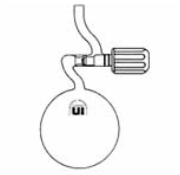
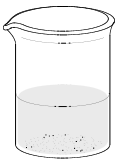
Medium Matters





Gas phase

Solution
(solvent + solute)

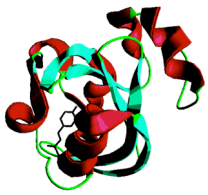
Rhodopsin

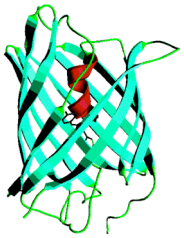
Increasing selectivity

How do biological media enforce selectivity?

1

Highly selective geometric isomerization occurs within a protein medium





Rhodopsin

Bacteriorhodopsin

Photoactive
yellow protein

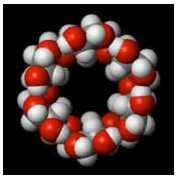
Green fluorescent
protein

How do a biological media enforce selectivity?

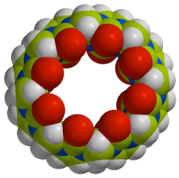
- by restricting the rotational and translational motions
- by pre-organizing the reactants
- by controlling the extent and the location of free space within a reaction cavity

2

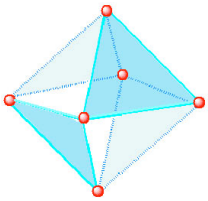
Water Soluble Hosts as Confined Media



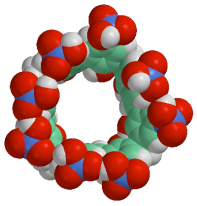
Cyclodextrins



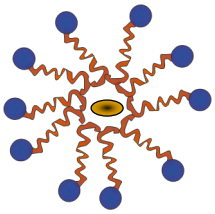
Cucurbiturils



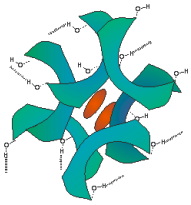
Pd Nano Cage



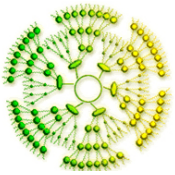
Calixarenes



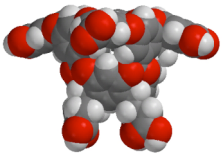
SDS / CTAC



NaCh / NaDCh



Dendrimers



Octa acid

3

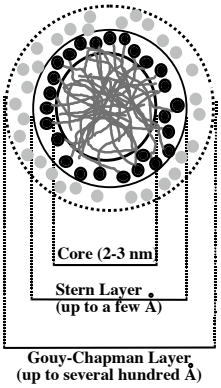
- Ability to solubilize substrates in water
- Weak interactions
- Confinement

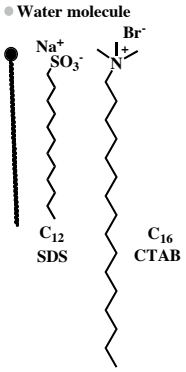
How can we achieve such a high level of selectivity in photochemical reactions in a laboratory?

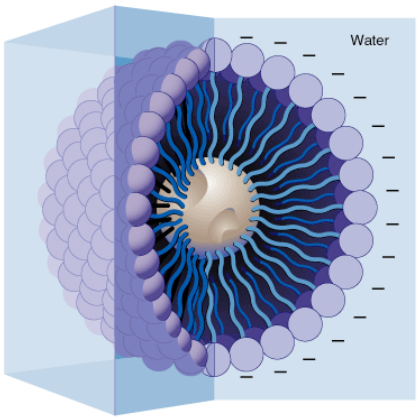
Are there any other media with some of the features of biological media?

