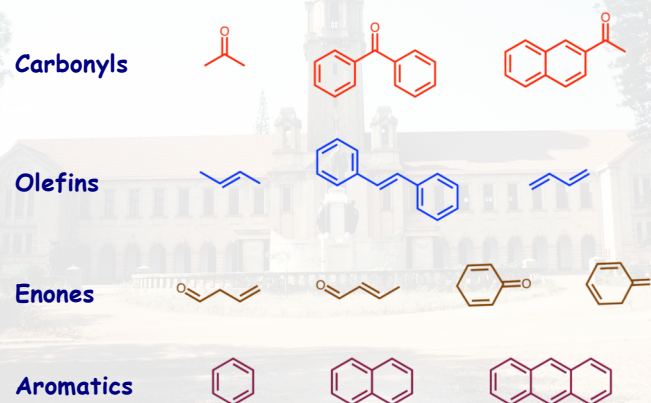


Supramolecular Photochemistry

Chapter 13, Turro book

Examples of Common Organic Chromophores

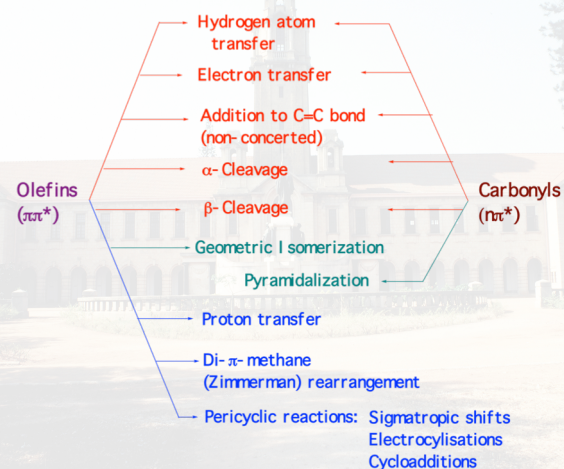


How does 'light energy' compare with chemical bonds?

Bond	Dissociation energy kcal/mol	Wavelength nm
O-H	104	275
C-H	95	300
C-C	82	350
C-Br	66	435
O-O	38	750

3

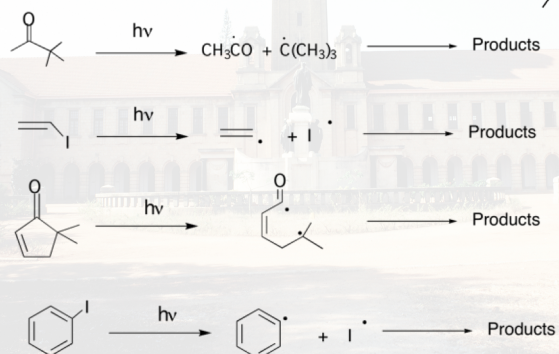
Photochemistry: Common Photoreactions



4

Photochemistry: Primary Photoreactions (1)

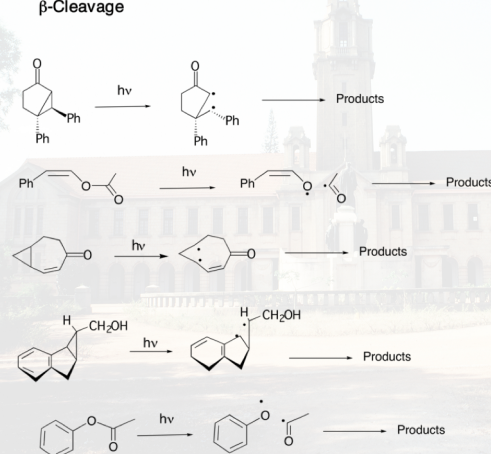
α -Cleavage



5

Photochemistry: Primary Photoreactions (2)

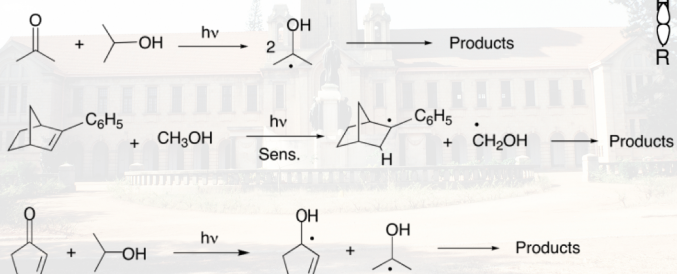
β -Cleavage



6

Photochemistry: Primary Photoreactions (3)

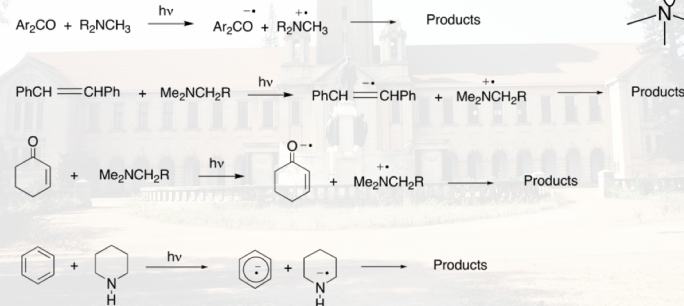
Hydrogen Abstraction



7

Photochemistry: Primary Photoreactions (4)

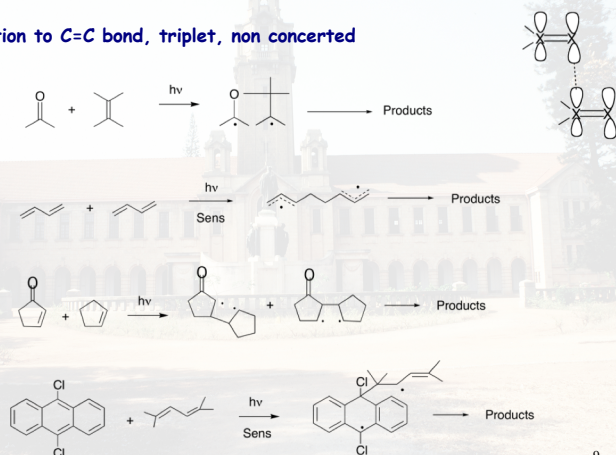
Electron Transfer



8

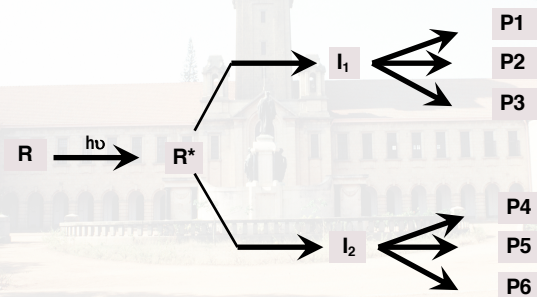
Photochemistry: Primary Photoreactions (5)

Addition to C=C bond, triplet, non concerted



9

Photochemistry often yields multiple products



Controlling Photochemical Reactions Through Conventional Means

- Nature of the excited state, $n\pi^*$ and $\pi\pi^*$
- Nature of the spin state, S_1 and T_1
- Level of the excited state, S_1 and S_2 ; T_1 and T_2

Controlling Photochemical Reactions

- **Electronic barrier:** Electronic configuration ($n\pi^*$ vs. $\pi\pi^*$)
- **Spin barrier:** Spin configuration (S^1 vs. T^1)

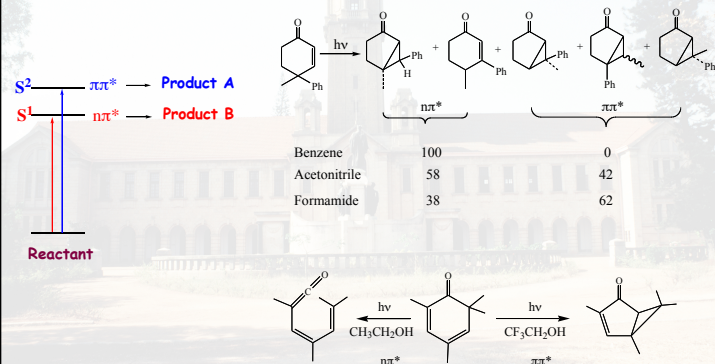
$$\Delta G^\# = \Delta H^\# - T\Delta S^\#$$

- **Enthalpic barrier:** Presence of activation energy
- **Entropic barrier:** Changes in conformational, rotational and translational freedom

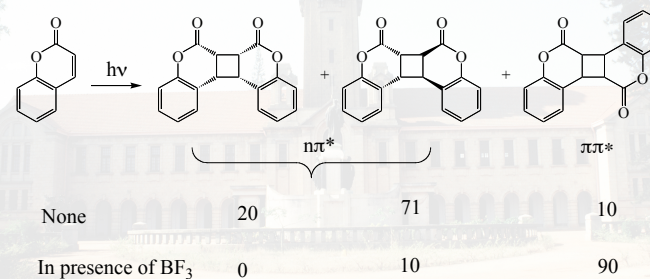
$$\Phi_p = k_r / \Sigma k$$

- **Competition:** Radiative, radiationless and other reactive modes

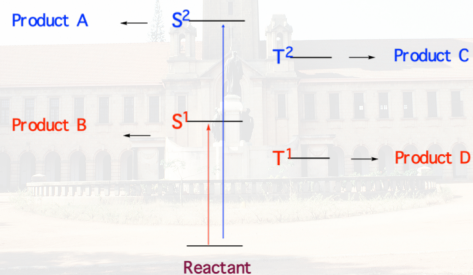
Controlling nature of reactive state with solvents



