Supramolecular Chemistry of Nanomaterials

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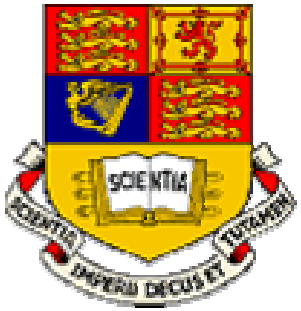
Ramon Vilar

Lecture 4 – Supramolecular Containers



Molecular containers

One of the most attractive features in enclathrating molecular aggregates is the discovery of new physical and chemical properties of molecules due to aggregate formation in the restricted micro environment of the cages. In this lecture, we will investigate some of such “molecular containers”. Specifically, we will cover the following topics:

- Carcerands
- Hemicarcerands
- Self-assembling capsules
- Metalla-cages and capsules

Carcerands

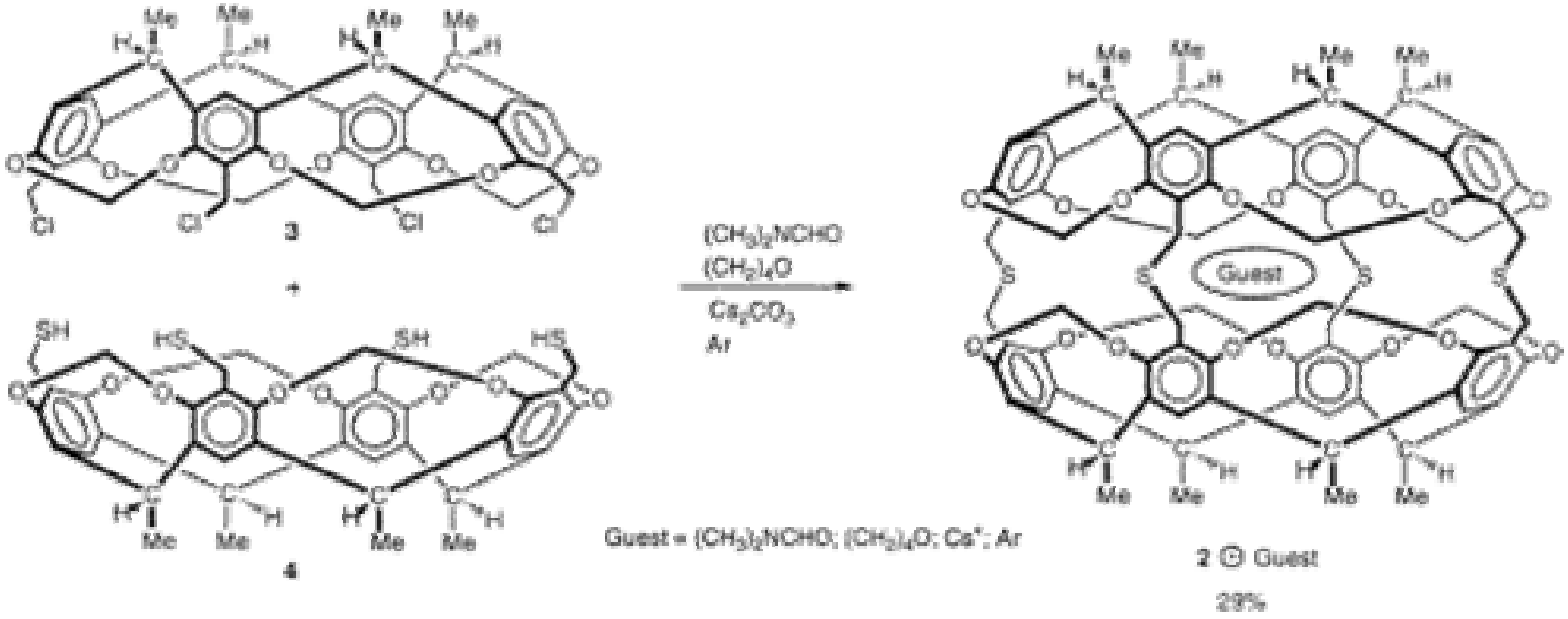
A *carcerand* is defined as a closed molecular container or capsule without portals of significant size through which guests can either enter or leave. Guest species within a carcerand are therefore permanently trapped within the internal volume, unless covalent bond breakage within the host occurs.

A carcerand that contains a guest to give an incarcerated host-guest complex is termed *carceplex*.

(Carcerand comes from the latin *carcer* which means prison)

Jasat and Sherman, *Chem. Rev*., 1999, **99**, 931

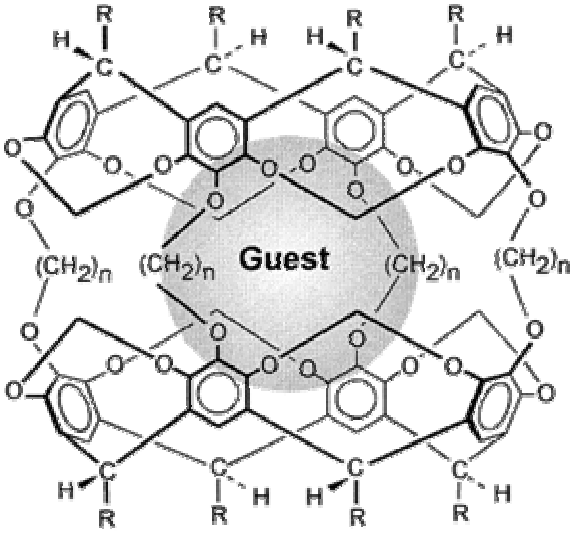
In the early 1980s Cram prepared the first carcerand by linking two *cavitands*:



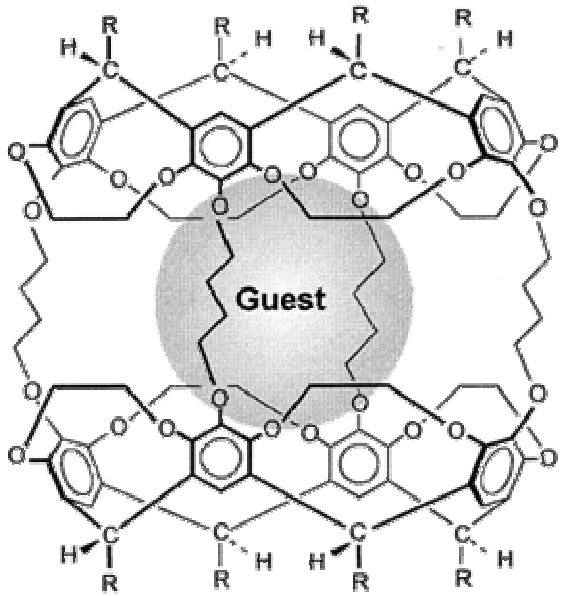
The excellent yields usually obtained in the preparation of many carceplexes is contrary to expectation based on the statistical coming together of so many reactants and the closure of so many rings. It is clear that their formation is not statistical at all, and that templated mechanisms are in operation.

The presence of a suitable template (guest) in the reaction mixture during the formation of all carceplexes is a critical prerequisite. In the absence of an appropriate template or in solvents that are too large to fit into the internal cavity, no carceplexes have been isolated. More importantly, the shell-closure process exhibits a high degree of selectivity when given a choice between two or more templates.

The acetal-bridged carceplexes shown in this slide which were prepared in remarkably high yields (up to 87%) from tetrol by bridging the two bowls with bromochloroalkanes in the presence of a suitable guest.



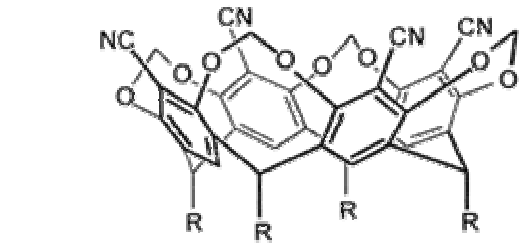
11•Guest n = 2 R = CH_2CH_2Ph
12•Guest n = 3 or $C_{11}H_{23}$



13•Guest R = $(CH_2)_4CH_3$

J. Am. Chem. Soc. 1991, **113**, 2194
J. Am. Chem. Soc. 1989, **111**, 4527

Carceplex can also be formed using transition metals to bring together the two halves (in the presence of the appropriate guest). An example of this has been reported by Dalcanale:



