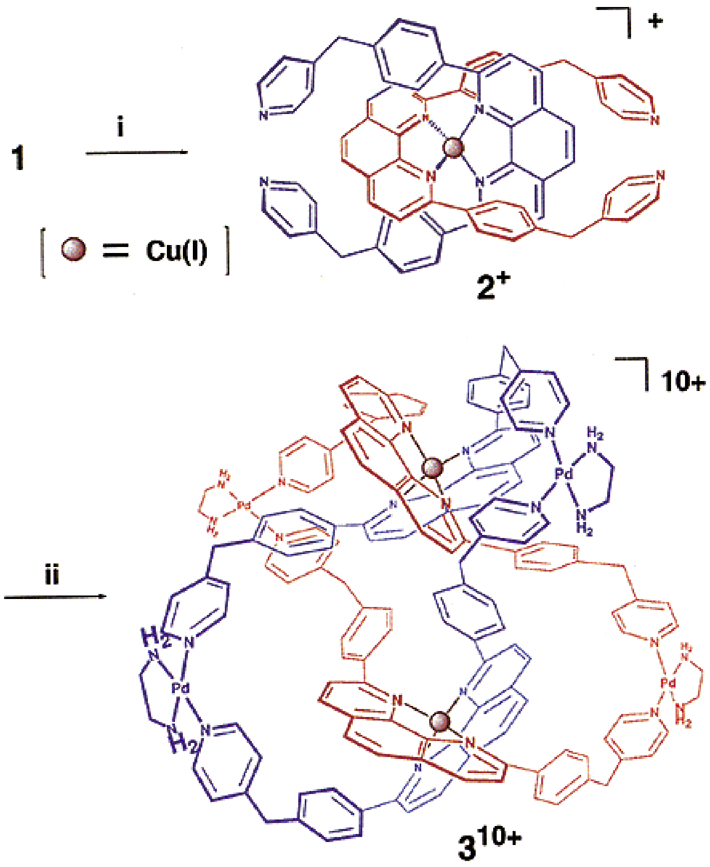
(1)