Controlling nature of reactive state with additives

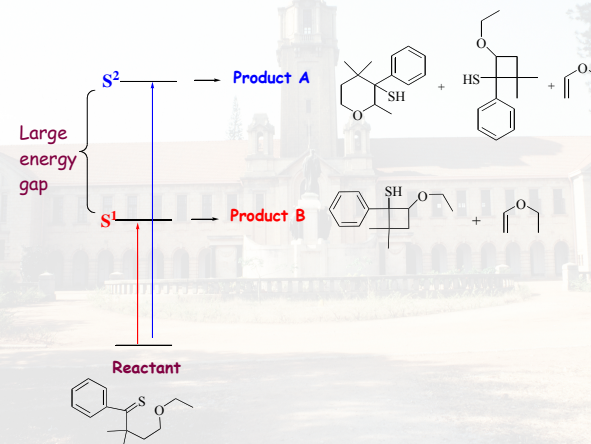


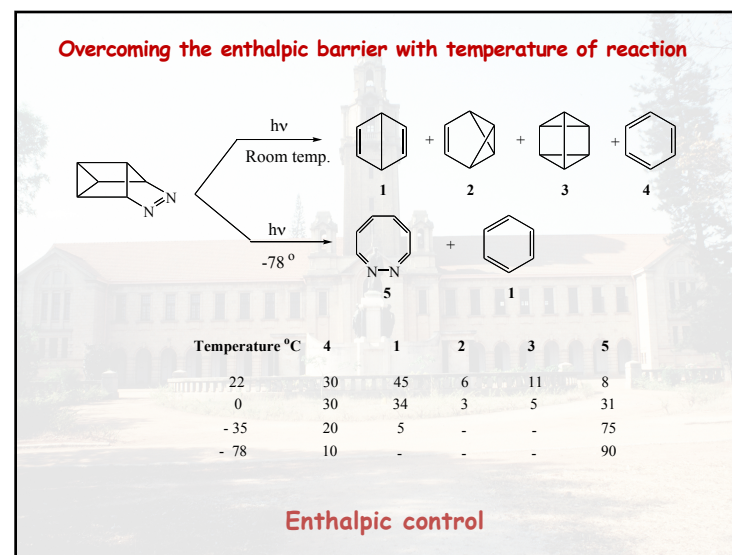
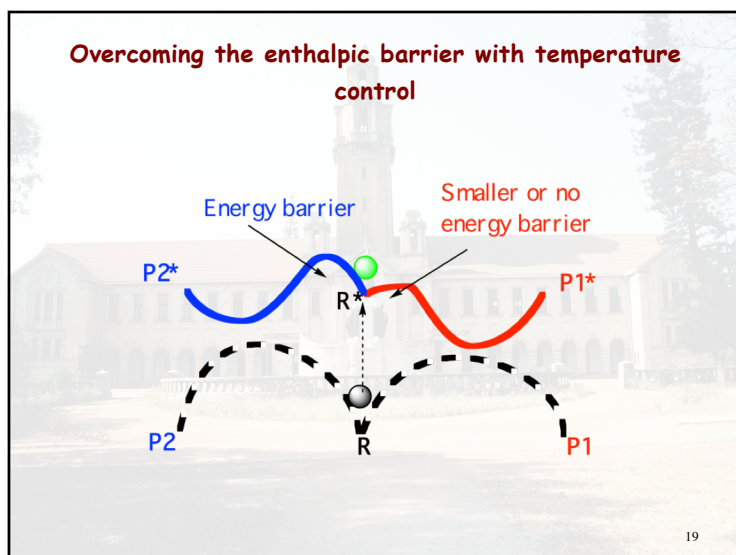
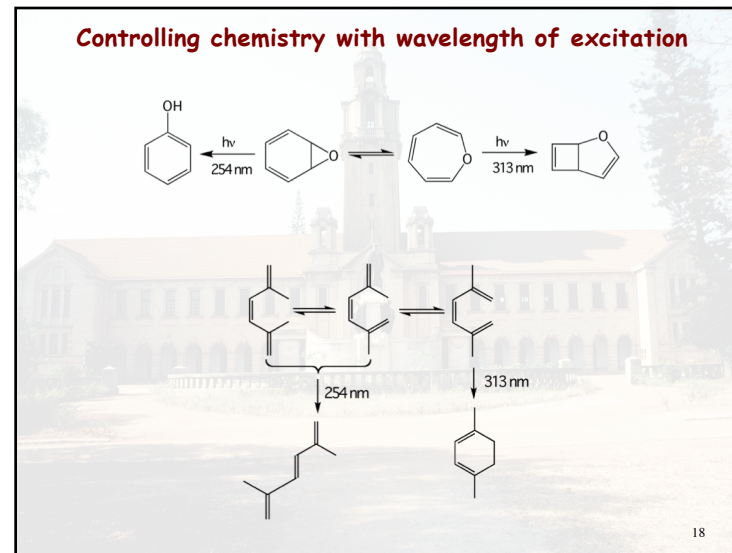
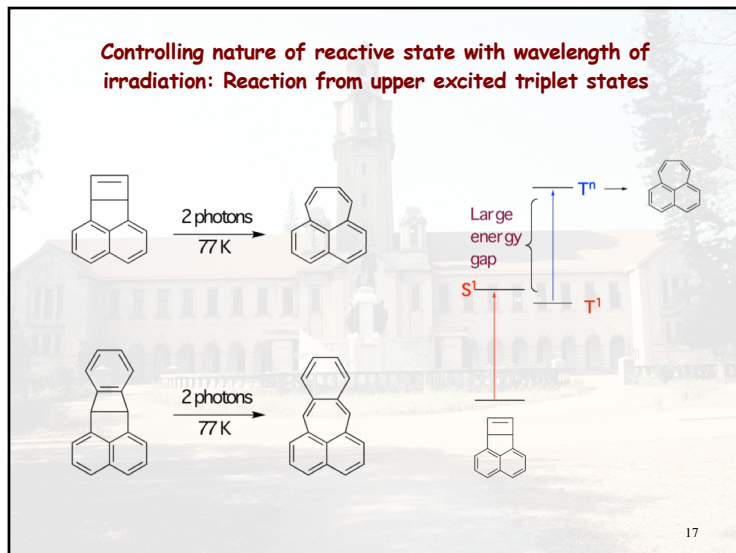
Large energy gap and violation of Kasha's Rule

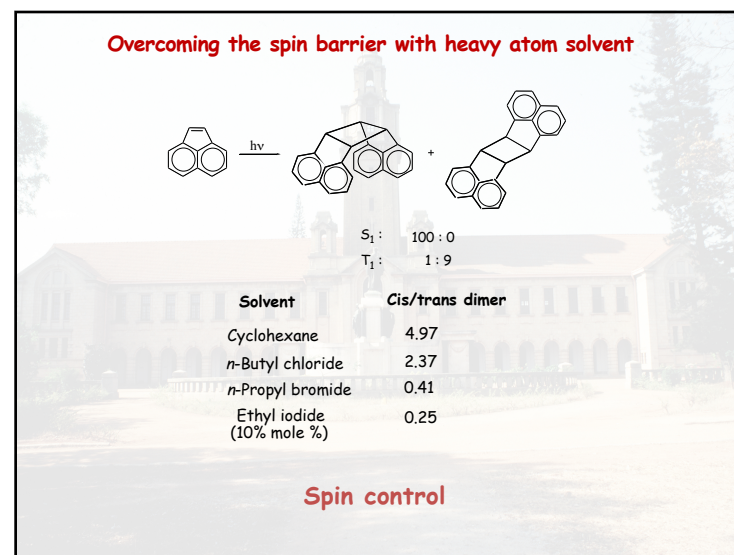
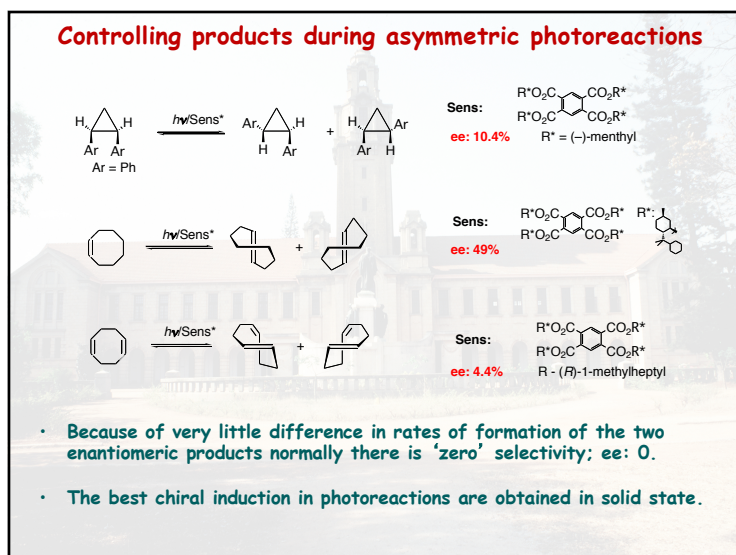
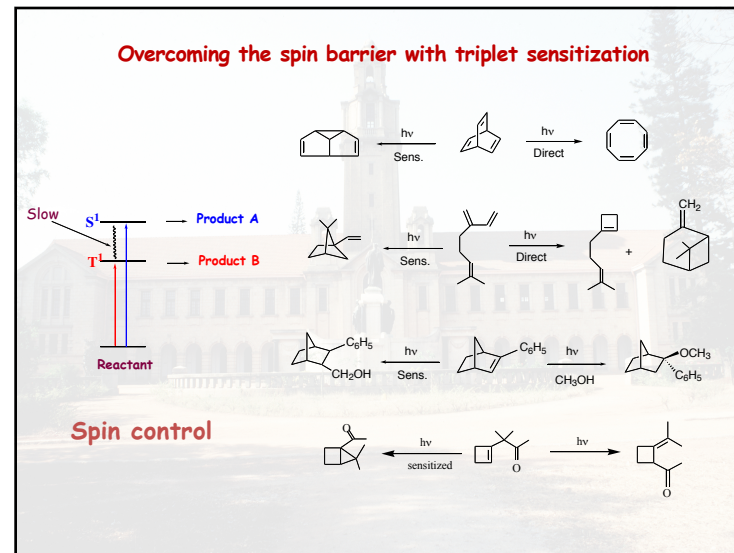
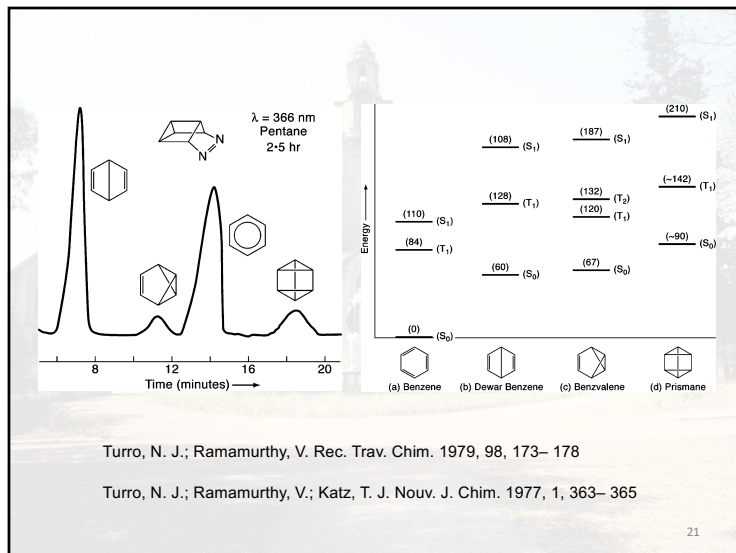


15

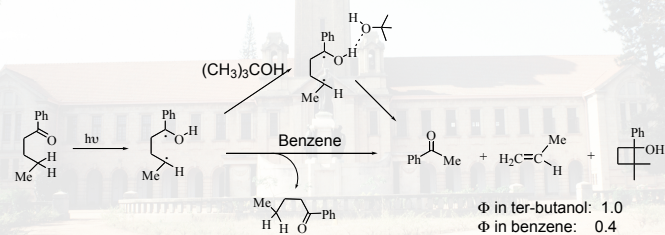
Controlling nature of reactive state with wavelength of irradiation Reaction from upper excited states



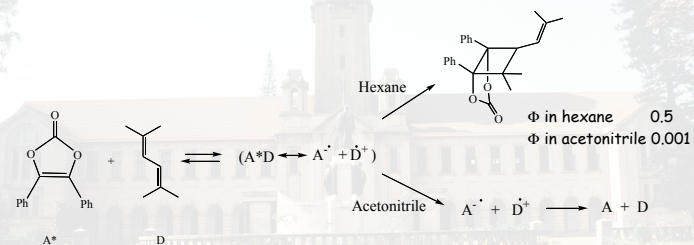




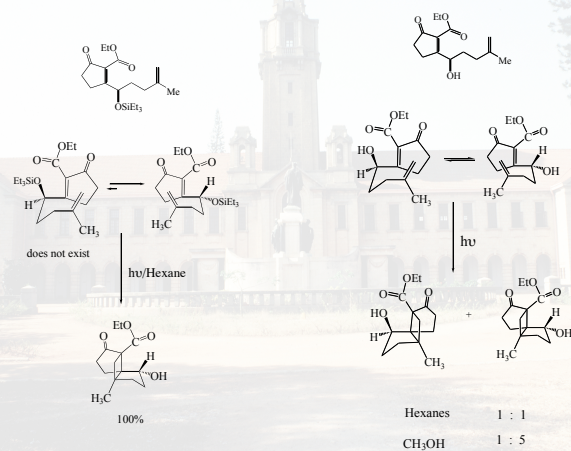
Cutting cut down competition with choice of solvent:
reduction of mobility-beginning of entropy control



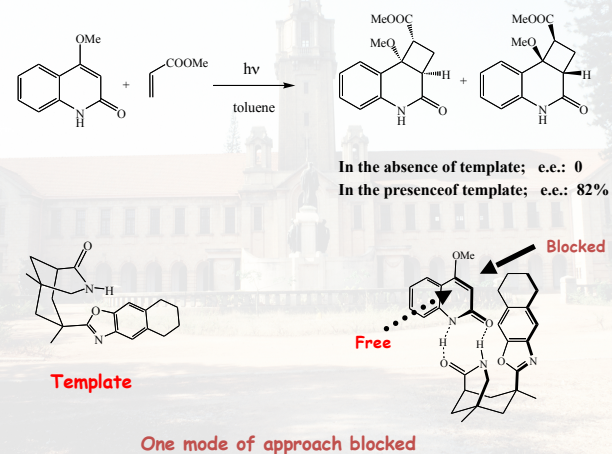
Cutting cut down competition with choice of solvent:
reduction of mobility-beginning of entropy control