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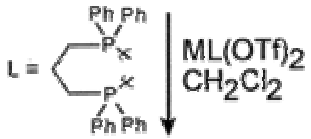
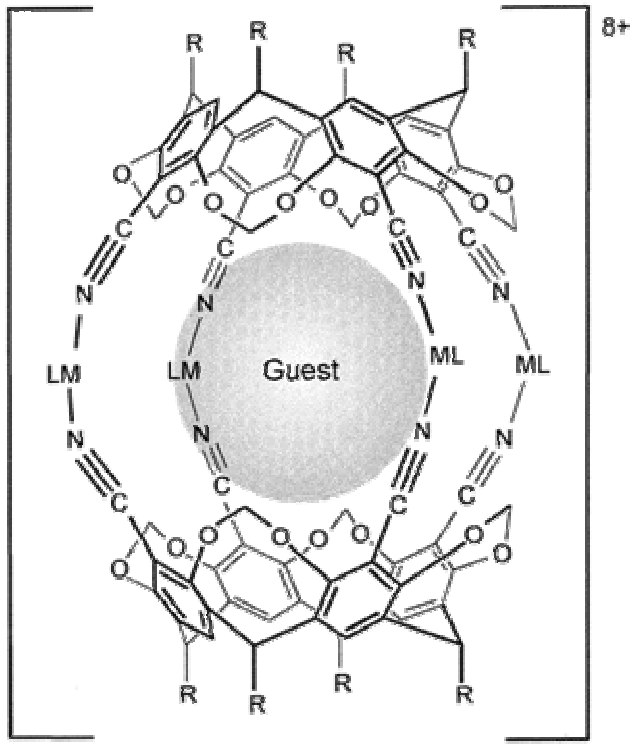




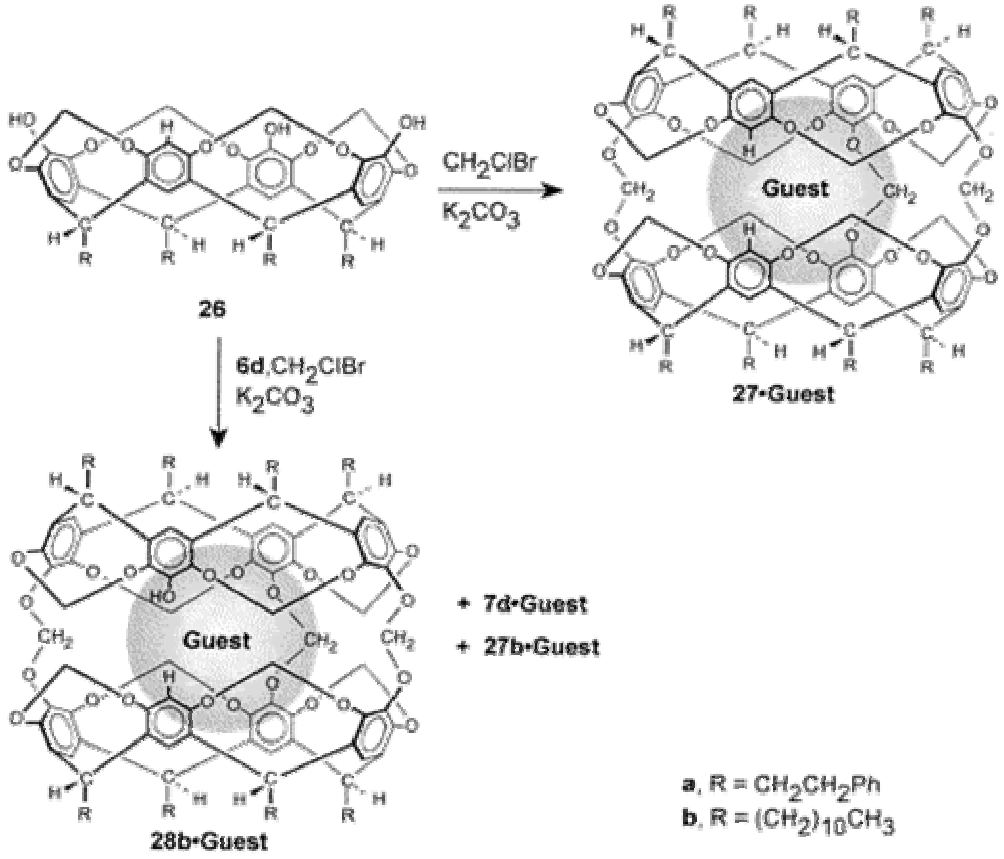
23•Guest

a M = Pd, R = $C_{11}H_{23}$
b M = Pt, R = $C_{11}H_{23}$
c M = Pd, R = C_6H_{13}

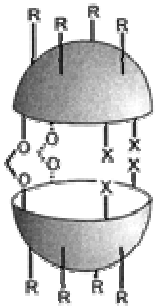
Angew. Chem., Int. Ed. Engl. 1997, **36**, 613

Hemicarcerands

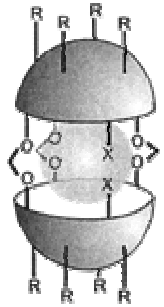
A *hemicarcerand* is a closed molecular container from which guests can enter and exit with a measurable activation barrier. In the presence of a guest species, hemicarcerands form hemicarceplexes.



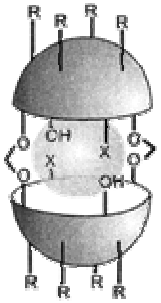
Recent examples of hemicarcerands include the direct synthesis of the pincer-like A,B-bis-bridged species and various tris-bridged derivatives.



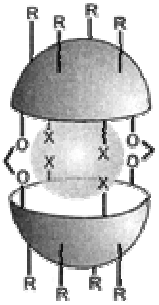
29a X = H
b X = OH
c X = OMe



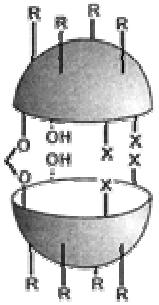
30a X = OMe
b X = OEt
c X = OBn
d X = OH