4

Cartoons of micelle structure

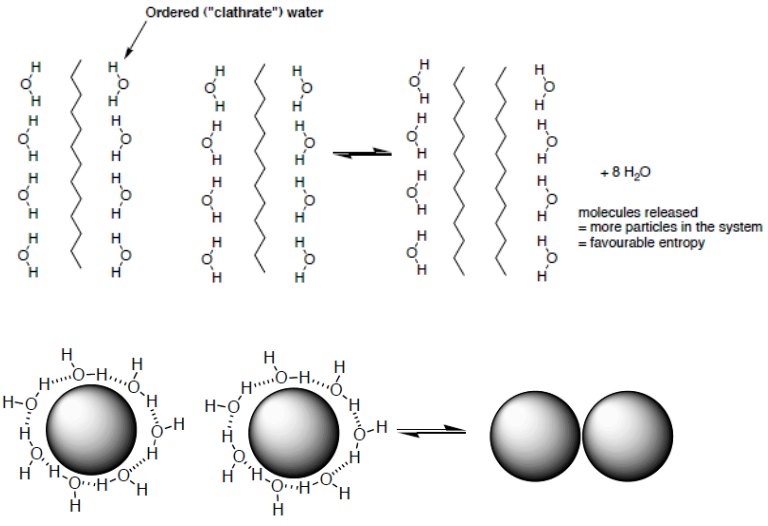






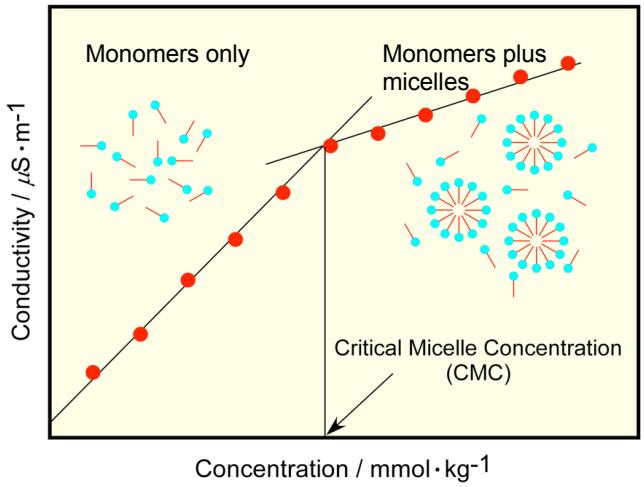
5

Why do micelles form at all?



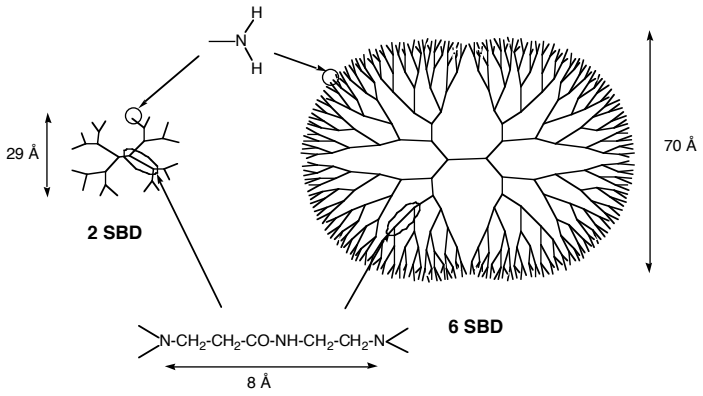
6

The critical micelle concentration phenomenon: Sudden break in properties near a certain concentration of surfactant



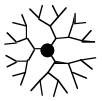
7

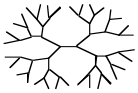
Dendrimers: Macromolecules as micelles



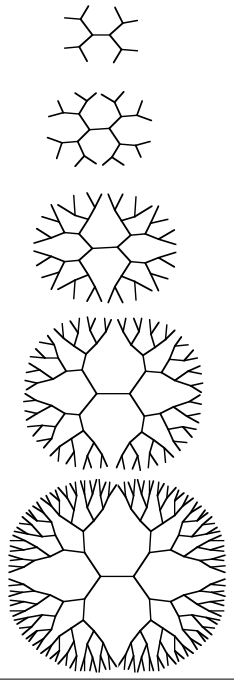
8

Generations of dendrimers



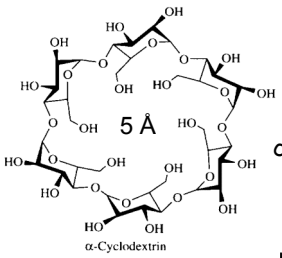


generation	surface groups	diameter (Å)	separation of the surface groups (Å)	surface groups
0.5	6	27.9	12.4	8
1.5	12	36.2	12.8	16
2.5	24	48.3	12.7	32
3.5	48	66.1	12.6	64
4.5	96	87.9	11.5	128
5.5	192	103.9	10.3	256
6.5	384	126.8	9.8	512
7.5	768	147.3	7.7	1024