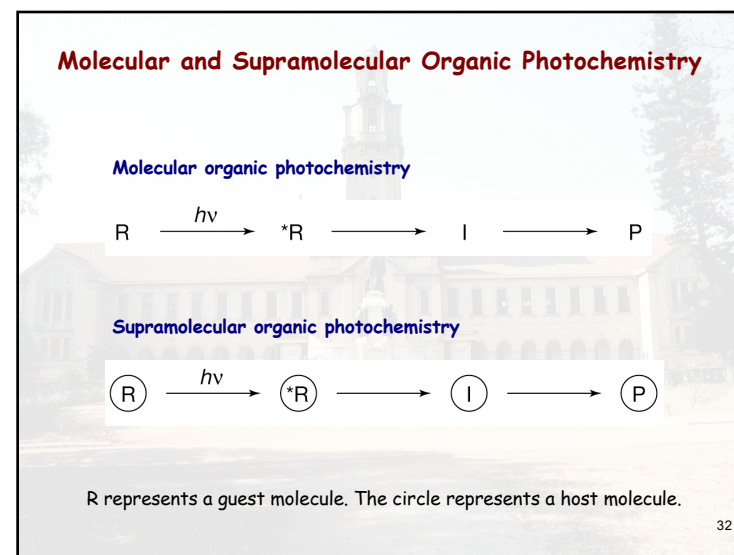
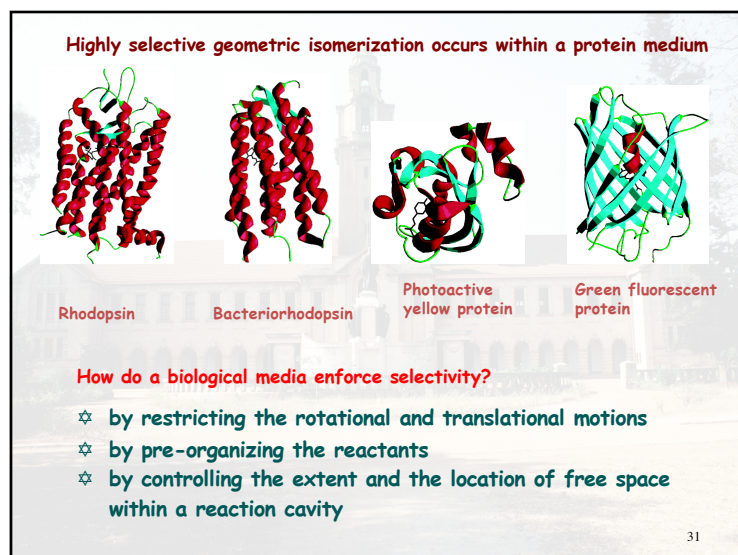
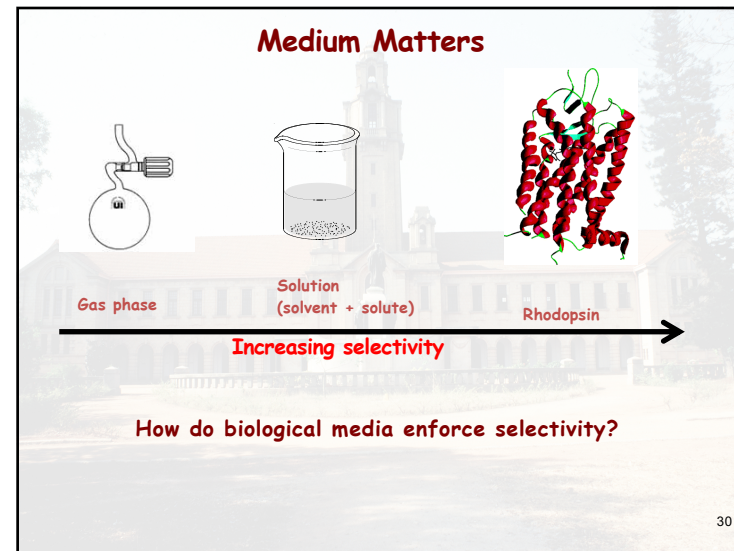
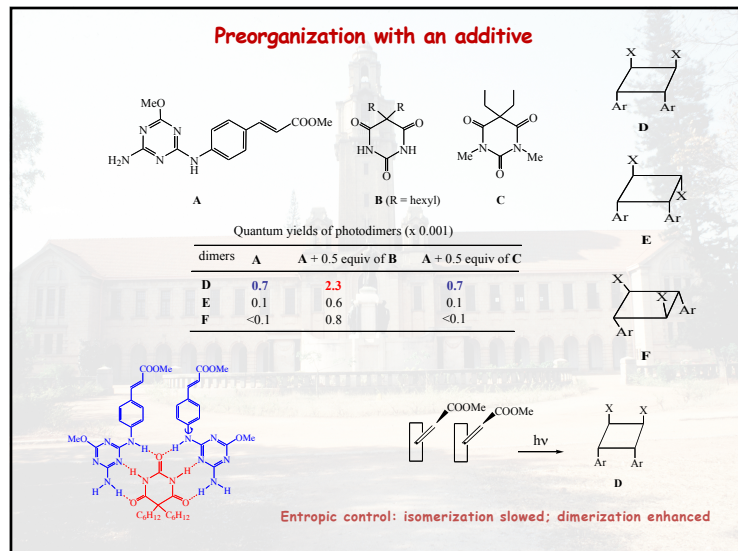


Cutting cut down competition with choice of solvent:
Conformational control



Preorganization with an additive

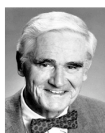




The beginnings of supramolecular organic chemistry: Cram, Lehn, Pedersen

The Nobel Prize in Chemistry 1987

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



Donald J. Cram

2/3 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

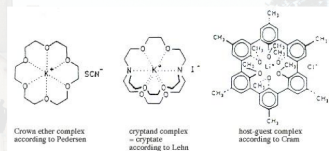


Charles J. Pedersen

1/3 of the prize
USA

Du Pont
Wilmington, DE, USA

b. 1901
(in Fusan, Korea)
d. 1989



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The Nobel Prize in Chemistry 2016

"for the design and synthesis of molecular machines"



Jean-Pierre Sauvage



J. Fraser Stoddart



Bernard L. Feringa

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Supramolecular Photochemistry



R. Breslow

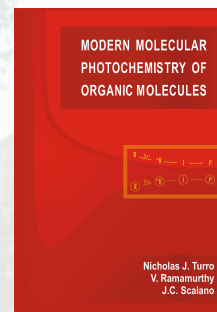


J. M. Lehn



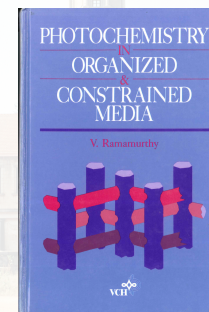
N. J. Turro

Reference books

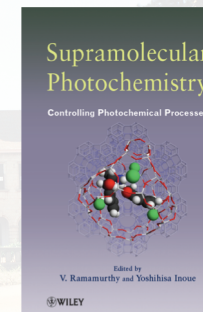


2010

Chapter 13



1991



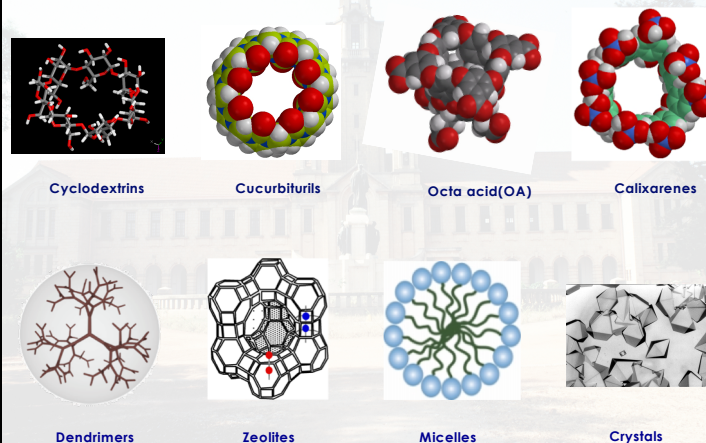
2011

Container Store



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Chemistry in bowls, baskets, cages and cavities



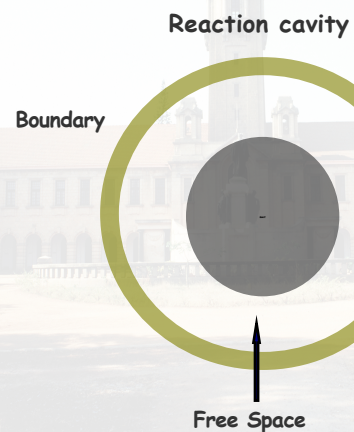
The guest@host paradigm



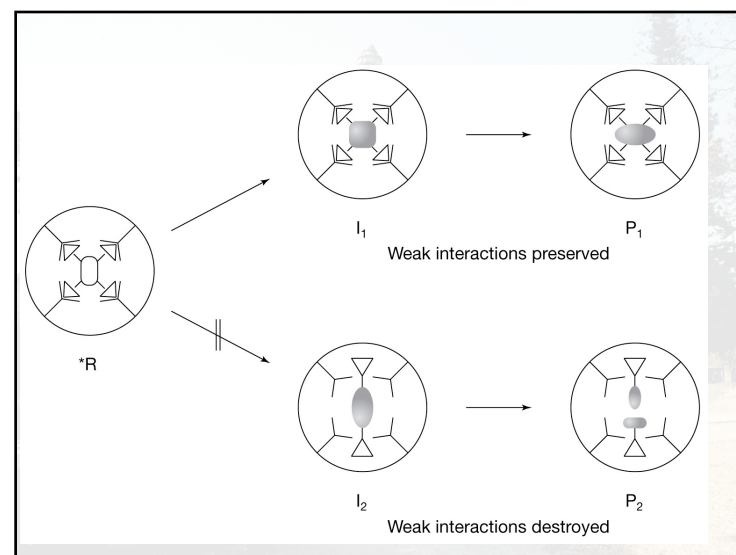
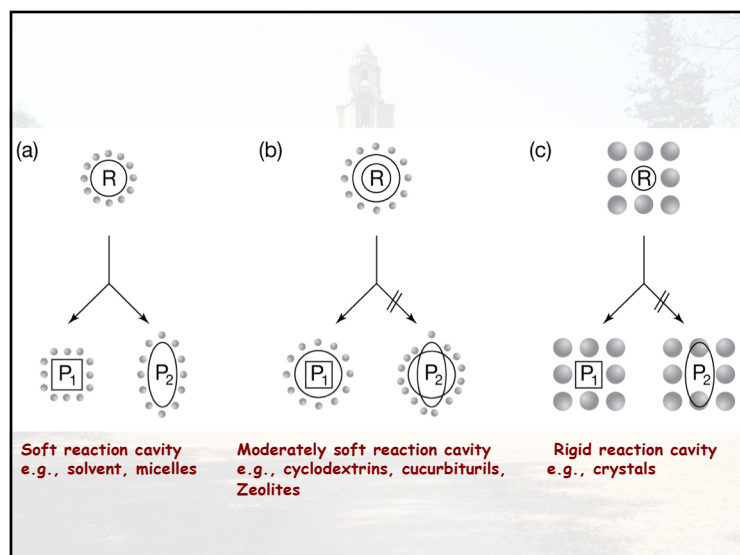
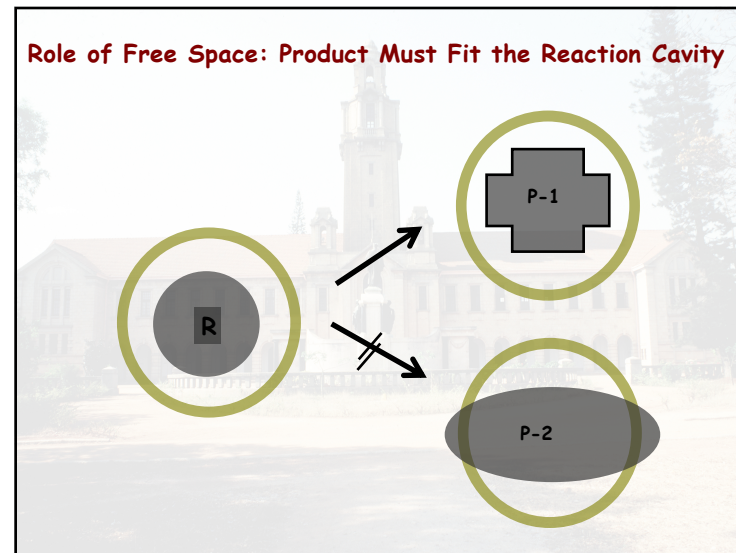
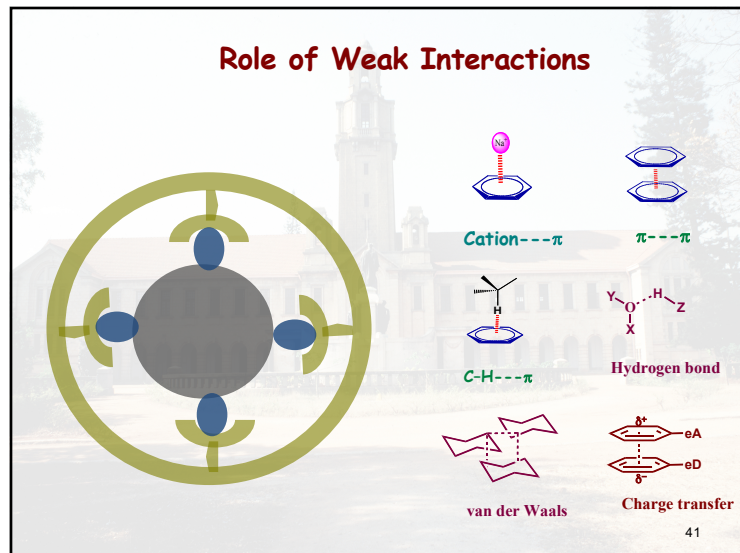
We'll be using this paradigm to discuss supramolecular systems