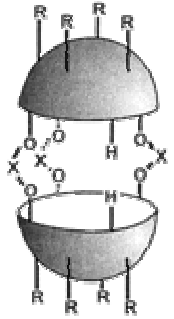
31a X= H
b X = OMe
c X = OEt



32a X = H
b X = OH



33a X = OH
b X = OMe

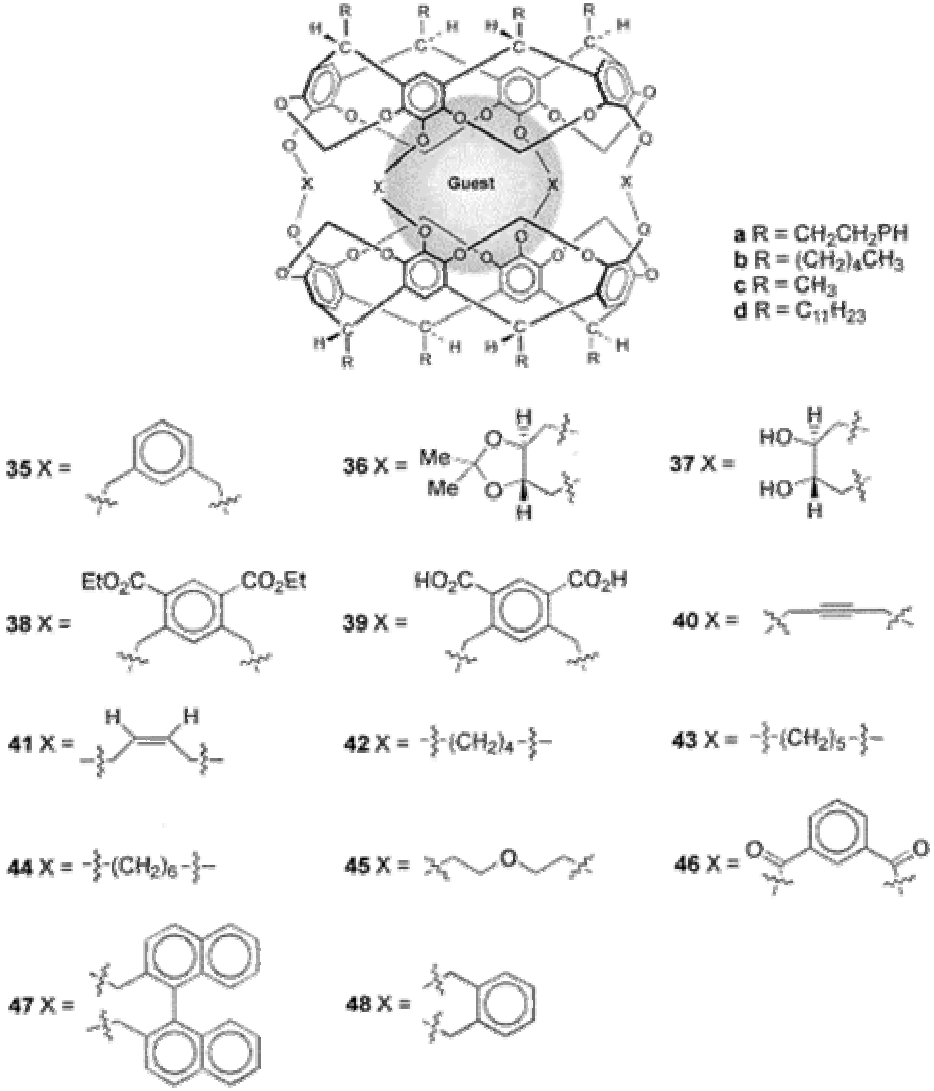


34a X = CH_2CH_2
b X = $CH_2CH_2CH_2$
c X = 1,2-$(CH_2)_2C_6H_4$

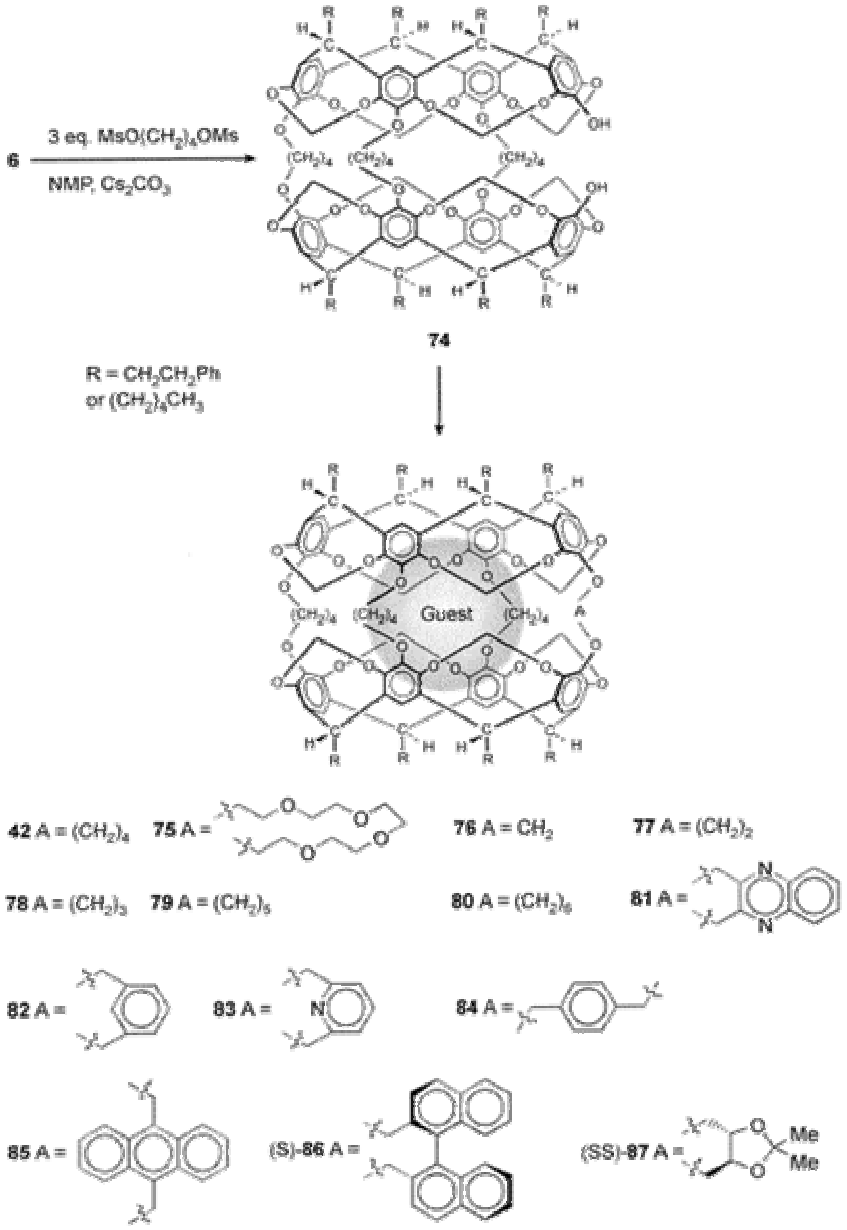
R = $C_{11}H_{23}$, CH_3, or CH_2CH_2Ph
Guest = DMSO, DMA or DMF

An alternative and more widely adopted approach to hemicarceplexes relies on expanding the distance between the two bowls by varying the interhemispheric linkers of a carceplex.

This approach generates cavities of various shapes and sizes; guests molecules can go through the relatively large spaces left between the portals.



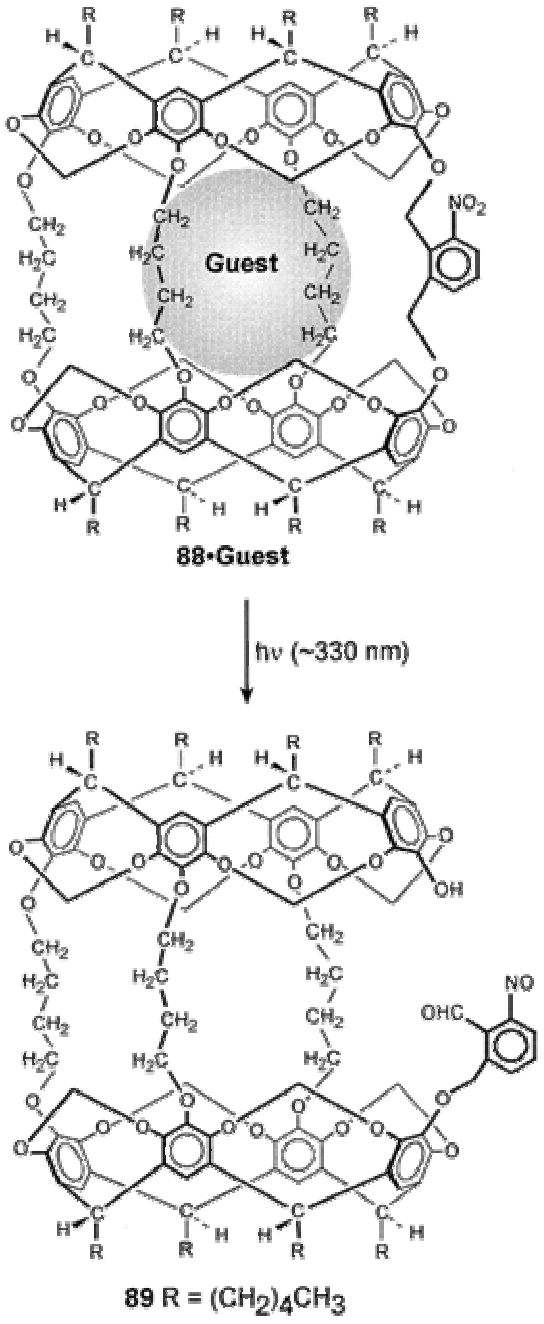
By careful choice of the experimental conditions it is possible to prepare dissymmetric hemicarcerands. These species are very attractive since they allow to tune the binding abilities of the container.



Cram, *J. Org. Chem*. 1996, **61**, 9323
Cram, *J. Am. Chem. Soc*. 1997, **119**, 11796

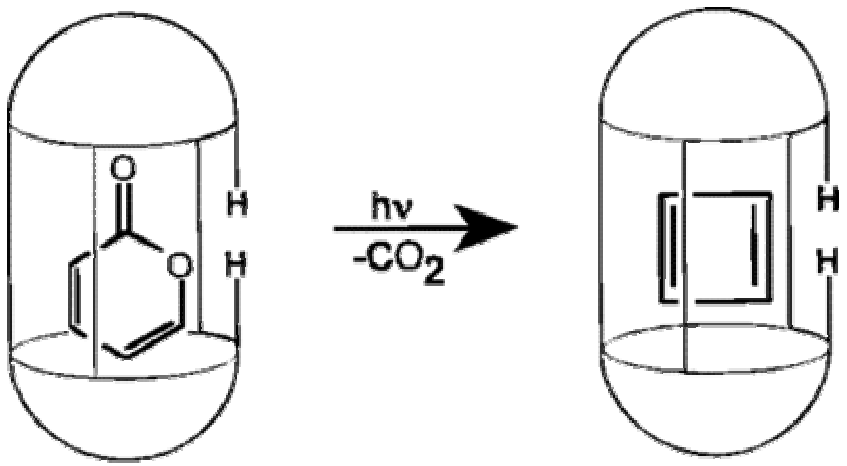
Dashaye has reported a series of hemicarceplexes which undergo bond cleavage at the adjacent benzylic position upon irradiation with UV light.

The rate of guest release for both complexes is linearly dependent on light intensity.