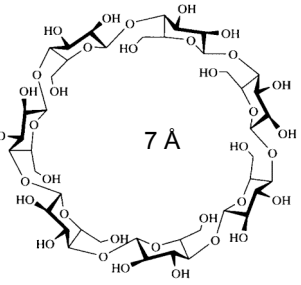
9

Water soluble organic hosts: Cyclodextrins

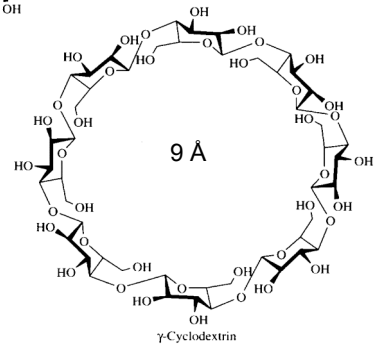


α-Cyclodextrin

D-glucopyranoside units connected into a cycle via 1,4-glycosidic linkages

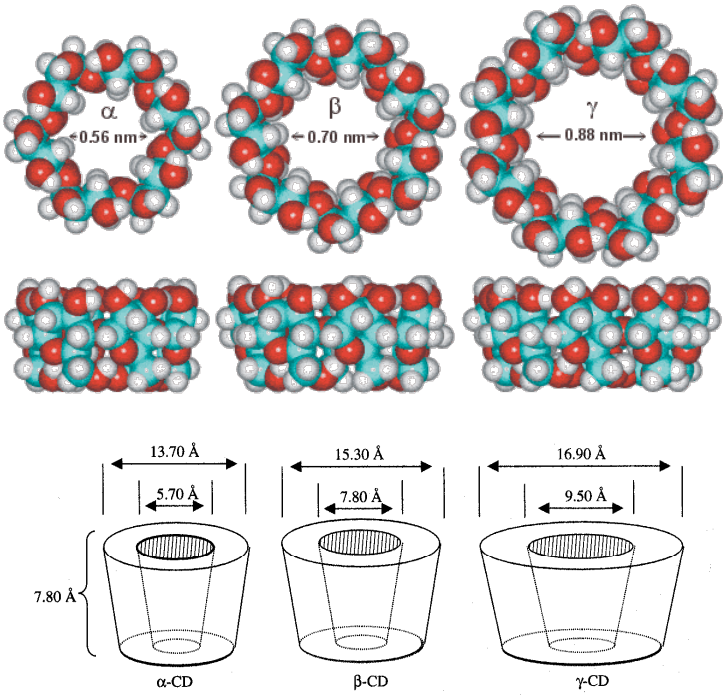


β-Cyclodextrin



γ-Cyclodextrin

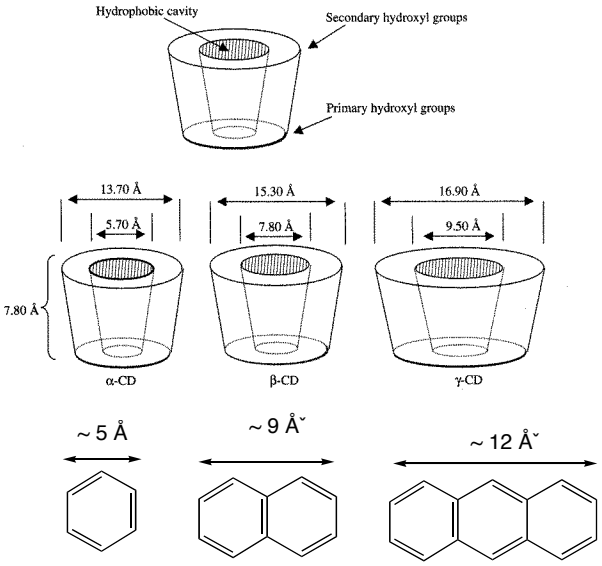
10



11

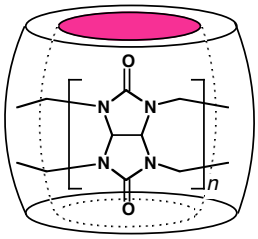
Cyclodextrins as supramolecular hosts

Cyclodextrin



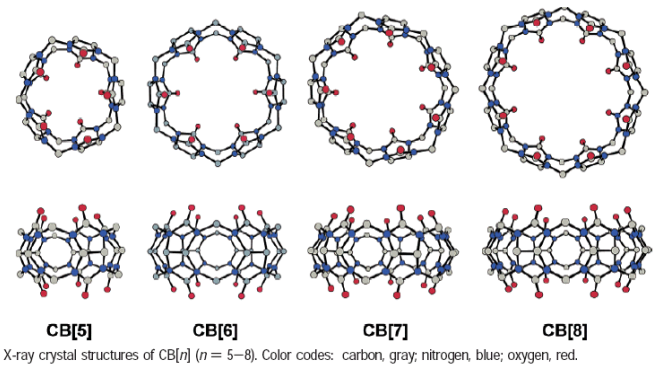
12

Water soluble organic hosts: Cucurbiturils



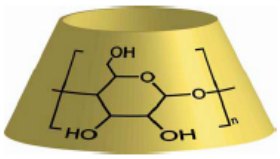
- Easily prepared by the condensation of glycoluril in acidic medium.
- Hexamer [CB6] known since early 1900's, first characterized in 1981.
- Kim and coworkers pioneered the synthesis and isolation of the higher CBs [*n* = 7, 8, 10] in 2000.

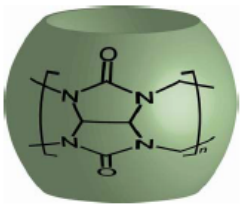
13



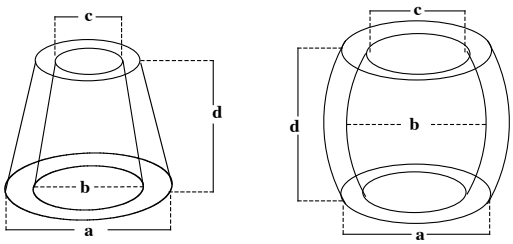
CB[5] CB[6] CB[7] CB[8]

X-ray crystal structures of CB[*n*] (*n* = 5–8). Color codes: carbon, gray; nitrogen, blue; oxygen, red.