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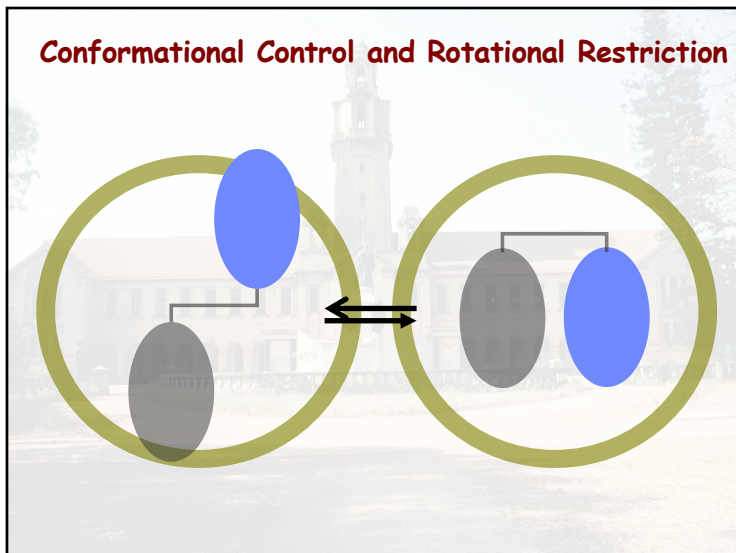
Supramolecular Containers



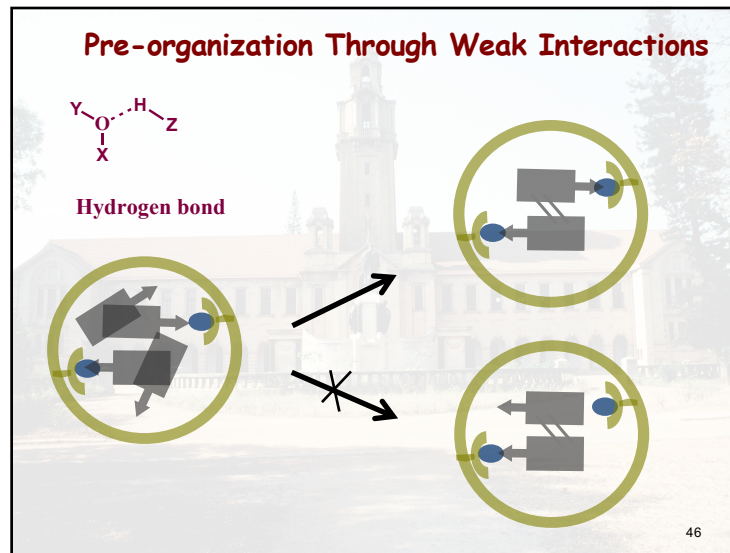
40



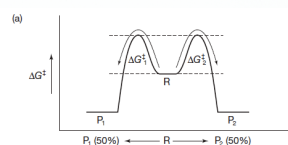
Conformational Control and Rotational Restriction



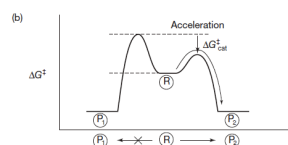
Pre-organization Through Weak Interactions



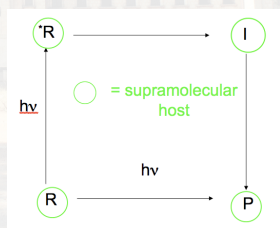
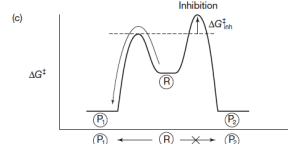
Energy diagram representation of supramolecular control of a reaction



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

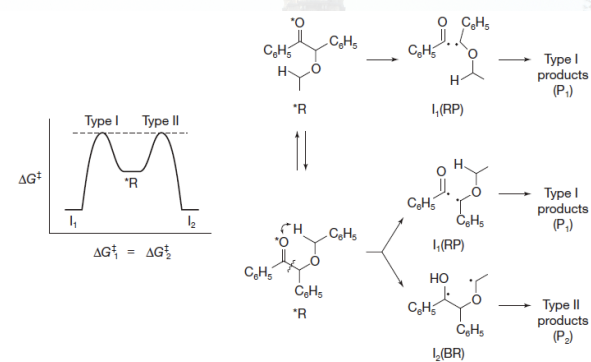


The "circle" (host) can accelerate (b) or inhibit (c) the rate of a reaction



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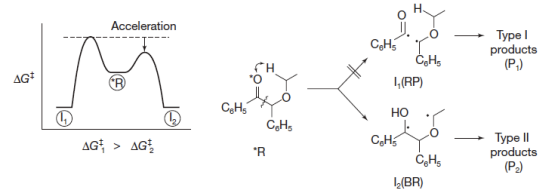
An exemplar of supramolecular control of a photoreaction with two competing paths



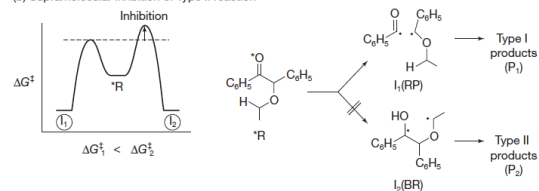
48

Acceleration and inhibition of the Type II photoreaction

(a) Supramolecular acceleration of Type II reaction



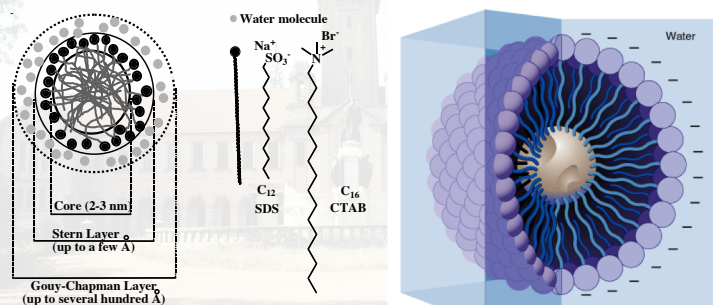
(b) Supramolecular inhibition of Type II reaction



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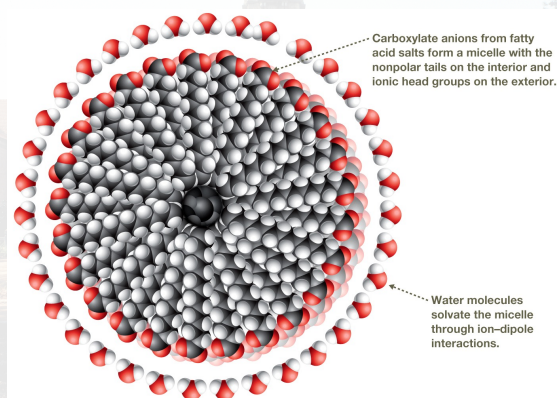
Supramolecular Hosts

Micelle structure

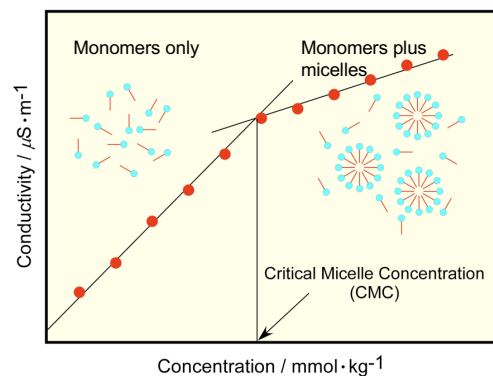


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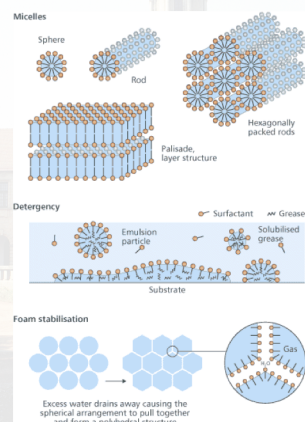
Micelles



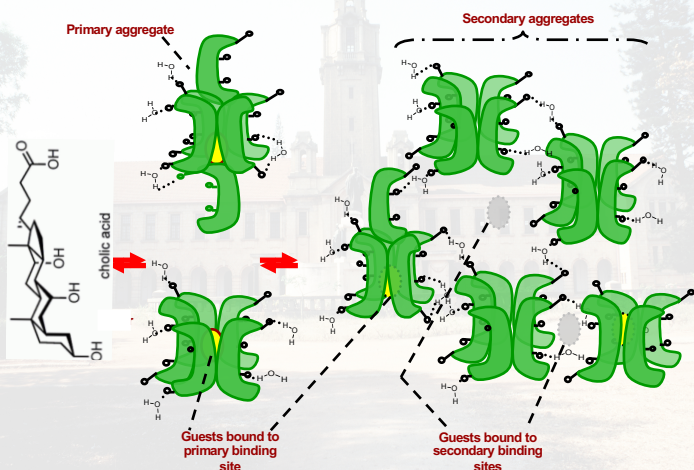
The critical micelle concentration phenomenon: Sudden break in properties near a certain concentration of surfactant



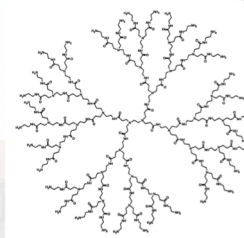
Structures formed from surfactants in aqueous solution



Cholic acid micelles--Bile salts

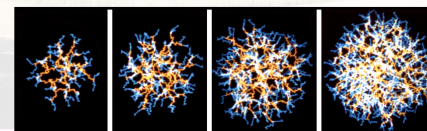


Dendrimers: covalent micelles



A dendrimer: a hyperbranched polymer

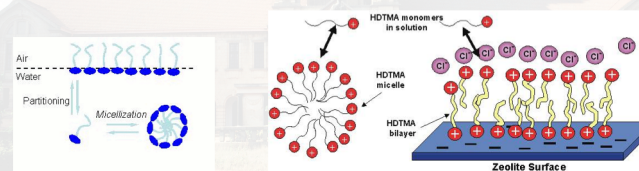
Generation increasing →



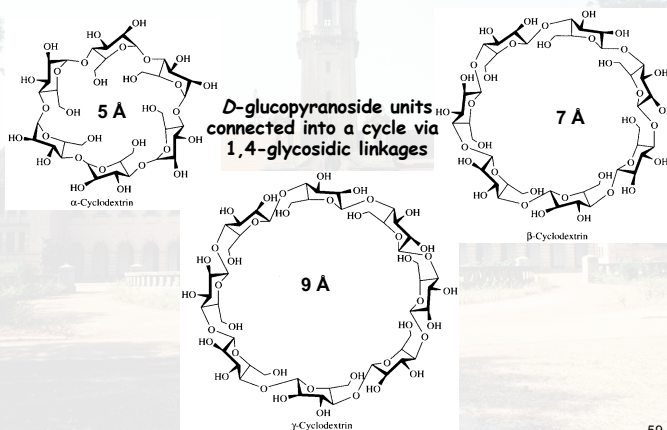
Generations of dendrimers

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

Surfactants gather at interfaces: the air/water interface and the water/solid interface

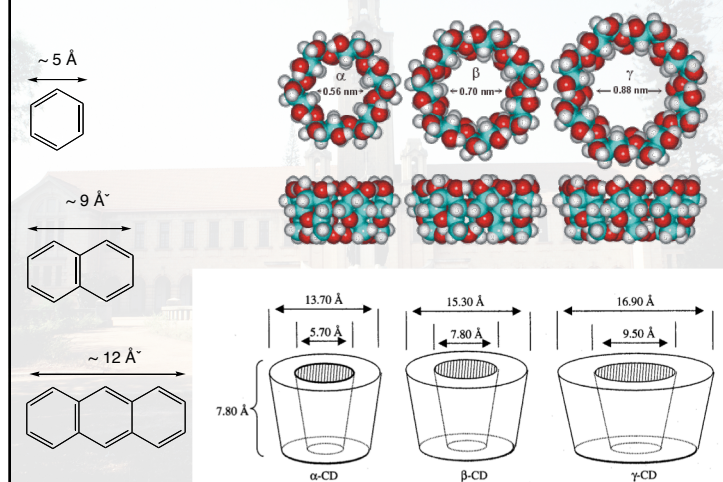


Water soluble organic hosts: Cyclodextrins

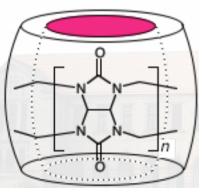


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Water soluble organic hosts: Cyclodextrins



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.