Deshayes, *Angew. Chem., Int. Ed. Engl*. 1998, **37**, 970

The internal cavity of hemicarceplexes represents a unique nanochamber within which novel chemical reactions may be explored. Unfortunately, due to the highly effective shielding ability of the shell's superstructure, the chemistry inside this chamber has largely been relegated to photochemical processes and reactions with small reactants that can readily traverse the portals. An elegant example of this is the stabilisation of cyclobutene reported by Cram:

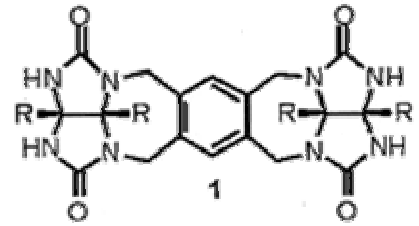


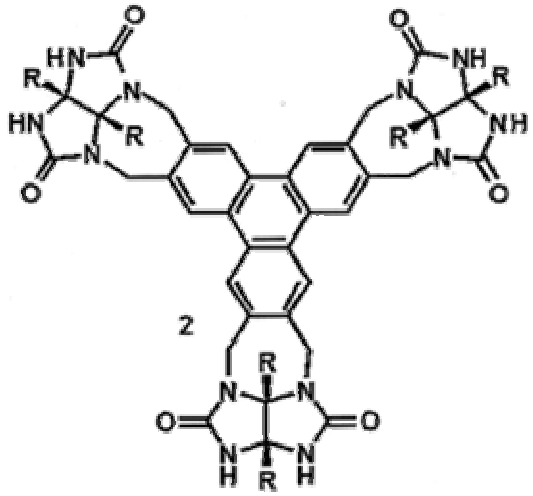
27a•α-pyrone

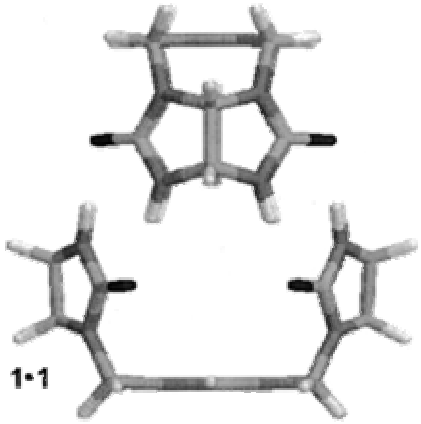
Cram, *Angew.Chem.Int.Ed.*, 1991, **30**, 1024

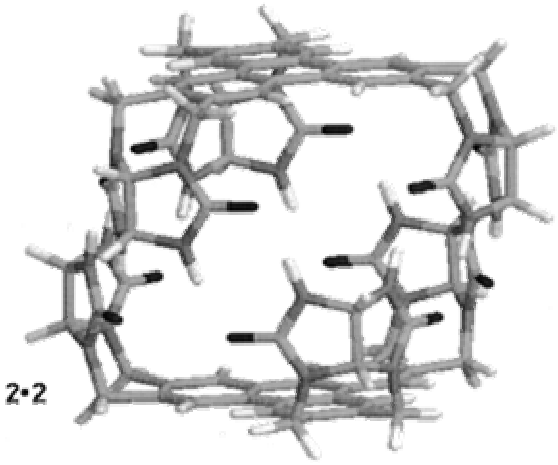
Self-assembling capsules

Another way of generating closed spherical molecules and capsules is by self-assembling two half-species by hydrogen bonding.

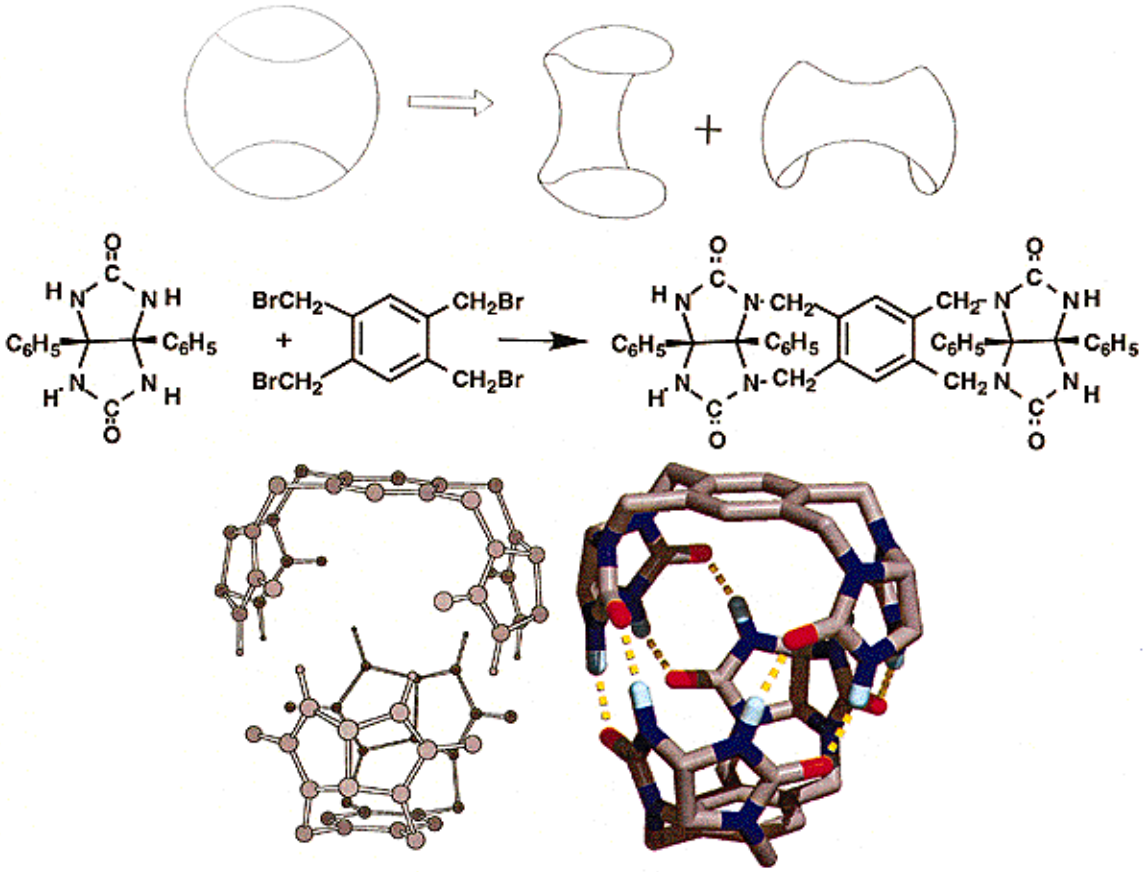






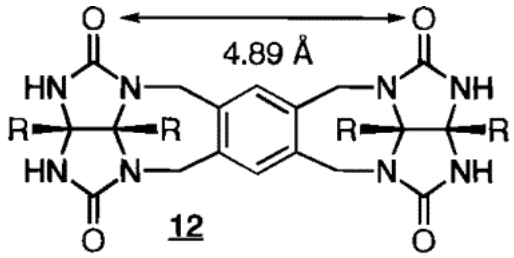


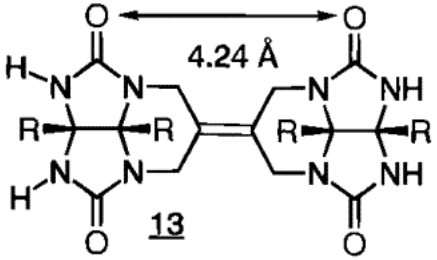
Over the last decade, Rebek has demonstrated that by using two mutually complementary curved building block it is possible to prepare hollow capsules (e.g. with the shape of a tennis ball):

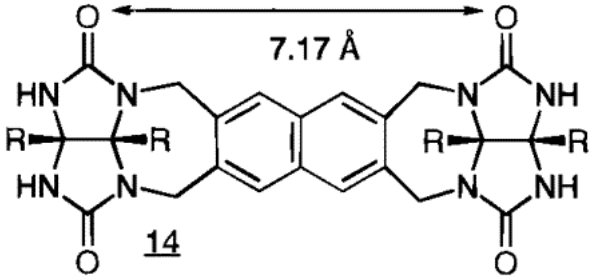


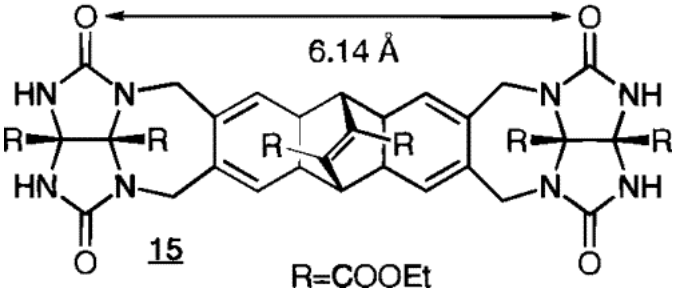
Rebek, *Acc.Chem.Res.*, 1999, **32**, 278

The length of the spacer allows to prepare cavities of different sizes. Such cavities can encapsulate selectively specific species. In some cases, this can lead to selective reactivity.