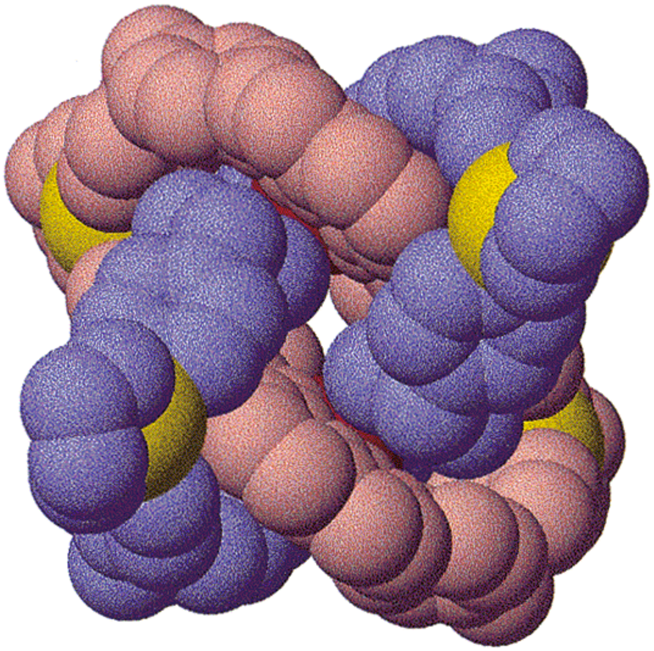



(a)
+
O
N
Cu
(b)
8+
H₂N
NH₂
Pd
N



M. Fujita and J.P. Sauvage, *J.Am.Chem.Soc.*, **1999**, *121*, 11014


1
i
= Cu(I)
+
2+
N
Pd
H2
ii
10+
3 10+



Self-assembly of metal nanoparticles

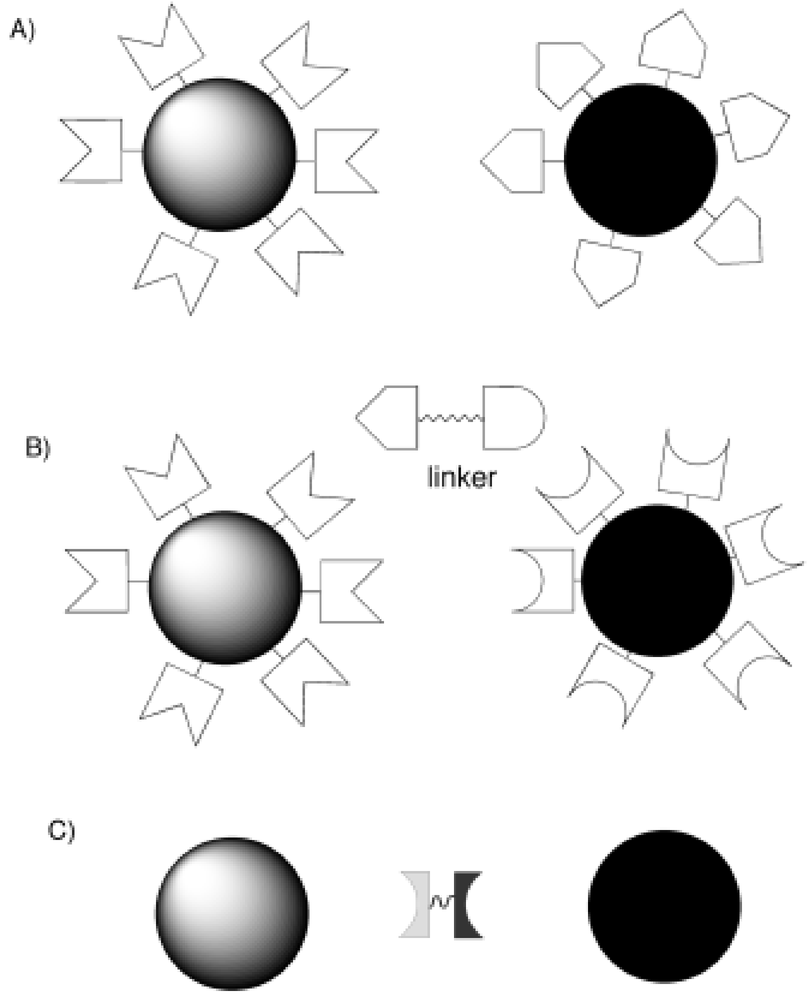
The previous section has dealt with the ability of the coordination Bond to direct the formation of specific assemblies.

Besides their “directing” properties metals are also very valuable As integral part of the