14

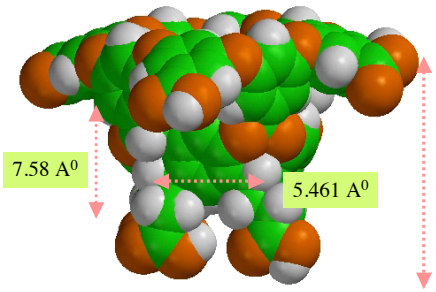


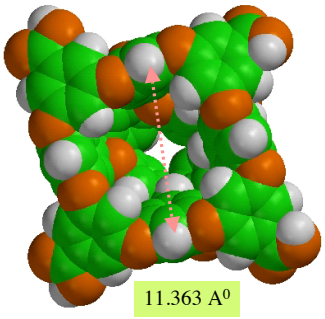
Cavity	a (A°)	b (A°)	c (A°)	d (A°)	Volume (A°^{3})
CB[6][b]	14.4	5.8	3.9	9.1	164
α–CD[a]	14.6	5.2	4.7	8.0	174
CB[7][b]	16.0	7.3	5.4	9.1	279
β–CD[a]	15.4	6.4	6.0	8.0	262
CB[8][b]	17.5	8.8	6.9	9.1	479
γ–CD[a]	17.4	8.3	7.5	8.0	472

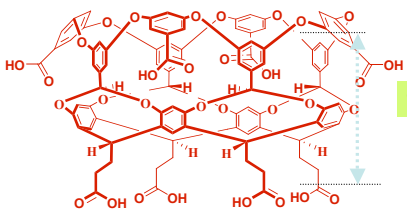
a) Szejtli, J. *Chem. Rev.*,**1998,** 98 (5), 1743 -1754,
b) Lee, J. W., Samal, S.; Kim, K., *Acc. Chem. Res.* (2003), 36(8), 621-630

15

Water soluble organic host: Octa Acid



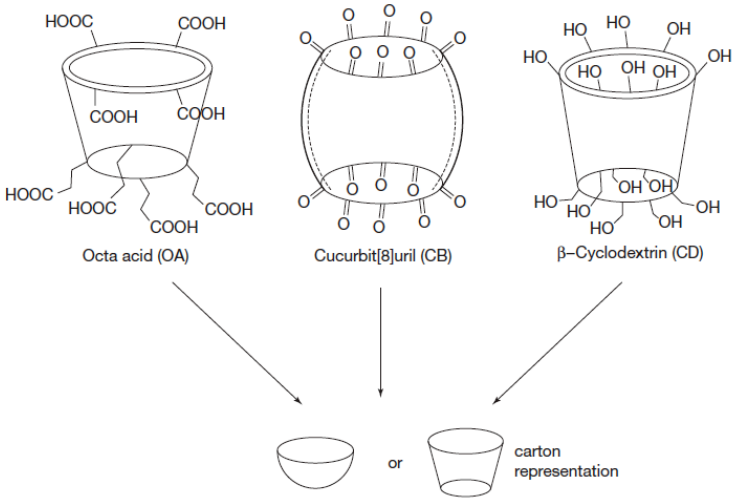




Soluble in sodium tetraborate buffer solution (10mM)-pH > 9

16

Octa acid (OA), Cucubituril (CB) and Cyclodextrin (CD) A comparison



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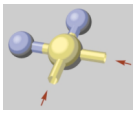
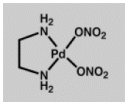
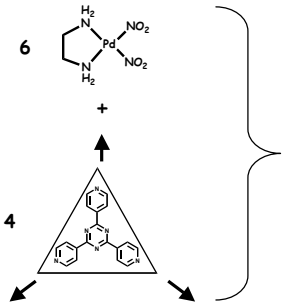
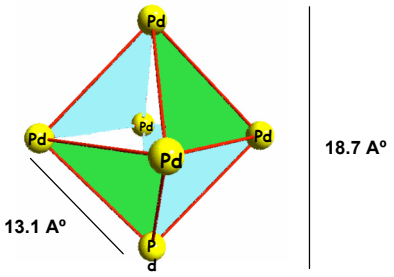
Water soluble inorganic host: Fijita's Pd host