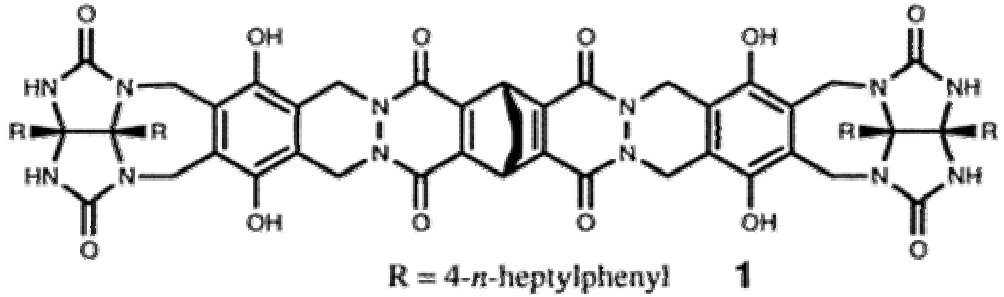




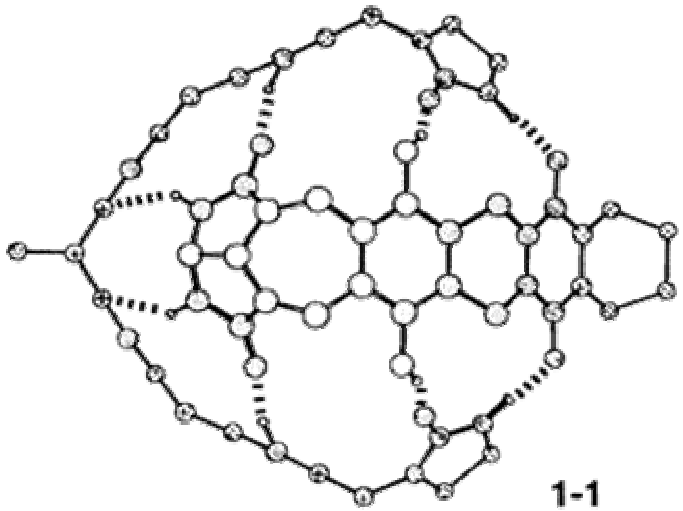




Rebek has demonstrated that this concave species self-assembles into a large cavity (a “soft-ball”) and which can encapsulate various organic species::



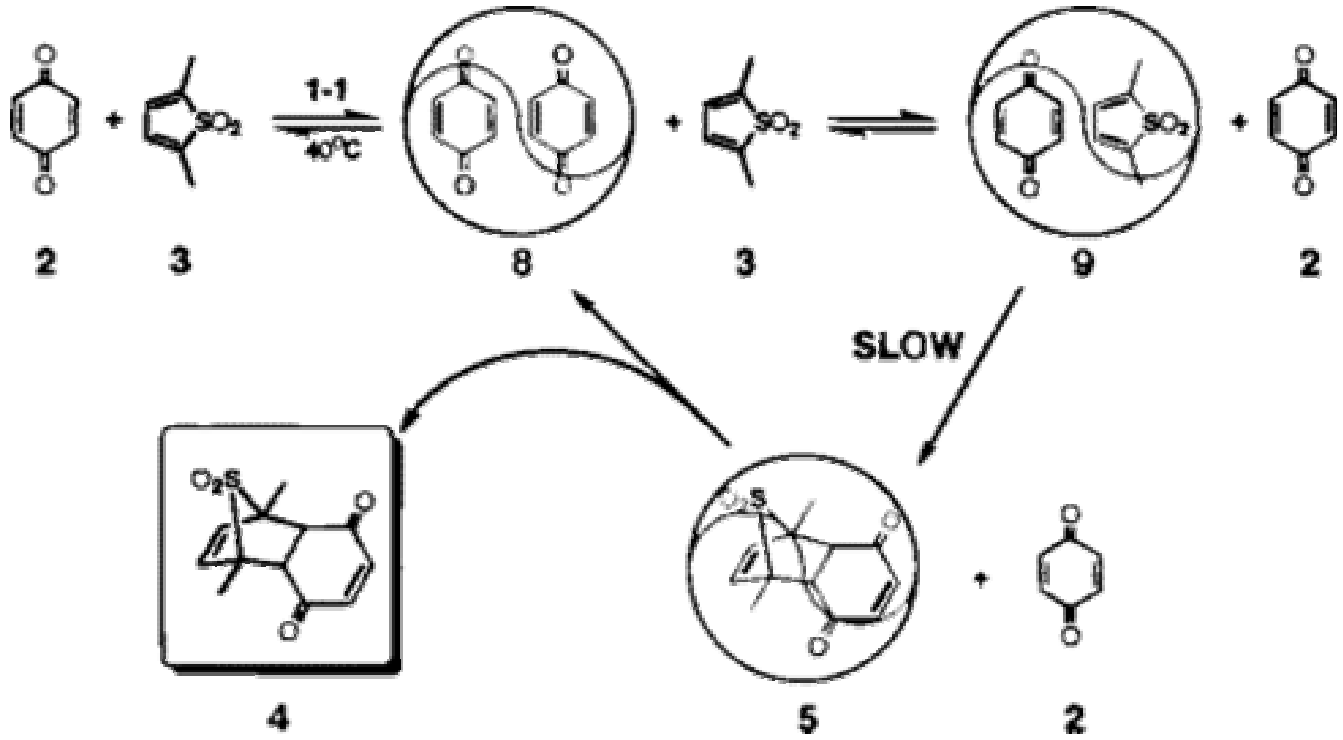
R = 4-*n*-heptylphenyl **1**



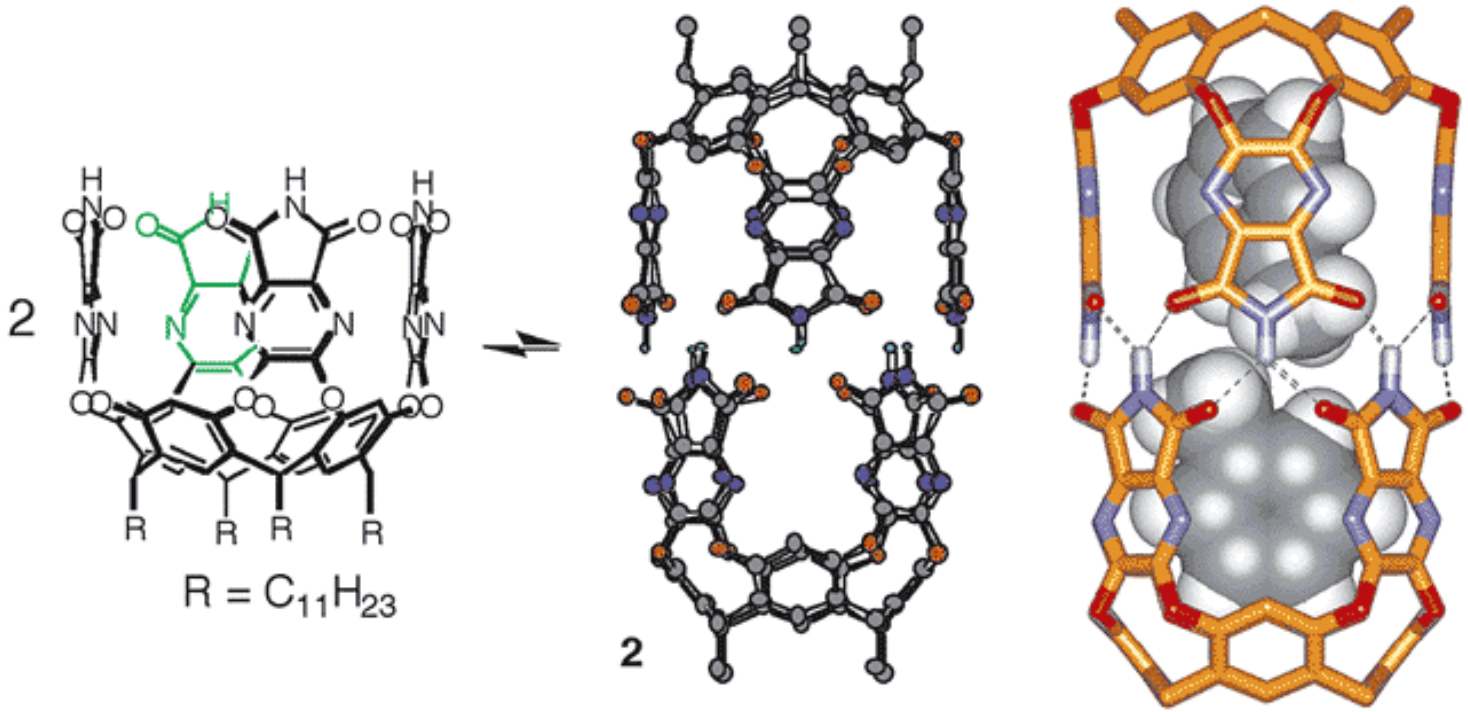
1-1

Rebek, J. Am. Chem. Soc., 1998, **120**, 7389

By encapsulating the appropriate species, it is possible to carry out a Diels-Alder reaction inside the cavity:

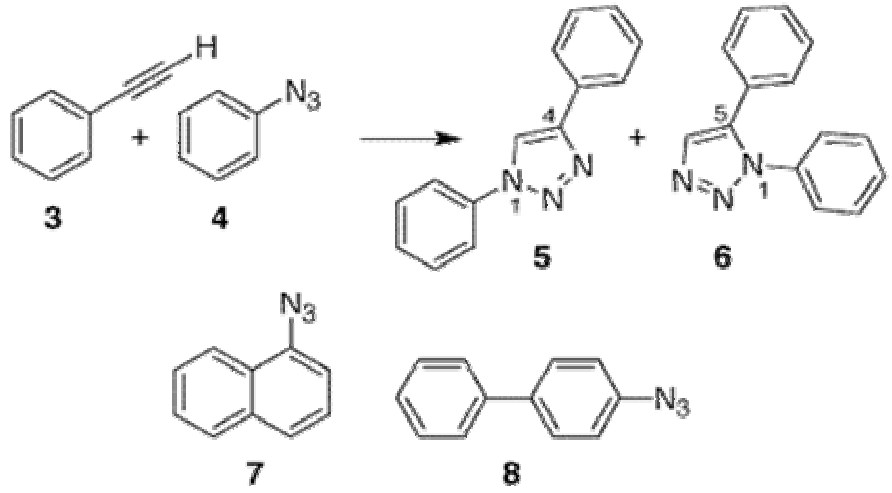


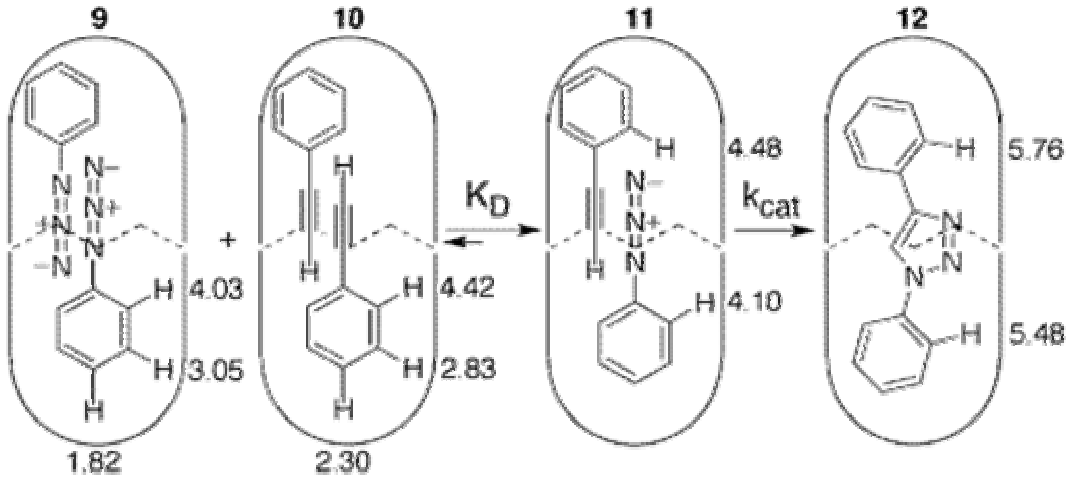
More recently Rebek has demonstrated that the capsule shown in this slide can be used as a selective nano-reactor for cycloaddition reactions:



Rebek, *Org. Lett.*, 2002, **4**, 327

The cycloaddition reaction shown in this slide gives, under normal conditions, a mixture of the two producs (5 and 6 in the scheme). However, in the presence of the capsule one of the products is favoured.



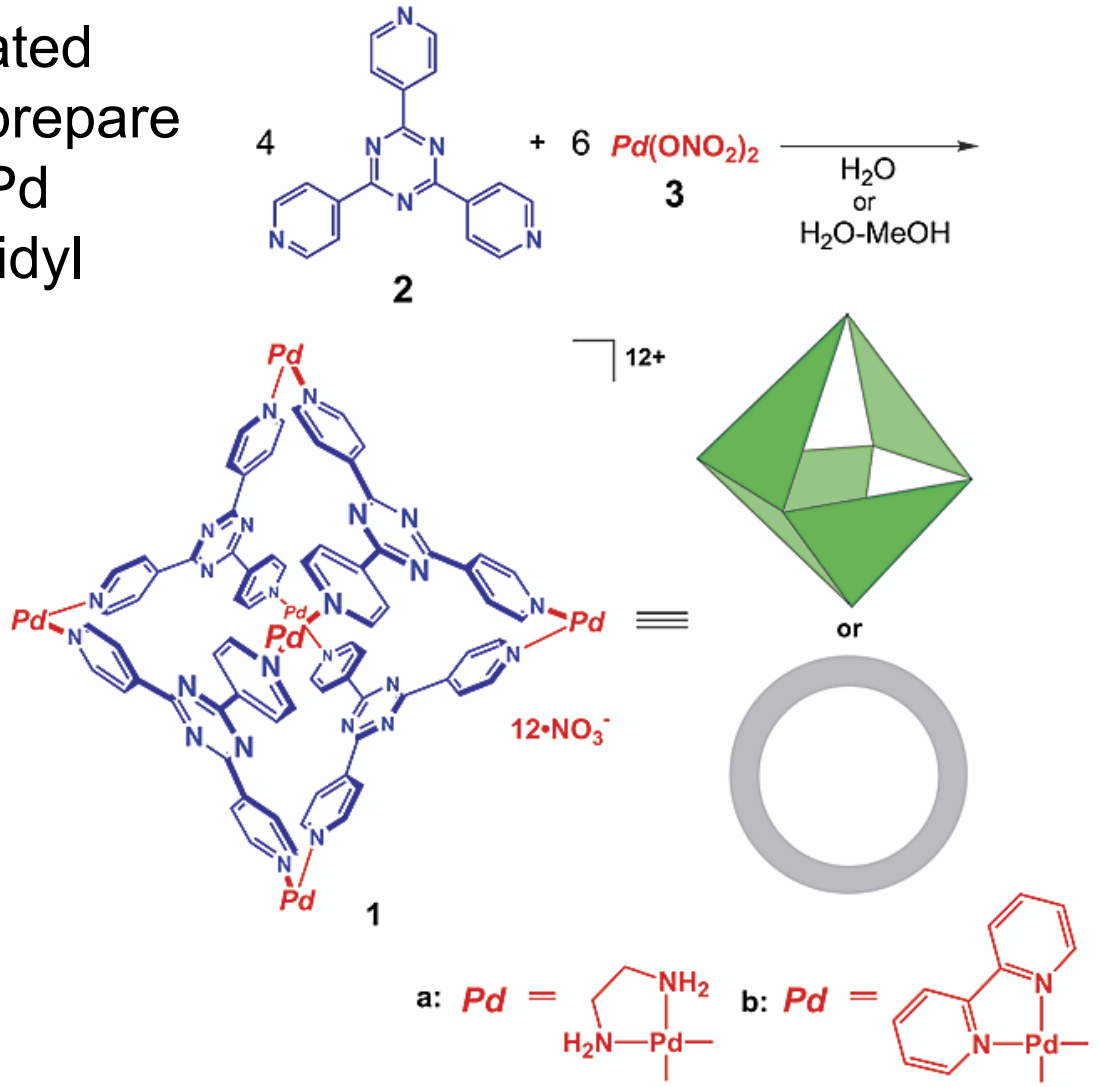


Metalla-cages and capsules

During the previous lecture the use of metals for the synthesis of cages and macrocycles has already been discussed. The pioneering work by Stang and Fujita has demonstrated that it is possible to control such self-assembling processes and prepare cages with large cavities.

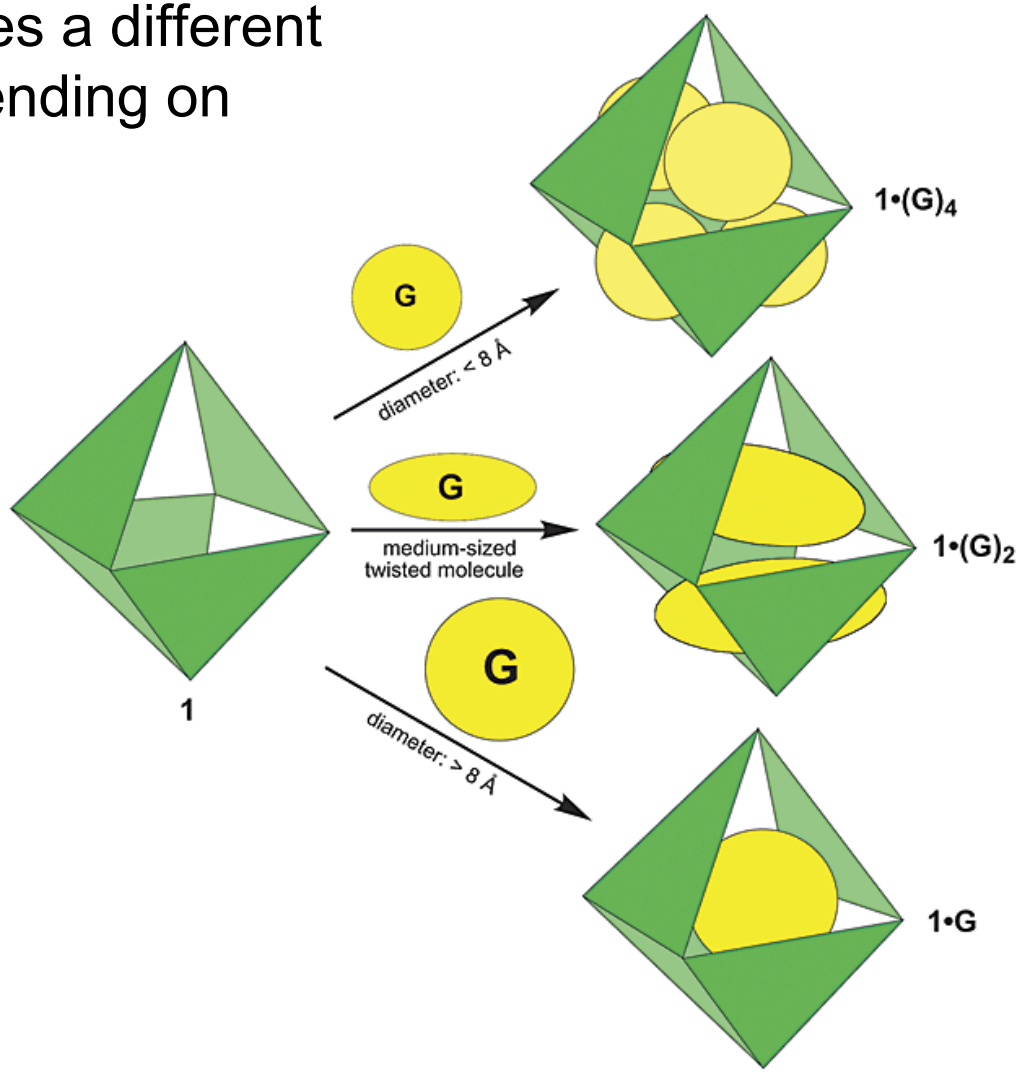
The synthetic strategies to such cages have been already Discussed (see notes fro lecture 3). In this section some examples where organic species are encapsulated in such large cavities will be presented. Such encapsulated species are in a different environment and, consequently, their reactivity can be modified.