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Water soluble organic hosts: Cucurbiturils

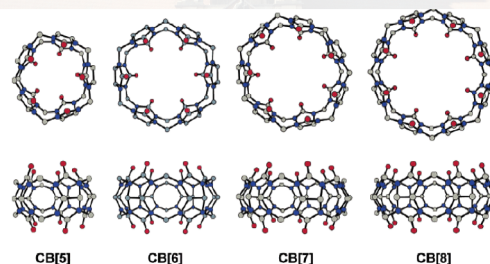
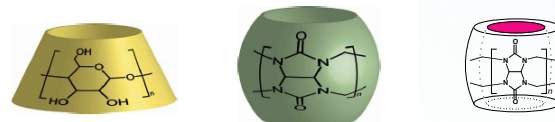
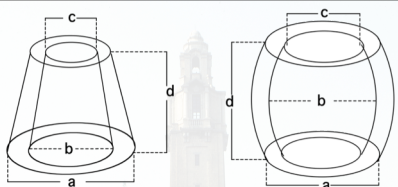


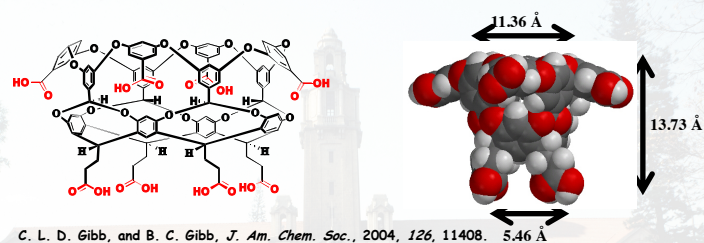
FIGURE 1. X-ray crystal structures of CB[n] ($n = 5-8$). Color codes: carbon, gray; nitrogen, blue; oxygen, red.



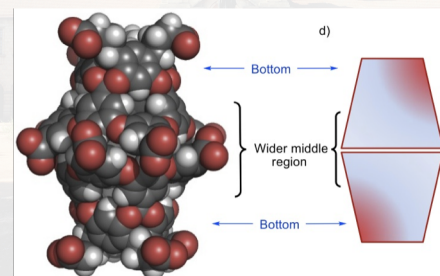
Cavity	a (Å)	b (Å)	c (Å)	d (Å)	Volume (Å ³)
CB[6] ^a	14.4	5.8	3.9	9.1	164
α -CD ^a	14.6	5.2	4.7	8.0	174
CB[7] ^b	16.0	7.3	5.4	9.1	279
β -CD ^a	15.4	6.4	6.0	8.0	262
CB[8] ^b	17.5	8.8	6.9	9.1	479
γ -CD ^a	17.4	8.3	7.5	8.0	472

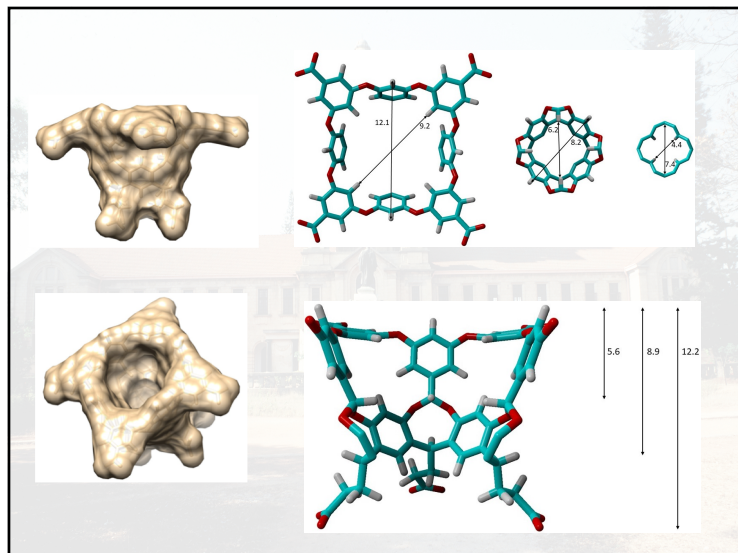
a) Saeghi, J. Chem. Rev. 1998, 98 (5), 1743-1754.
b) Lee, J. W., Sarraf, S.; Kim, K., Acc. Chem. Res. (2003), 36(8), 621-630

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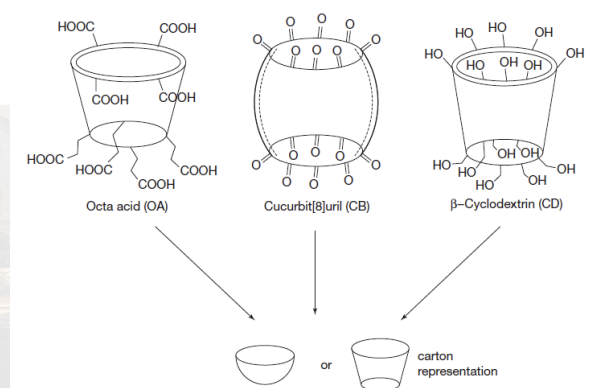


C. L. D. Gibb, and B. C. Gibb, *J. Am. Chem. Soc.*, 2004, 126, 11408.



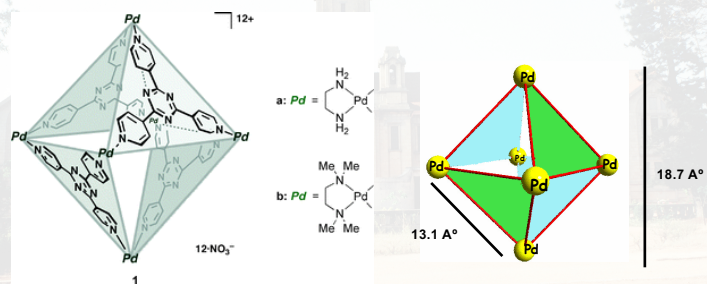


Octa acid (OA), Cucurbituril (CB) and Cyclodextrin (CD) A comparison



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Water soluble inorganic host: Fujita's Pd host



Discovery of zeolites



Baron Cronstedt 1722-1765

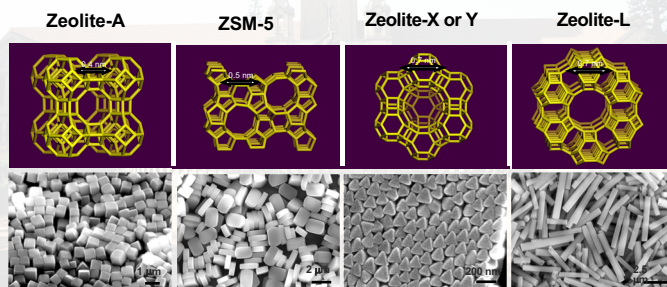


A zeolite, as found in Nature

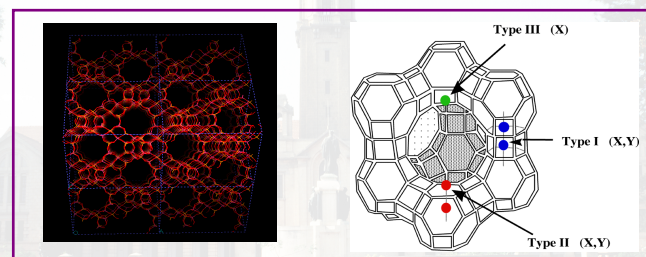
Cronstedt discovered "boiling stones" which he called "zeolites" from the Greek: zeo (boil) and lithos (stone).

Zeolites: Synthetic

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.



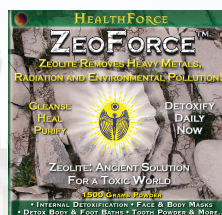
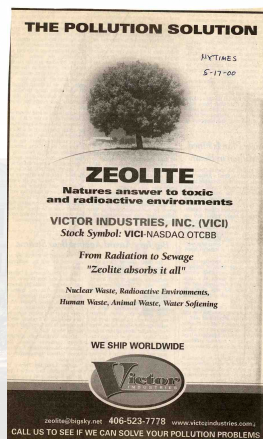
Characteristics of Faujasites (Zeolites)



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

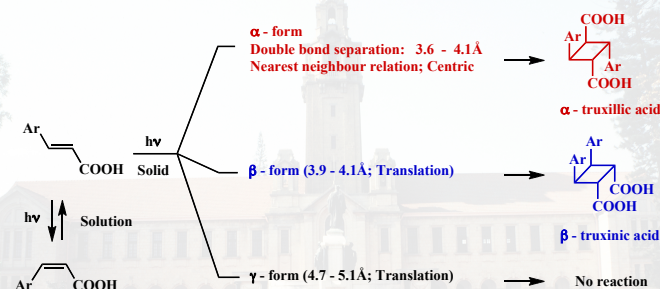
70

The solution to pollution: zeolites



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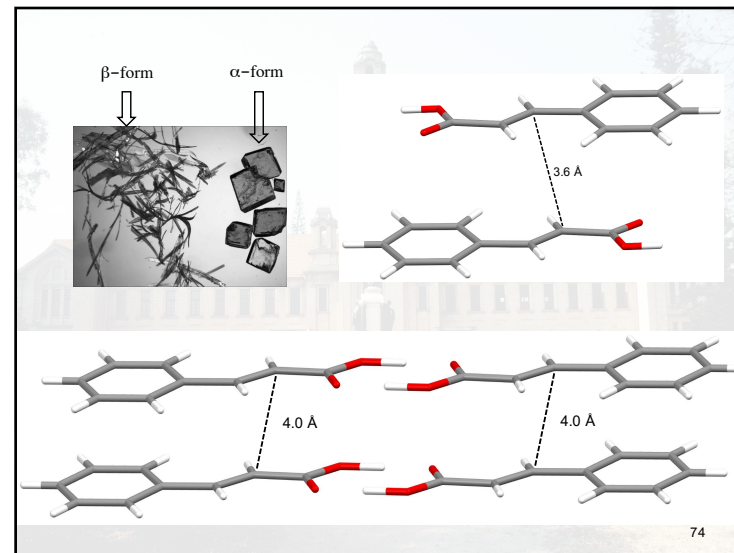
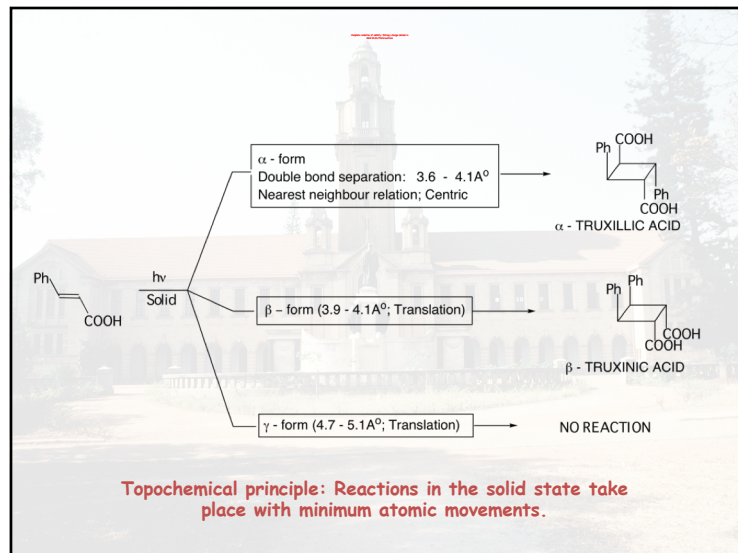
Photodimerization of *trans*-Cinnamic acids



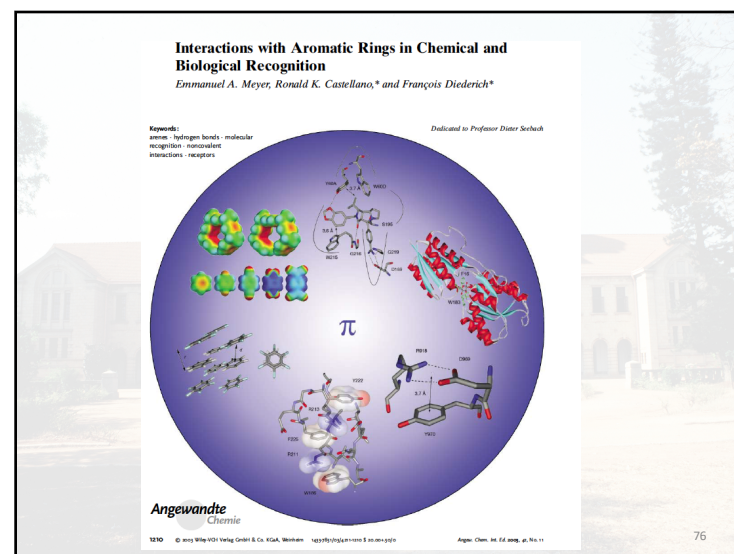
Topochemical principle: Reactions in the solid state take place with minimum atomic movements.