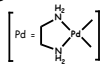






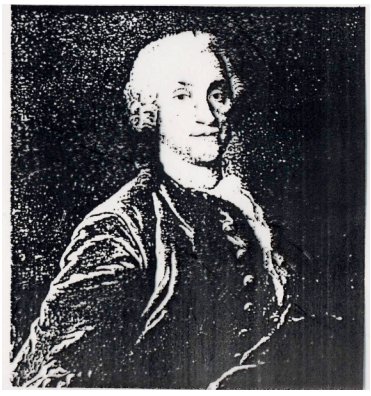


M_6L_4 Octahedral cage



18

Discovery of zeolites



Baron Cronstedt 1722-1765

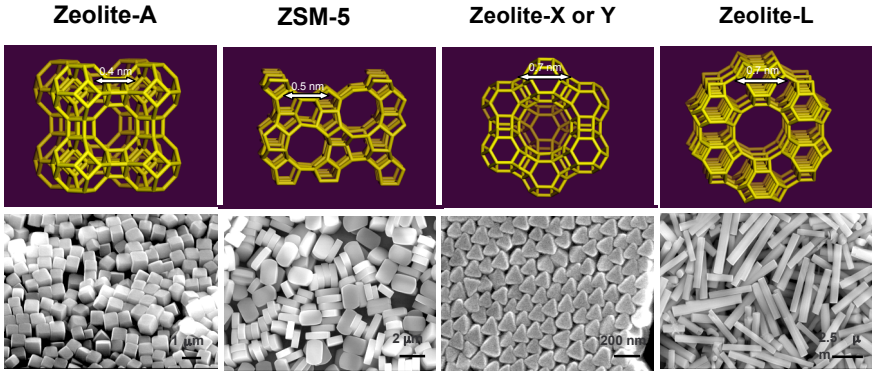
A zeolite, as found in Nature

Cronstedt discovered "boiling stones" which he called "zeolites" from the Greek: zeo (boil) and lithos (stone).

19

Zeolites: Sythetic

More than 65% of the earth's crust consists of 3D crystalline polyaluminosilicates (3D-CPAS): feldspar, zeolite, and ultramarine. Zeolite is a class of 3D-CPAS having nanochannels and nanocavities.



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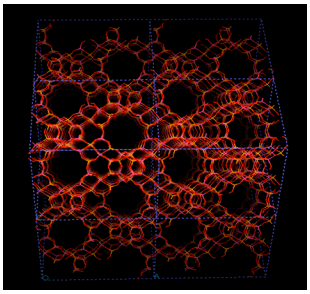
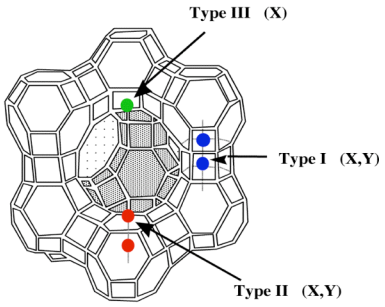
21

Characteristics of Faujasites (Zeolites)

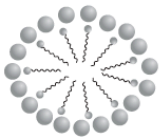
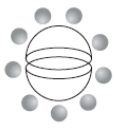
$M_x(AlO_2)_x\,(SiO_2)_y.ZH_2O$





- Microporous solid
- Large surface area
- Well defined channels/cages
- Si/Al ratio = 2.4
- Type I - 4 cations /supercage
- Type II- 4 cations /supercage

Nomenclature of elementary supramolecular hosts

Name of Host	Definition (Refers to the Host)	Schematic Structure (Large Spheres Represent Solvent)
Micelle	An assembly of small molecules, held together by noncovalent bonding that can completely surround a small guest molecule. Examples: sodium dodecyl sulfate (SDS), hexadecyl trimethyl ammonium chloride (HDTCl) (Sections 13.16 and 13.21)	
Cavitand	A molecule possessing a structurally intrinsic permanent cavity that can contain a small guest molecule by partially surrounding it. Examples: cyclodextrins (CDs) and cucurbiturils (CBs) (Sections 13.10 and 13.16)	
Capsule	An assembly of two cavitands that can structurally organize noncovalently to completely surround a small molecule. Examples: CD and octa acid (OA) (Sections 13.10, 13.11, 13.14, and 13.16)	

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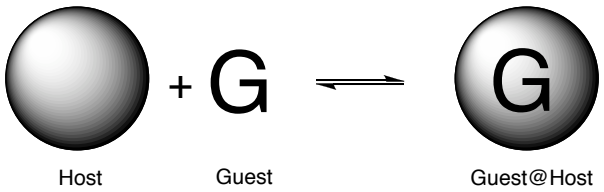
The enzyme guest@host paradigm



We'll be using this paradigm to discuss supramolecular systems

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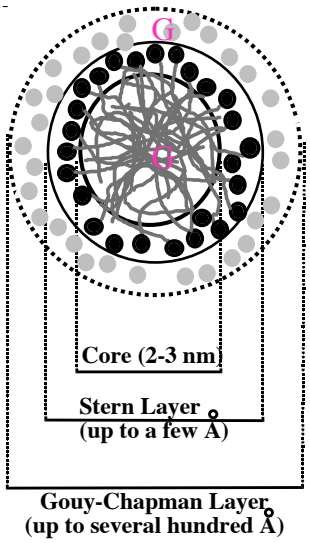
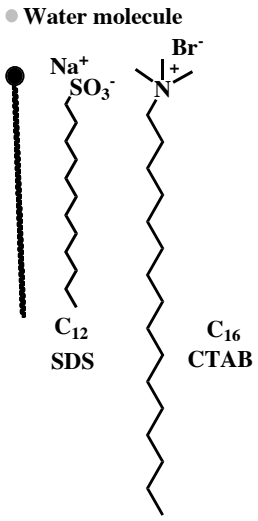
Schematic representation of a guest@micelle complex