final assemblies. This is due to their unique optical, chemical and magnetic properties.

One of the areas that has received enormous attention over the last decade, is the utilisation of supramolecular forces to organise in specific assemblies, metal-containing nanoparticles.

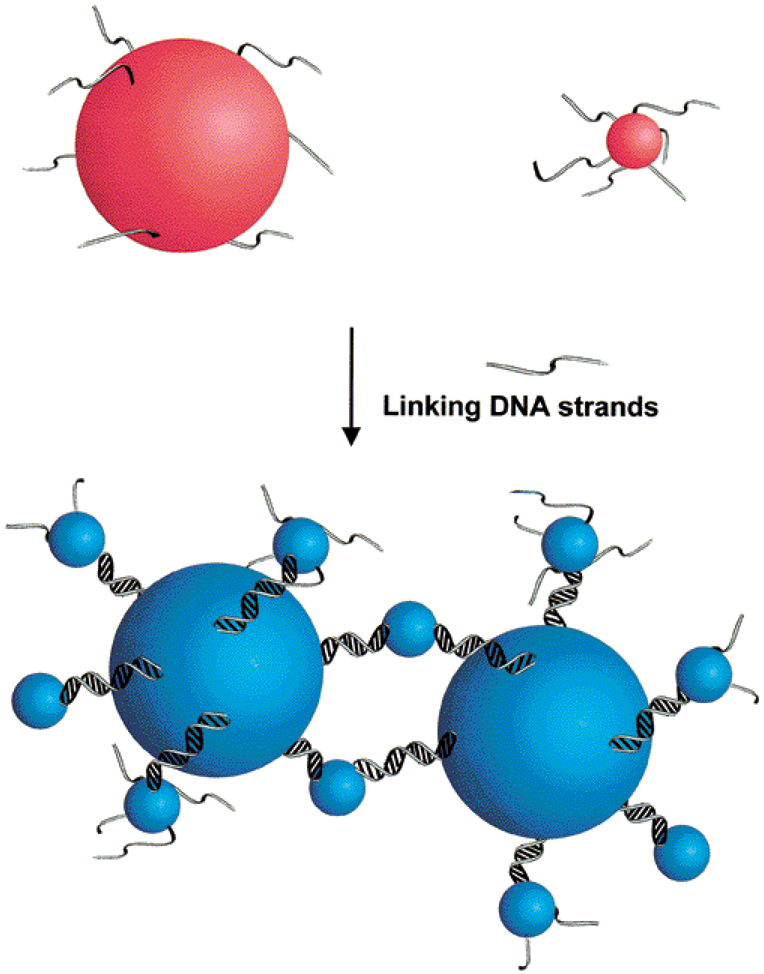
The challenge ahead is to be able to control the way in which this nanometer-size particles are organised (enormous applications in electronics, sensors, etc).