Fujita has demonstrated that it is possible to prepare large cavities using Pd centres and poly-pyridyl ligands.



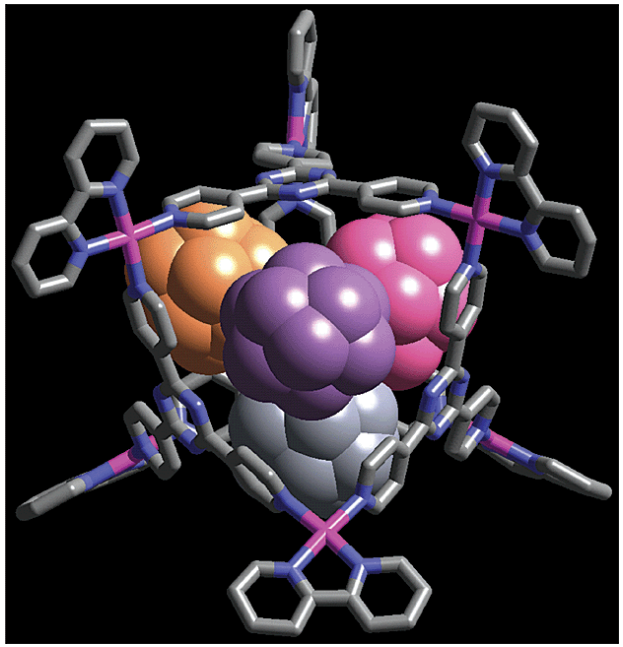
Fujita, *J. Am. Chem. Soc.*, 2002, **124**, 13576

Such cage encapsulates a different number of guests depending on their size:

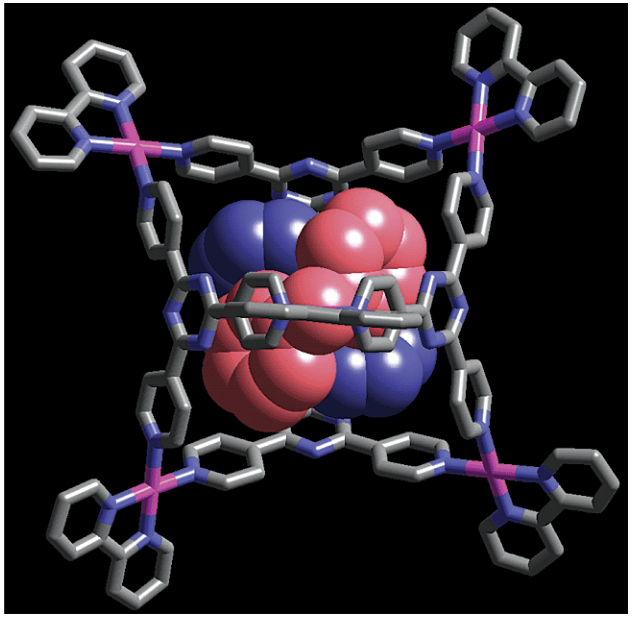


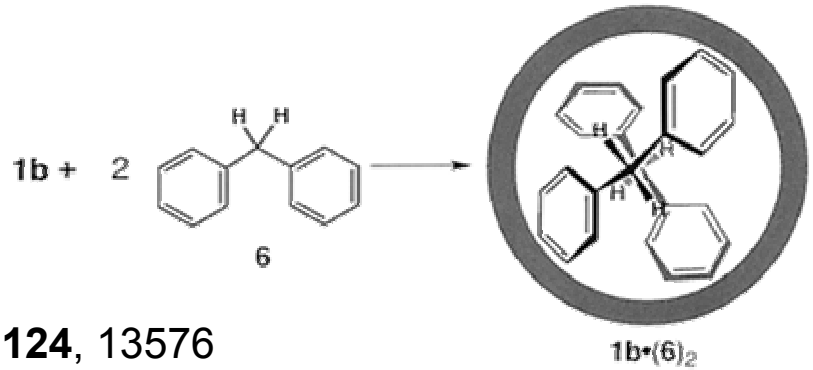
Fujita, *J. Am. Chem. Soc.*, 2002, **124**, 13576

Enclathration of spherical guest molecules: 1:4 complexation



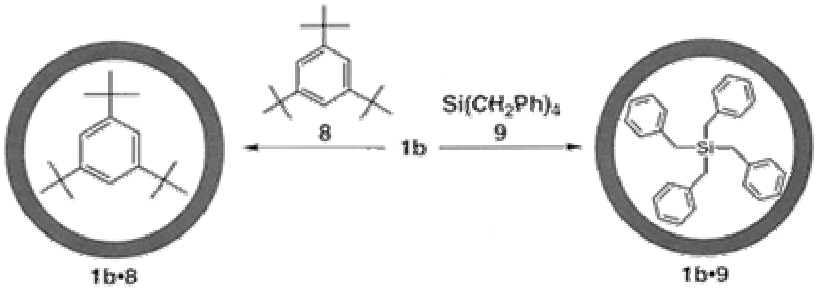
Enclathration of medium bending molecules: 1:2 complexation