Surfactant monomers



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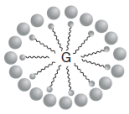
Nomenclature of elementary supramolecular guest@host complexes

Name of guest@host Complex	Definition (Refers to Solution)	Schematic Structure (Large Spheres Represent Solvent)
Micelleplex	Guest@micelle complex. Examples: DBK@SDS (DBK = dibenzyl ketone), cylopentenone@deconate	
Cavitandplex	Guest@cavitand complex. Examples: cinnamic acid@CB	
Capsuleplex (Hemicapsulplex)	Guest@capsule complex. Examples: DBK@OA_2, $anthracene_2$@OA_2	
Hemicarceplex	Guest@carcerand complex (portals are large enough for guests to exit (ex) or enter the host cavity). $k_{ex} > k_{photo}$ Examples: biacetyl@Cram's carcerand	
Carceplex	Guest@carcerand complex (portals are too small for guest to exit or enter the host cavity). $k_{ex} < k_{photo}$ Examples: cyclobutadiene@Cram's carcerand	

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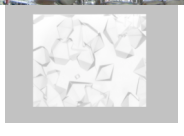
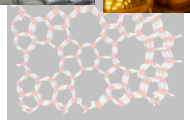
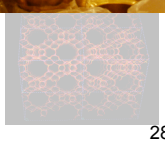
Container Store





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Container Store

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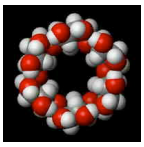
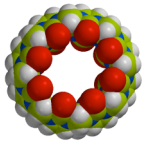
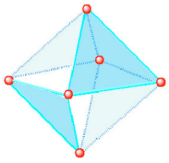
Supramolecular Containers



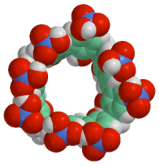
Cyclodextrins



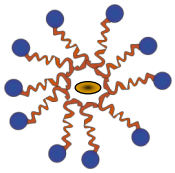
Cucurbiturils



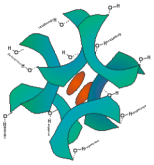
Pd Nano Cage



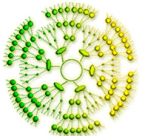
Calixarenes



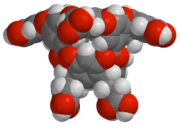
SDS / CTAC



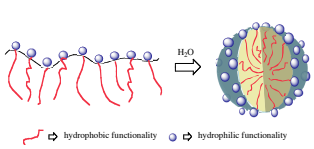
NaCh / NaDCh



Dendrimers

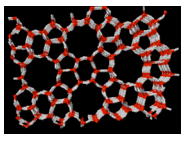


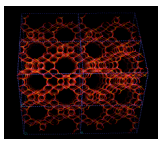
Octa acid



Water soluble polymer

Crystals





Zeolites

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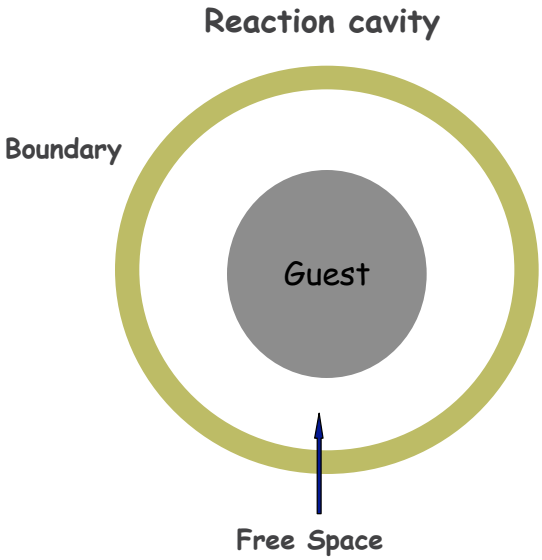
Supramolecular Containers



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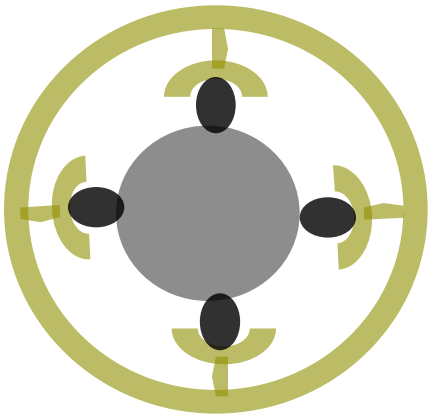
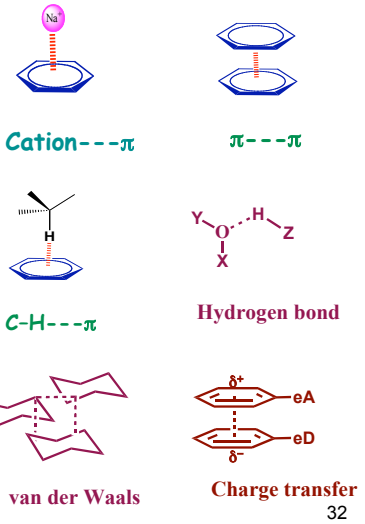
Role of Weak Interactions