Certain nanoparticles and
nanorods (e.g. Au, Ag, CdSe)
can nowadays be prepared
using simple synthetic procedures.
These species (between 2 and
30 nm) can then be functionalised
with the appropriate ligands
(containing functionalities with
supramolecular capabilities)
to form assemblies.

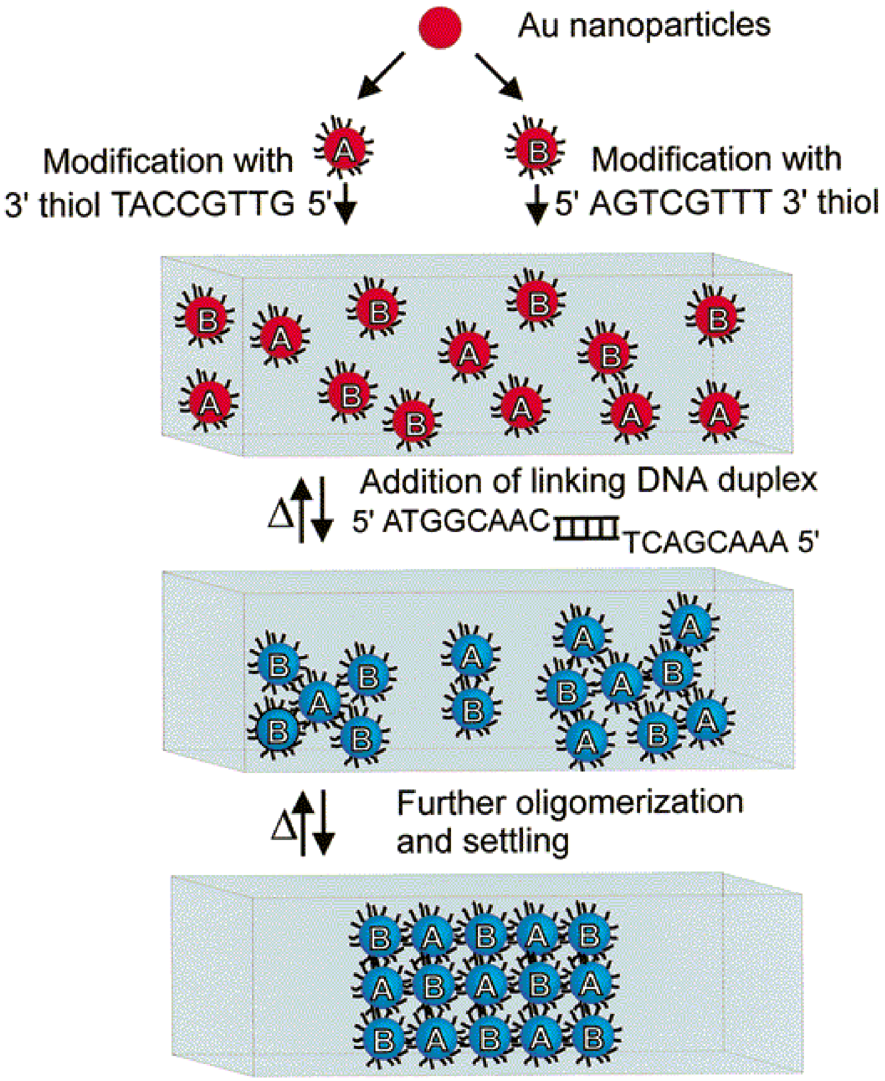


Niemeyer, *Angew. Chem. Int. Ed.*, 2001, **40**, 4129

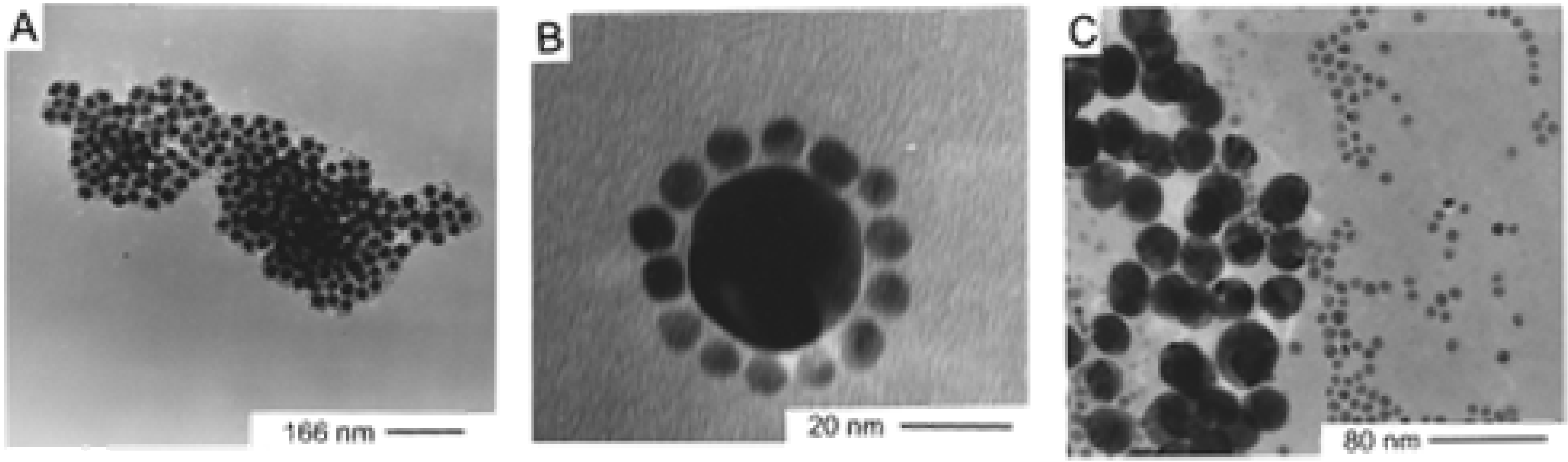
An example of this are the DNA-functionalised gold nanoparticles reported by Mirkin:



Mirkin, *Inorg. Chem.*, 2000, **39**, 2258

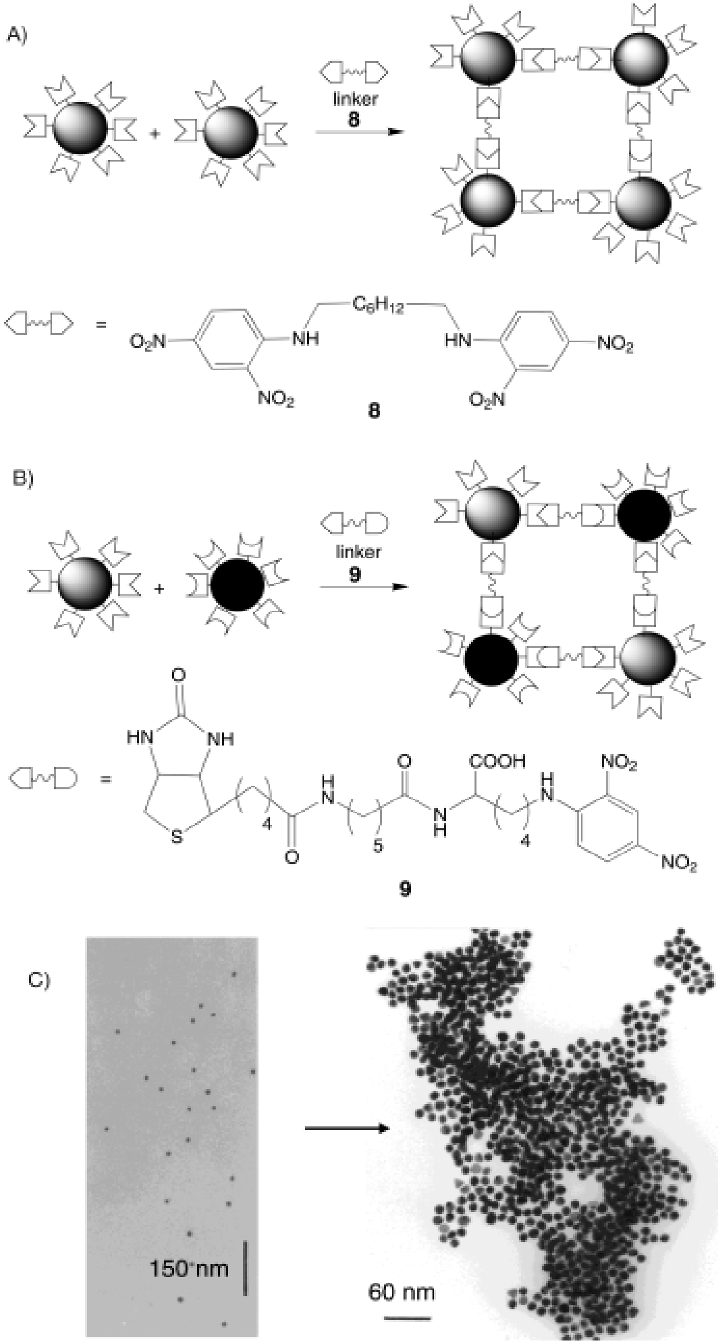

Au nanoparticles
Modification with
3' thiol TACCGTTG 5'
Modification with
5' AGTCGTTT 3' thiol
A
B
Addition of linking DNA duplex
5' ATGGCAAC
TCAGCAAA 5'
Δ
Further oligomerization
and settling
Δ

TEM pictures of the DNA-linked nanoparticle assemblies reported
By Mirkin:

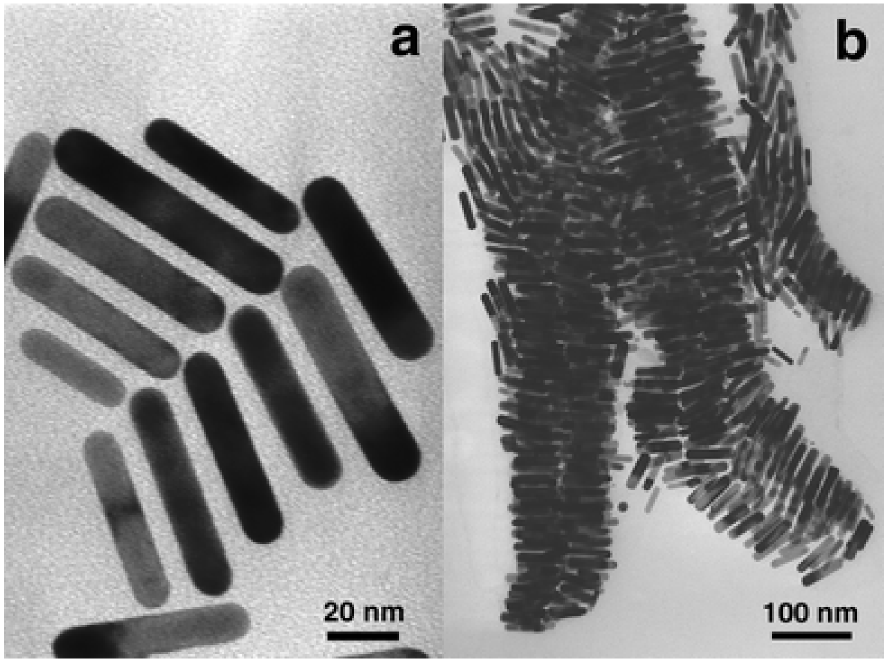


Cross-linking of Ag and Au nanoparticles functionalized with IgG molecules. Bivalent linkers with two terminal hapten groups, allow the directed assembly of homo-oligomeric (A) or heterodimeric (B) aggregates, respectively. The TEM images (C) were obtained from colloidal Au/antibody aggregates before (left) and after (right) the addition of linker 8.

S. Mann, *Adv. Mater*. 1999, 11, 449



Metal nanorods have also attracted much interest since their asymmetric structure can introduce anisotropy into a nano-assemble. This in turn can have interesting applications in nano-electronics. However, the synthesis of such structures is not trivial. Some interesting DNA-functionalised nanorods and their assemblies have been recently reported by Mann:



Mann, *Chem. Commun*., 2001, 1264