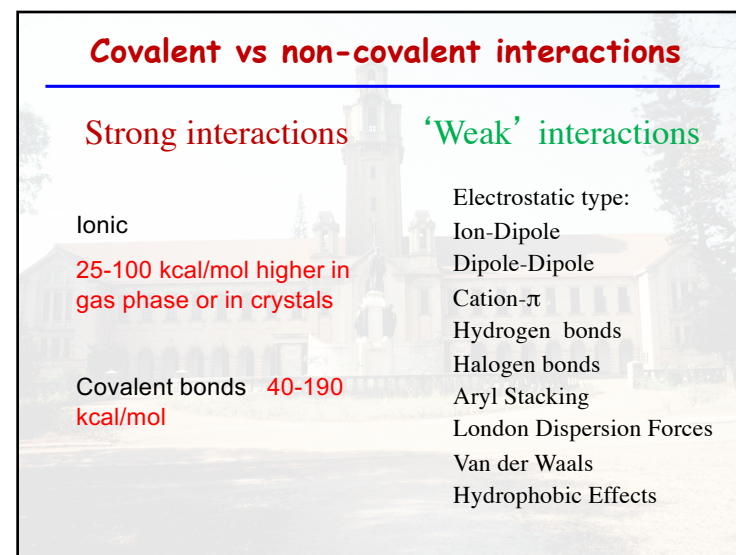
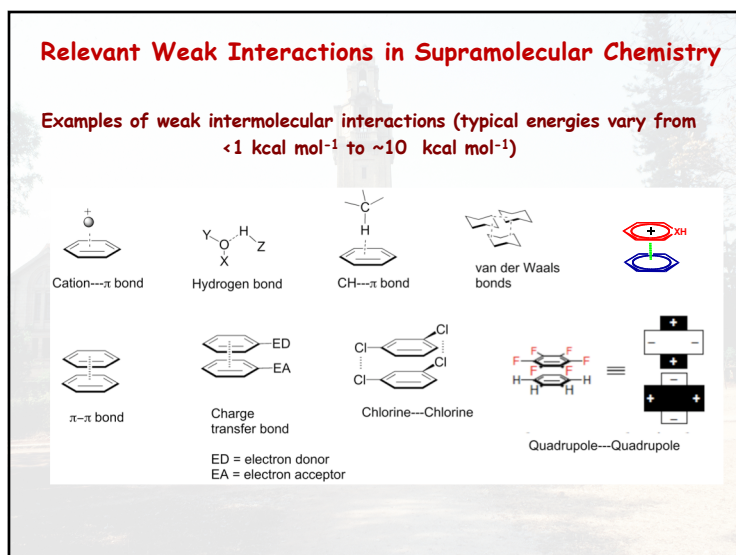
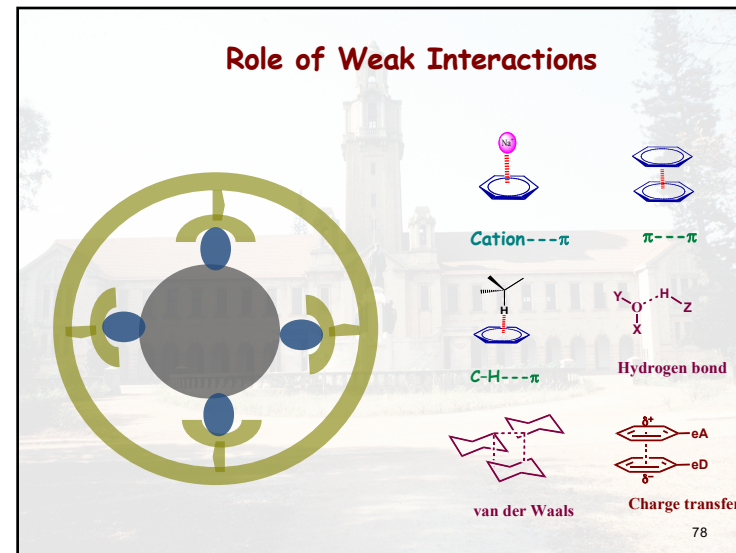
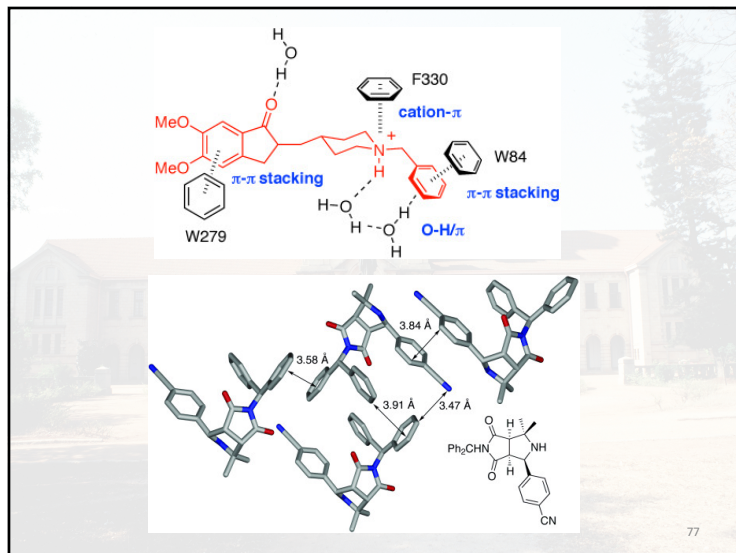
G. M. J. Schmidt et al. 'Solid State Photochemistry, A Collection of Papers', Verlag Chemie, 1976.

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Supramolecular Weak Interactions





Electrostatic defined

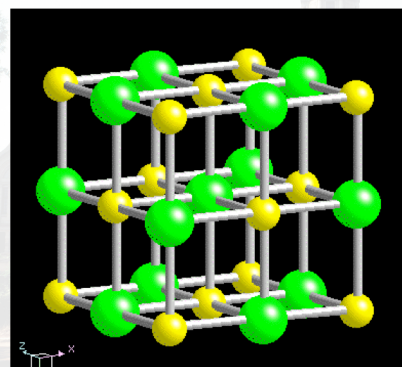
Coulombic attraction or repulsion between charges or partial charges that exists prior to the interaction and remain unchanged in the interaction

$$E = \frac{q_1 q_2}{4\pi\epsilon\epsilon_0 r}$$

Dielectric constant of the medium

The two charges

Ion-Ion



Ionic bonds

25 - 100 kcal/mols

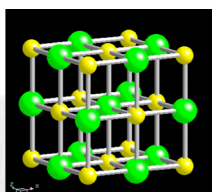
comparable in strength to covalent bonds

Lattice energy

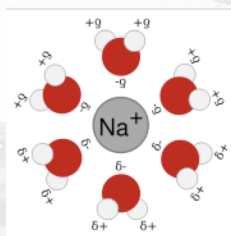
Yet these compounds Dissolve in water and other polar solvents!

NaCl mp = 800 ° C

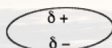
Solvation



H₂O



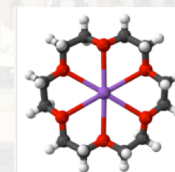
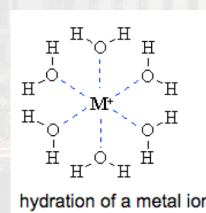
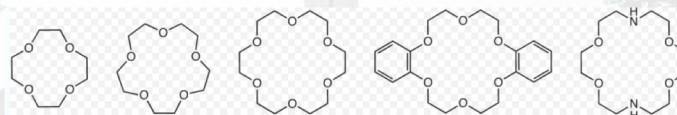
NaCl mp = 800° C



Note the shape of the solvent can affect the solubility. Water can arrange itself well around Na⁺ and Cl⁻.

Ion-Dipole

Quite useful for molecular recognition and sensing
~ 10 - 50 kcal/mol (50-200 kJ/mol)



Water like interior
Alkane exterior

18-crown-6 K⁺

Dipole-Dipole Forces

- Dipole-dipole interactions result from the approach of two polar molecules.
- If their positive and negative ends approach, the interaction is an attractive one.
- If two negative ends or two positive ends approach, the interaction is repulsive.
- In a liquid or a solid, the molecules are mostly oriented with the positive and negative ends together, and the net force is attractive.

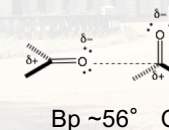
Dipole-Dipole

Interaction between molecules with permanent dipoles
~ 1-15 kcal/mol (5-50 kJ/mol)



or

Ketones are a good example but their low bp shows this is a relatively weak interaction

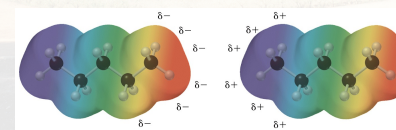
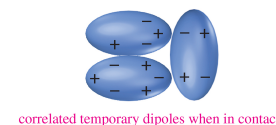


London Dispersion Forces

- One of the Van der Waal forces
- A temporary dipole moment in a molecule can induce a temporary dipole moment in a nearby molecule.
- An attractive dipole-dipole interaction results for a fraction of a second.
- Main force in nonpolar molecules
- Larger atoms are more polarizable.

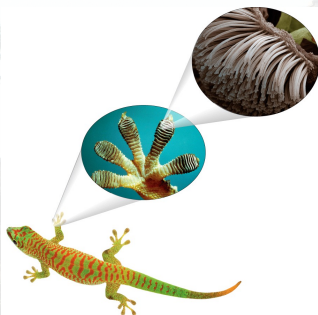
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London Dispersion Forces



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London Dispersion Forces

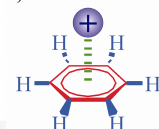


- The greater the surface area of a molecule, the more temporary dipole attractions are possible
- Consider the feet of Gecko. They have many flexible hairs on their feet that maximize surface contact
- The resulting London dispersion forces are strong enough to support the weight of the Gecko

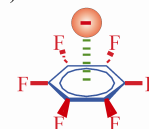
Geckos can climb effortlessly on almost every surface. Their ability to do so is attributed to ultrafine hairs on their feet, which give rise to a very large contact surface area. This allows for rather strong dispersion forces, one of the intermolecular interactions we will examine in this chapter.

Cation- π and Anion- π

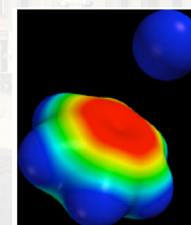
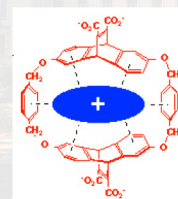
a)



b)



$\sim 1 - 20$ kcal/mol

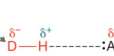


$\sim 25\%$ of Tryptophan residues in proteins make cation- π interactions

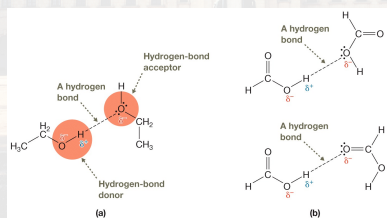
Hydrogen Bonding

- **Hydrogen bonding** occurs between a **hydrogen-bond donor** and a **hydrogen-bond acceptor**.

Hydrogen-bond donor (D = N, O, or F) Hydrogen-bond acceptor (A = N, O, or F)



A hydrogen bond



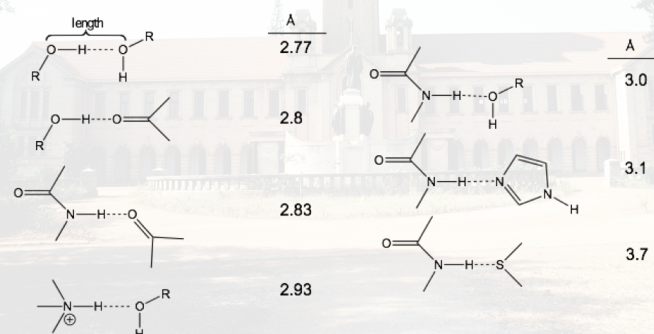
Hydrogen bonds: Directionality

X-H \cdots (lp) A

proton donor

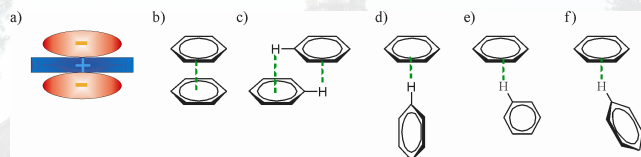
proton acceptor

Highly directional (180°); Specific lengths



Aryl stacking interactions

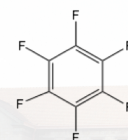
0 - 15 kcal/mol



Interaction often depend on one ring being more electron rich and the other electron poor. In this case only the face orientation b is favored. In other cases it is the edge-to-face or T-shaped.