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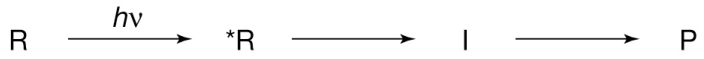
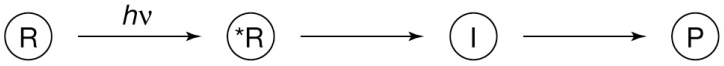
Molecular and Supramolecular Organic Photochemistry

Molecular organic photochemistry



Supramolecular organic photochemistry



R represents a guest molecule. The circle represents a host molecule.

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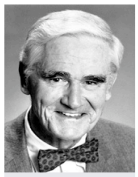
The beginnings of supramolecular organic chemistry: Cram, Lehn, Pedersen

Chemistry

The Nobel Prize in Chemistry 1987

"for their development and use of molecules with structure-specific interactions of high selectivity"



Donald J. Cram

1/3 of the prize

USA

University of California
Los Angeles, CA, USA

b. 1919
d. 2001

Jean-Marie Lehn

1/3 of the prize

France

Université Louis Pasteur
Strasbourg, France;
Collège de France
Paris, France

b. 1939

Charles J. Pedersen

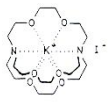
1/3 of the prize

USA

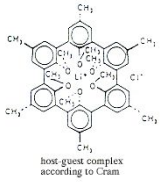
Du Pont
Wilmington, DE, USA

b. 1904
(in Fusan, Korea)
d. 1989

Crown ether complex
according to Pedersen



cryptand complex
= cryptate
according to Lehn



host-guest complex
according to Cram

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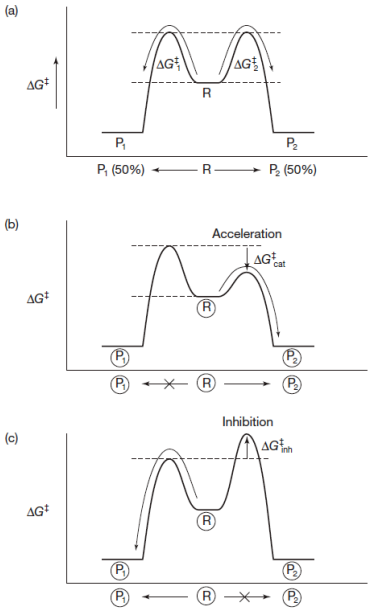
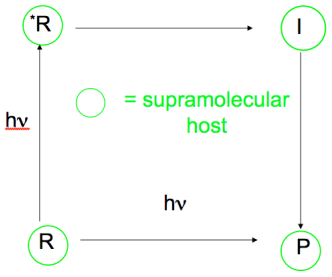
Energy diagram representation of supramolecular control of a reaction



The top reaction (a) is indiscriminate since the activation energies for R going to P_1 or P_2 are identical

The "circle" (host) can accelerate (b) or inhibit (c) the rate of a reaction



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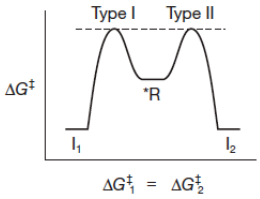
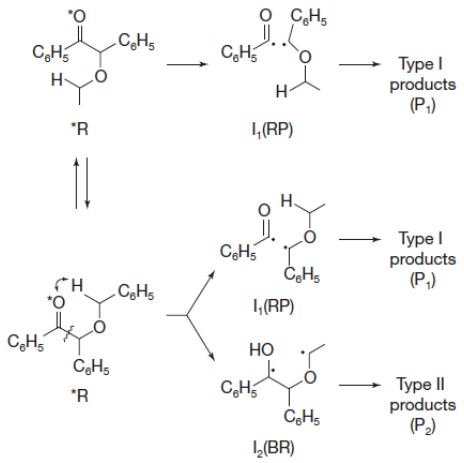
An exemplar of supramolecular control of a photoreaction with two competing paths