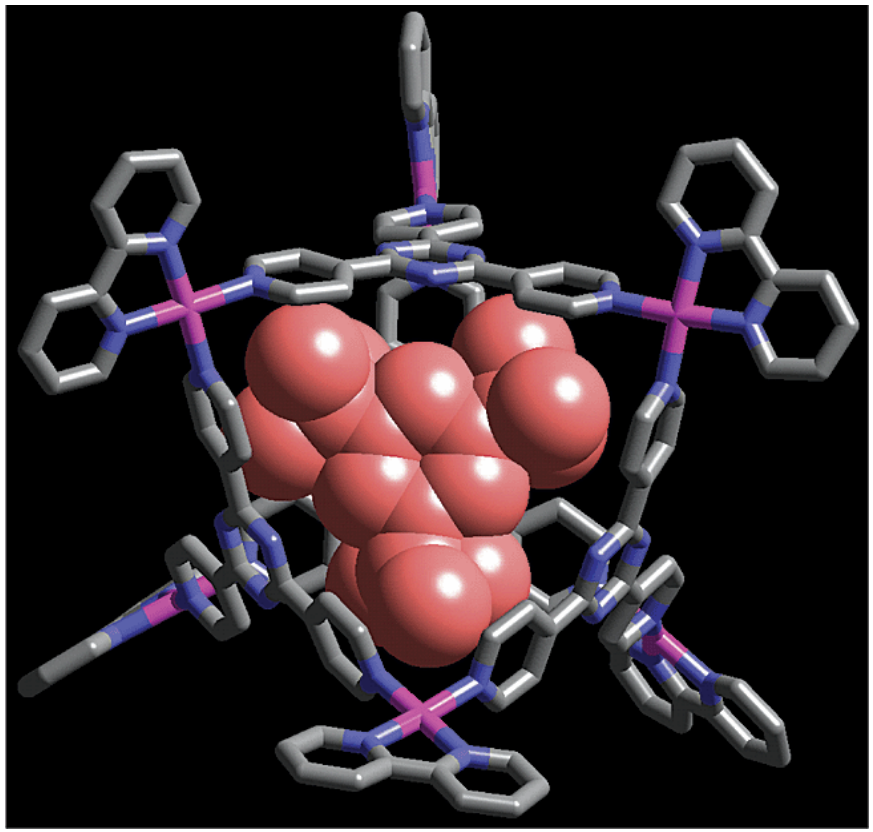




Fujita, *J. Am. Chem. Soc.*, 2002, **124**, 13576

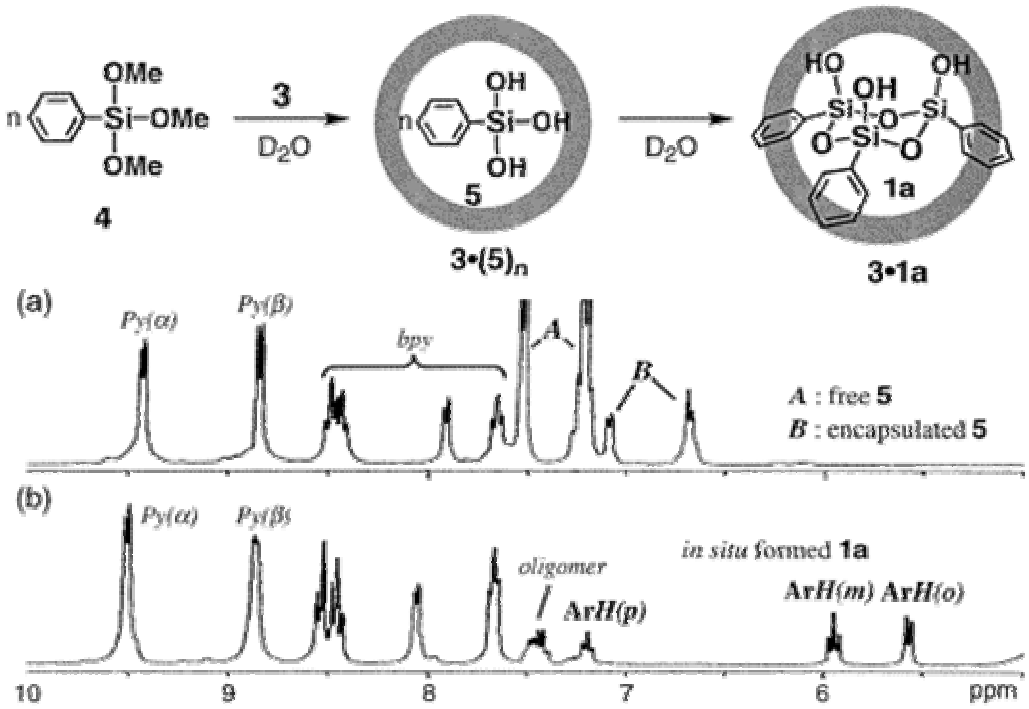
Enclathration of guest molecules that are larger than the portals of the cage: 1:1 complexation



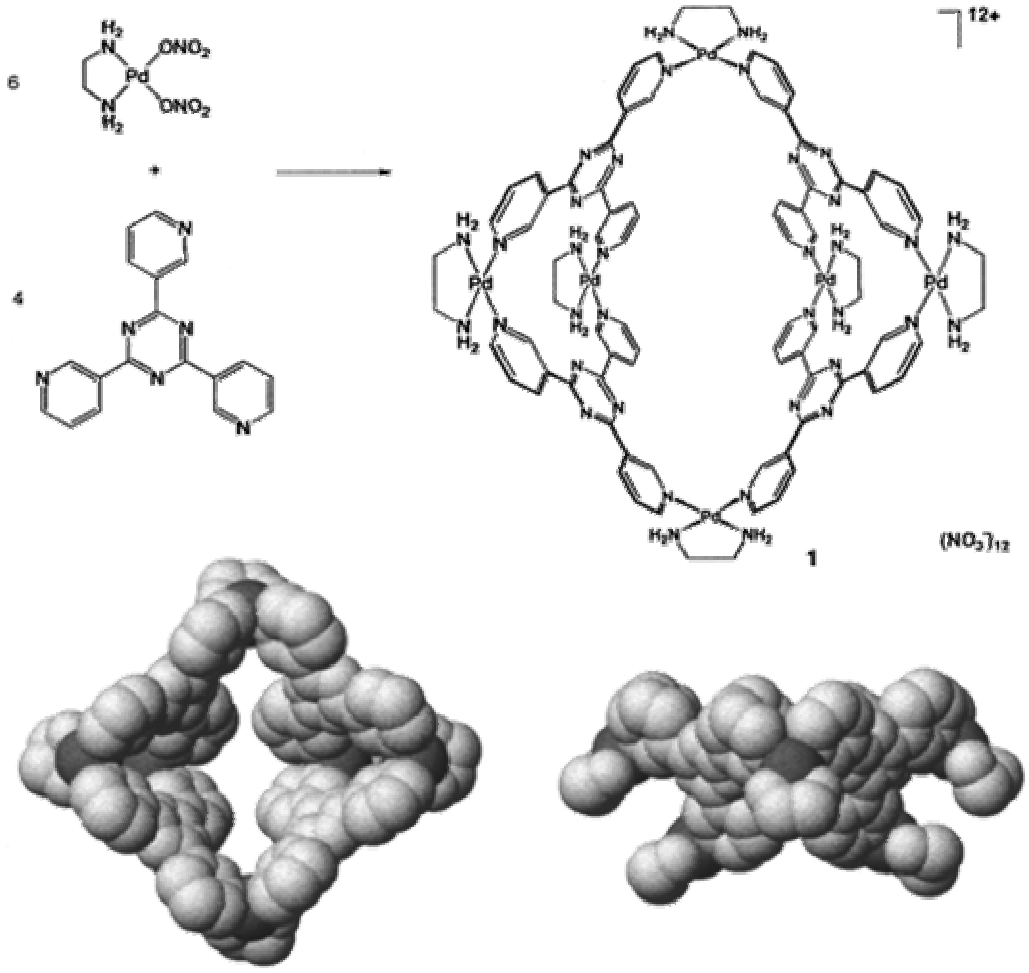


Fujita, *J. Am. Chem. Soc.*, 2002, **124**, 13576

Molecular capsules provide isolated microspace within the molecules where otherwise labile species are protected and can be considerably stabilized. The labile molecules are most effectively trapped in the capsules if they are prepared *in situ* from smaller components coming through small openings of the capsules.

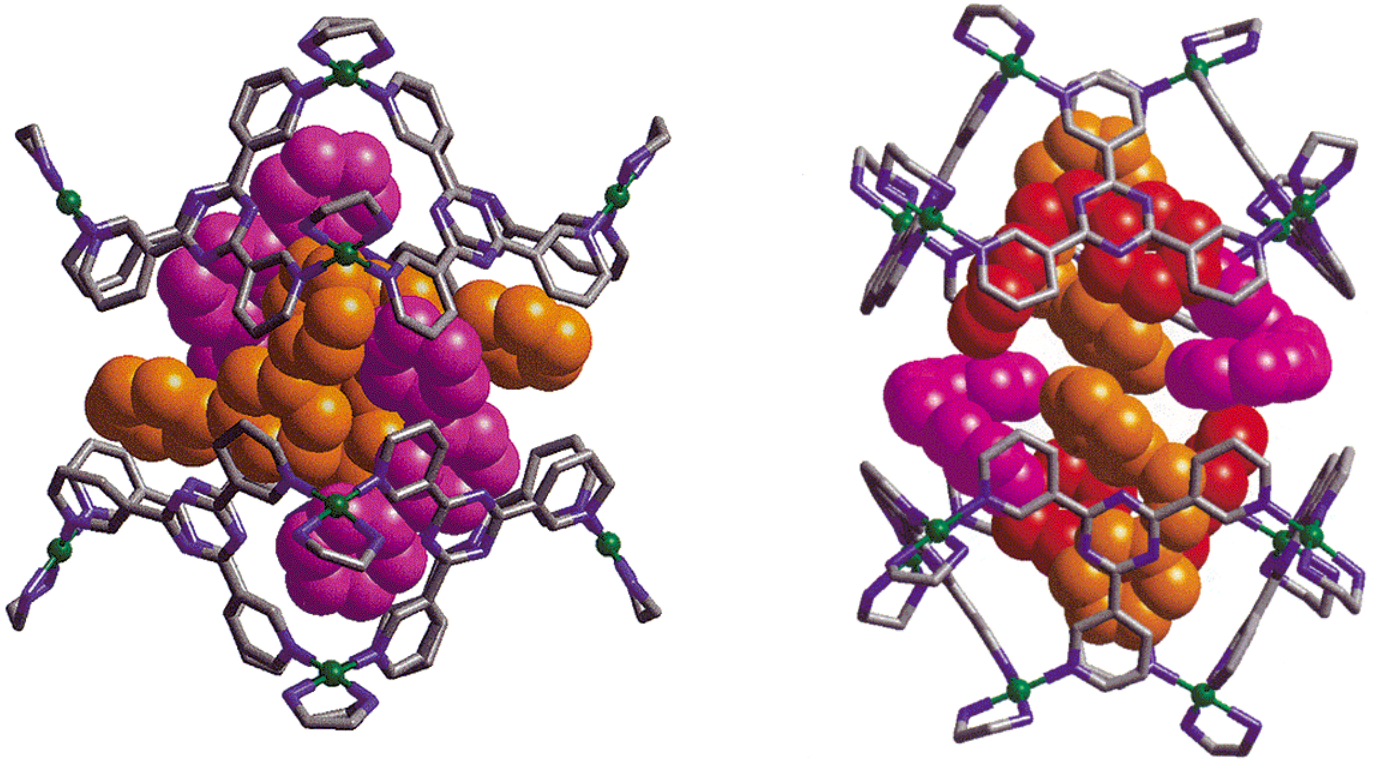


Fujita et al, *J. Am. Chem. Soc.*, 2000, **122**, 6311



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

The hydrophobic cavity of the capsule formed can trap neutral guests:



M. Fujita et al., *J. Am. Chem. Soc.*, 2000, **122**, 2665