For review see: Angew. Chem. Int. Ed. **2003**, 42, 1210-1250

Aryl stacking between e-rich and e-poor aromatics



e- poor = acceptor

Acceptor

Donor



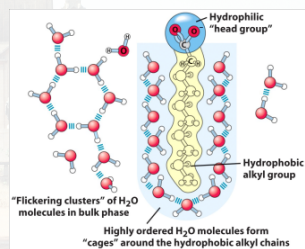
e- rich = donor

Acceptor

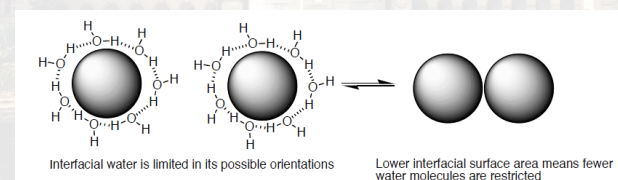
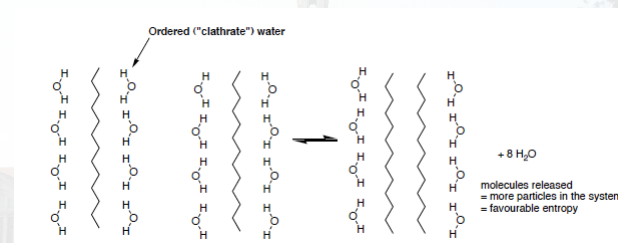
Donor

Hydrophobic Effects

The hydrophobic interaction is mostly an **entropic** effect originating from the disruption of highly dynamic **hydrogen bonds** between molecules of liquid water by the nonpolar solute.



Why do micelles form at all?

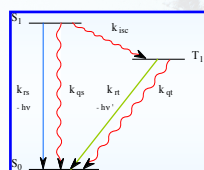
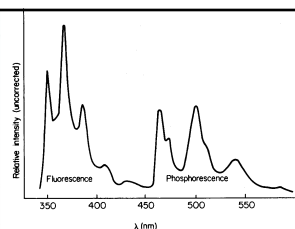


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Supramolecular Photochemistry Introduction and Photophysics

Supramolecular Photophysics

- Manipulating photophysics of organic molecules through weak interactions and confinement
- Use of organic photophysics in understanding supramolecular structures
- Supramolecular organic photophysics: Sensors, molecular motors, etc.

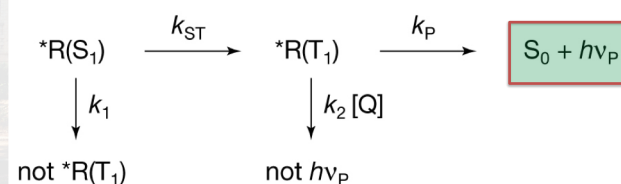
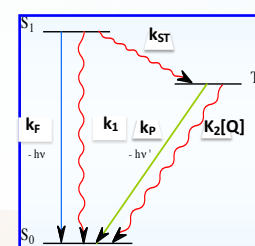


Fluorescence:

- High radiative rate constant, 10^{-10} to 10^{-8} s^{-1}
- Precursor state (S_1) has a short lifetime
- Not susceptible to quenching

Phosphorescence:

- Low radiative rate constant, 10^{-6} to 10 s^{-1}
- Precursor state (T_1) has long lifetime
- Very much susceptible to quenching
- Emission quantum yield depends on S_1 to T_1 crossing



The heavy atom effect on spin transitions

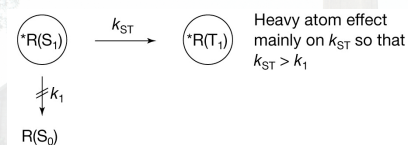
The “heavy atom” effect is an “atomic number” effect that is related to the coupling of the electron spin and electron orbit motions (spin-orbit coupling, SOC).

Most commonly, the HAE refers to the rate enhancement of a spin forbidden photophysical radiative or radiationless transition that is due to the presence of an atom of high atomic number, Z .

The heavy atom may be either internal to a molecule (molecular) or external (supramolecular).

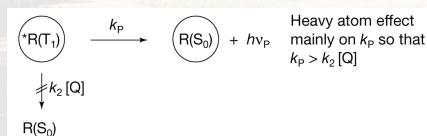
Strategy to record phosphorescence at room temperature through supramolecular approach

Stage 1



Make more triplets through the heavy atom effect

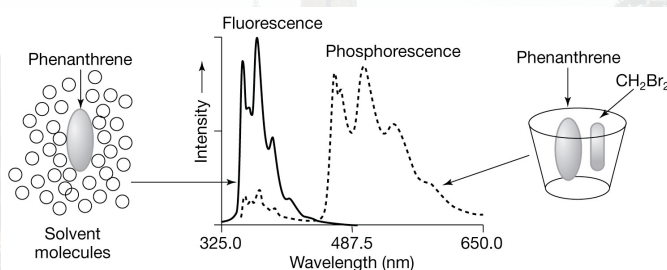
Stage 2



Make triplets emit faster in competition with quenching processes

Cyclodextrins as hosts

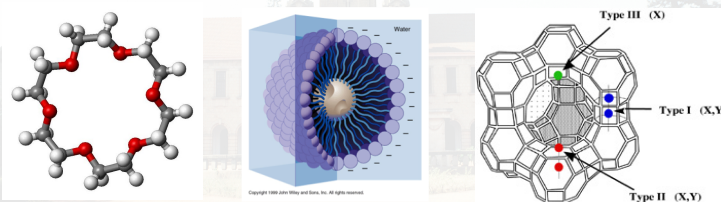
Phenanthrene@Cyclodextrin: effect of CH_2Br_2 as co-guest



Induced Intersystem Crossing Depends on the SOC: Cations as the heavy atom perturber

Atom	Ionic Radius of the Cation (Å)	Spin-Orbit Coupling ζ cm ⁻¹
Li	0.86 (+)	0.23
Na	1.12	11.5
K	1.44	38
Rb	1.58	160
Cs	1.84	370
Tl	1.40	3410
Pb	1.33 (2+)	5089

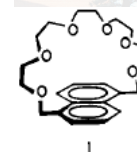
Crown ethers, micelles and zeolites contain cations



External heavy atom effect: Crown ether approach

Table II. Estimates^{a,b} of Rate Constants for Excited-State Processes of 1,5-Naphtho-22-crown-6 (**1**) in Alcohol Glass^c at 77 K with Alkali Metal Chloride Salts Added in 5:1 Molar Excess (Crown at $1.00 \times 10^{-4} F$)

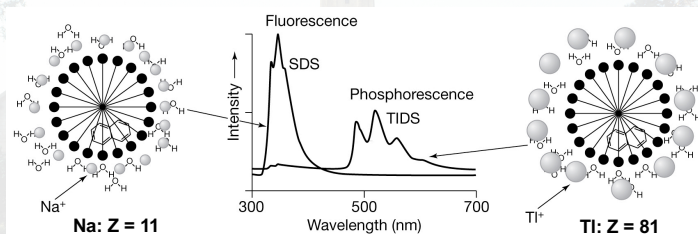
Salt added	$10^{-6}k_f$	$10^{-6}k_{nr}$	$10^2k_p^d$	k_{dt}^d
None	3.1	25	8.7	0.37
NaCl	2.6	32	6.7	0.41
KCl	2.3	35	5.8	0.39
RbCl	1 ^e	52	12.	0.50
CsCl	1 ^e	670	81.	1.57



^a All rate constants in s^{-1} . ^b $k_f = \phi_f \tau_f^{-1}$; $k_{nr} = (1 - \phi_f) \tau_f^{-1}$; $k_p = \phi_p (1 - \phi_f)^{-1} \tau_p^{-1}$; $k_{dt} = \tau_p^{-1} - k_p$. ^c See note 4. ^d With $\phi_f + \phi_{isc} = 1.0$ assumed. ^e Estimated from 77 K UV absorption spectra.

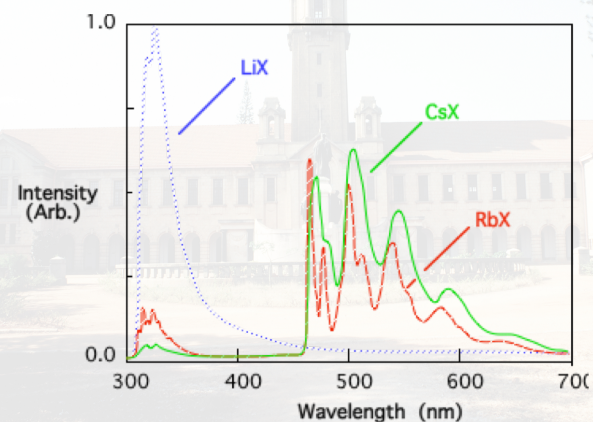
Micelles as hosts

Naphthalene@SDS micelle: effect of heavy atom counterions

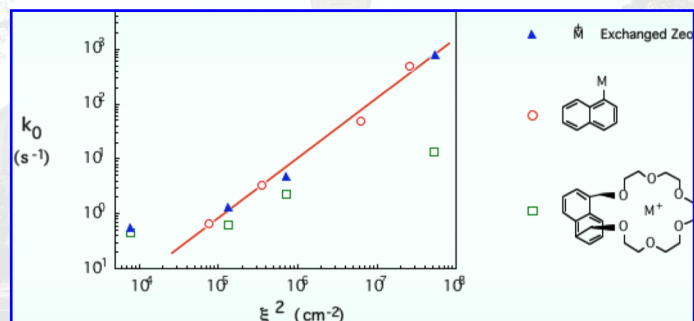


Heavy atom produces more triplets and the triplets produced phosphoresce at a faster rate

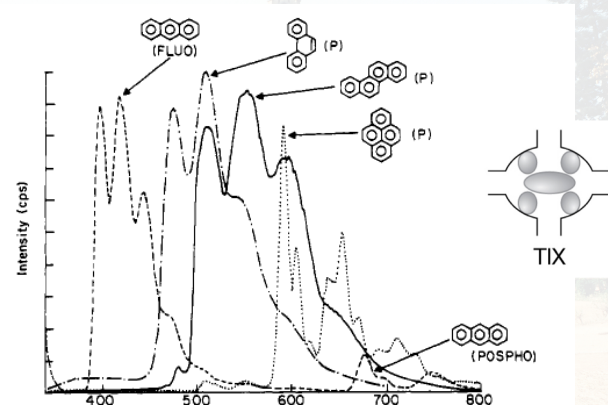
Emission Spectra of Naphthalene Included in MY Zeolites



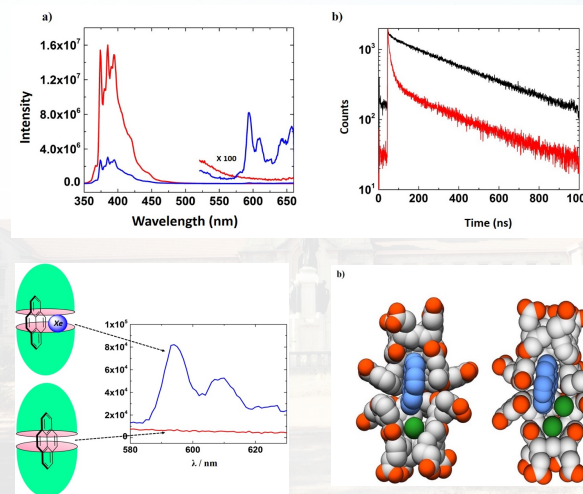
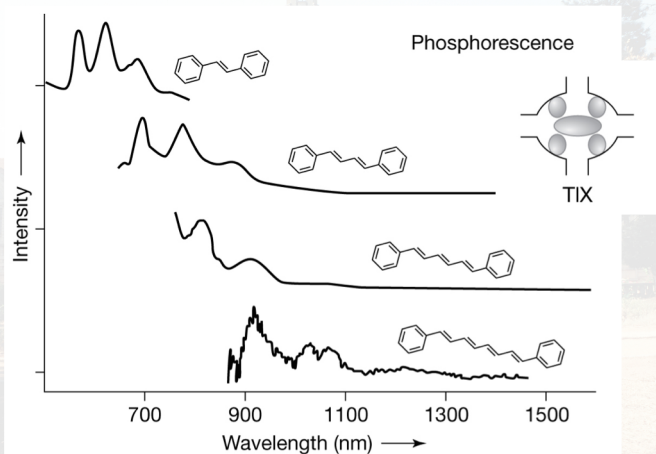
External Heavy Atom Effect on Triplet Decay Rates of Naphthalene