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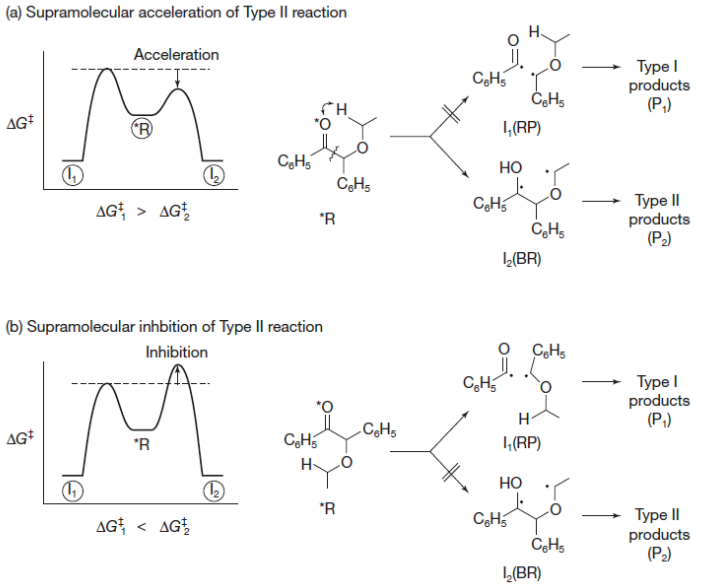
Acceleration and inhibition of the Type II photoreaction



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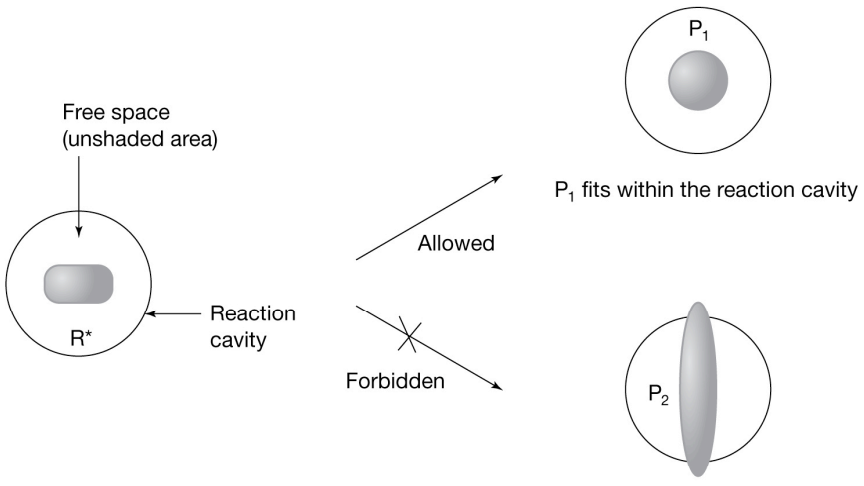
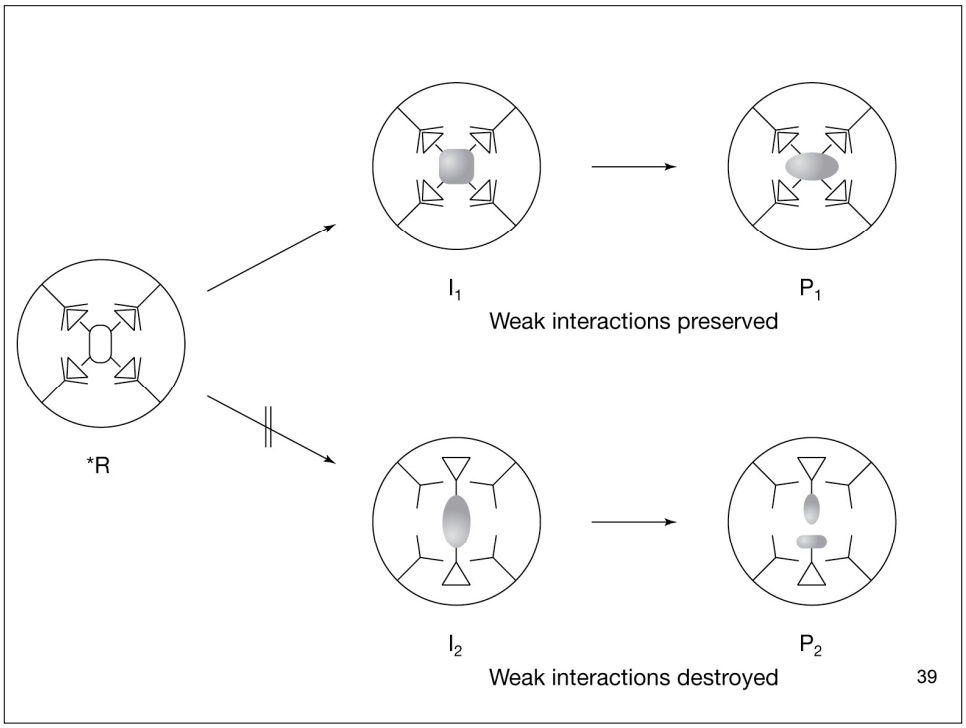
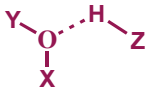




Pre-organization Through Weak Interactions



Hydrogen bond