Room temperature phosphorescence

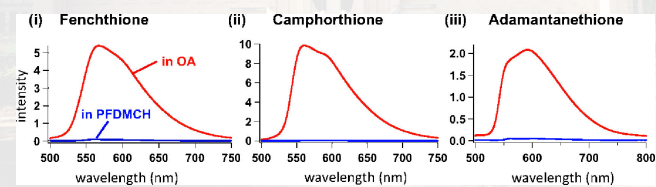
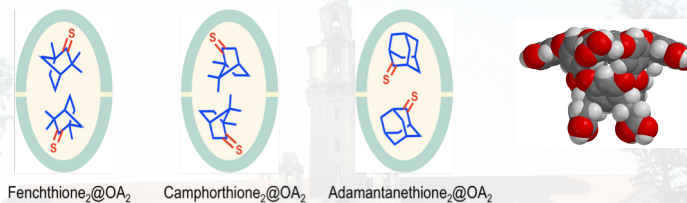
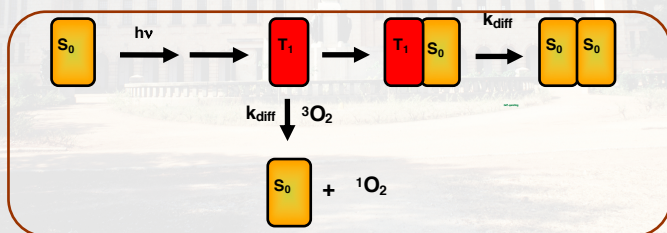
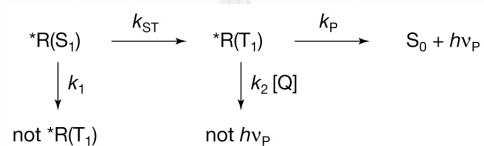


Phosphorescence from Diphenyl Polyenes



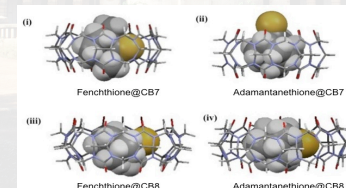
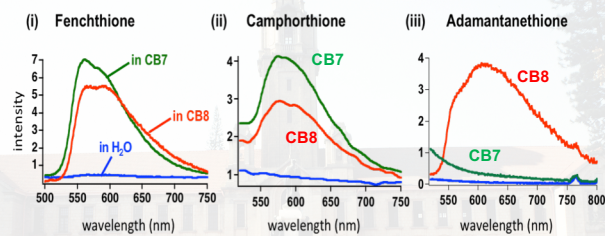
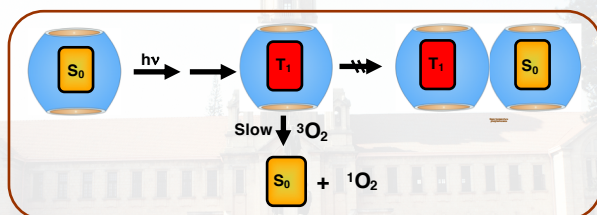
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Diffusion controlled self-quenching and oxygen-quenching in solution

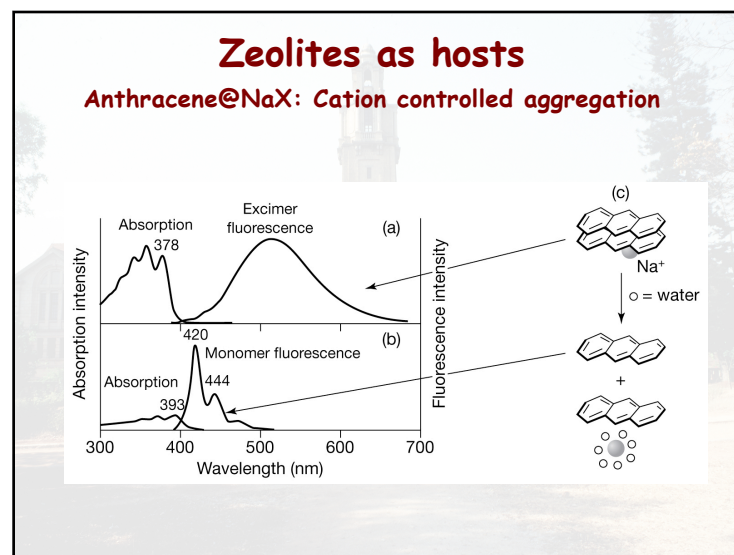
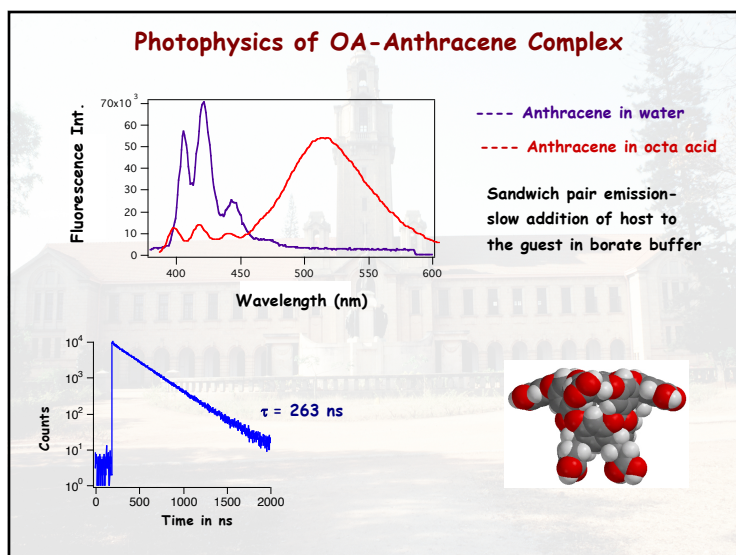
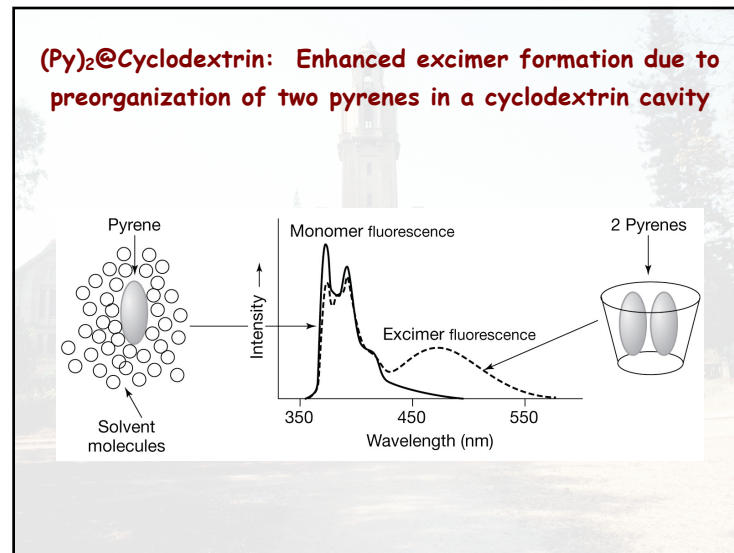
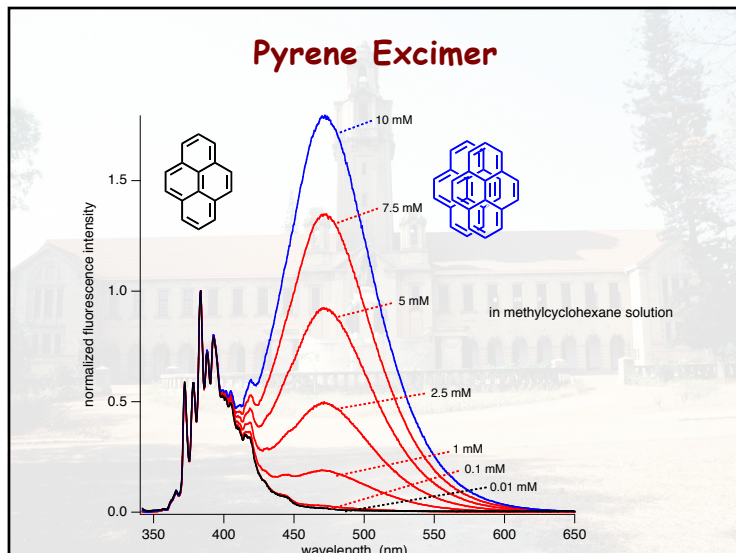


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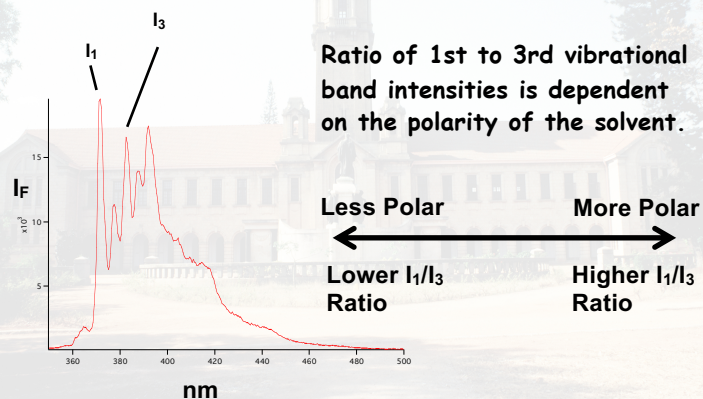
Prevention of self quenching and oxygen quenching with the help of containers



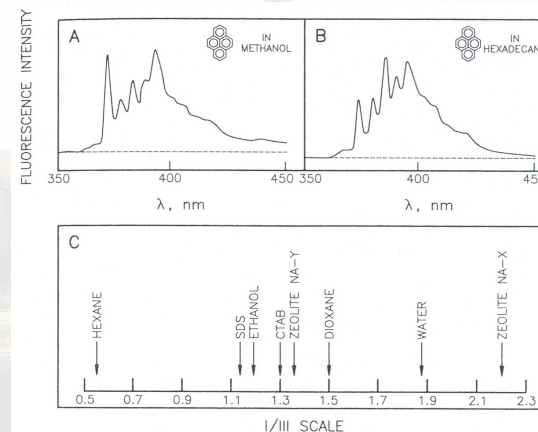
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Fluorescence Response to Solvent Polarities



Pyrene as a polarity probe



Stabilizing Unstable Molecules

Cram's "taming" of cyclobutadiene

For many years attempts to isolate cyclobutadiene in solution at room temperature failed because one diene undergoes a very rapid Diels-Alder reaction with a second diene molecule (a dimerization)



Cram's idea was to synthesize cyclobutadiene in a host system that would provide supramolecular steric hindrance to prevent dimerization

Cram's breakthrough publication: "The Taming of Cyclobutadiene", Angew. Chem. 30, 1024 (1991)

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International Edition in English

30/8 1991

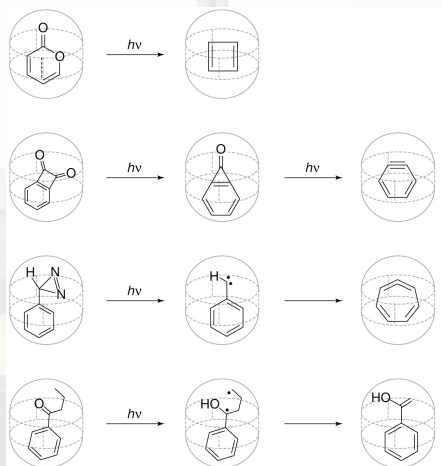
The Taming of Cyclobutadiene**

By Donald J. Cram*, Martin E. Tanner, and Robert Thomas

Cyclobutadiene, C_4H_4 , is the most reactive of organic molecules in its ability to dimerize, undergo Diels-Alder reactions, and undergo other reactions. No other organic compound combines such a strong tendency to react with other species, with such a propensity for dimerization.

** See also: Cram, D. J., Tanner, M. E., and Thomas, R., Angew. Chem. 1991, 103, 1024.

Stabilizing Unstable Molecules



Stabilizing Reactive Intermediates

