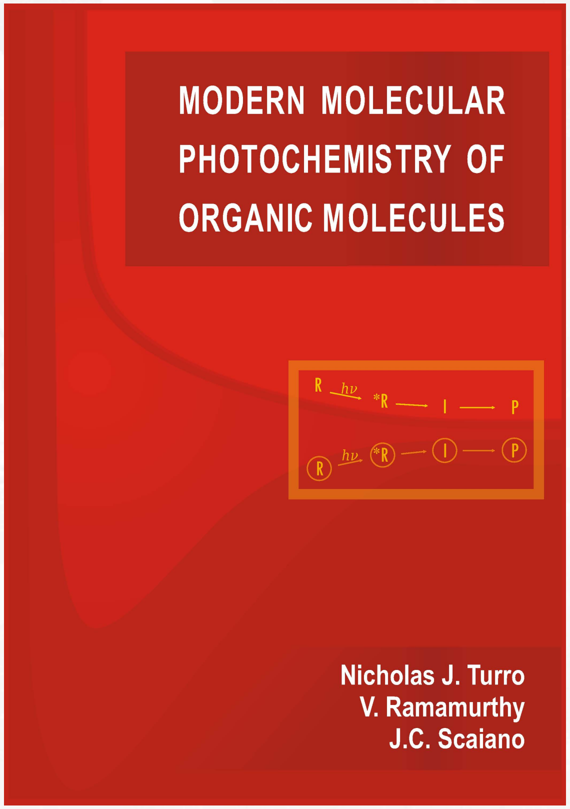
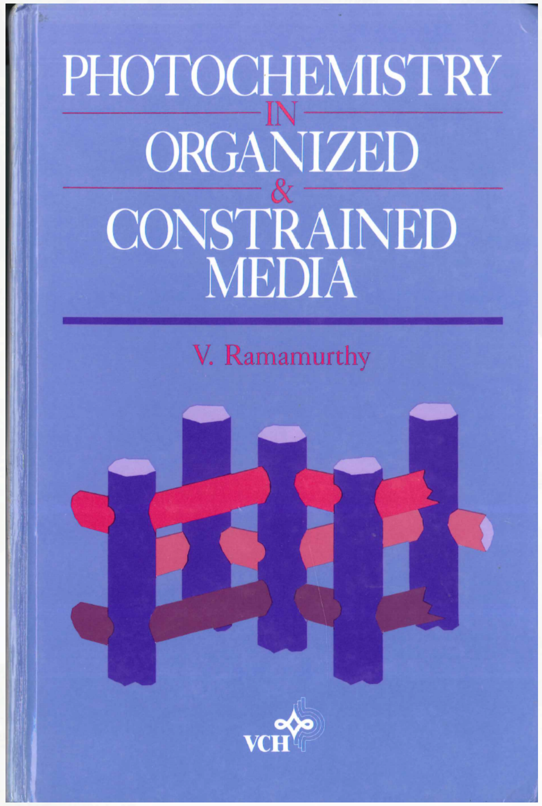
Supramolecular Photochemistry
Introduction and Photophysics

Reference books

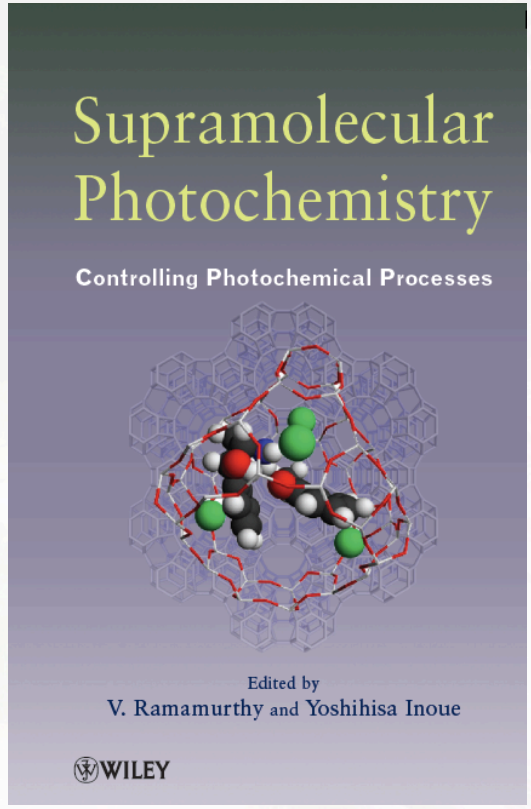


2010

Chapter 13

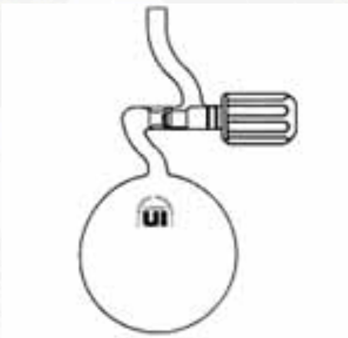


1991

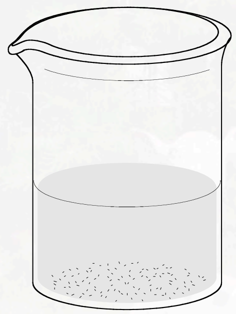


2011

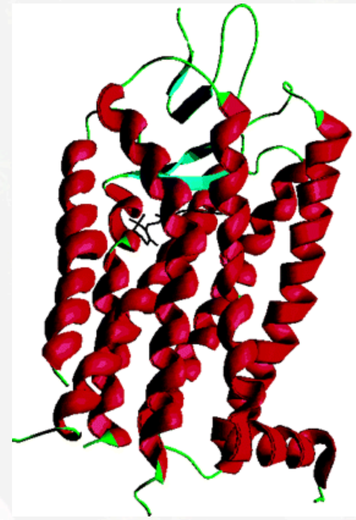
Medium Matters



Gas phase



Solution
(solvent + solute)

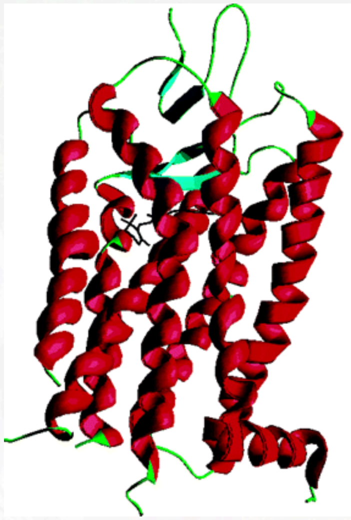


Rhodopsin

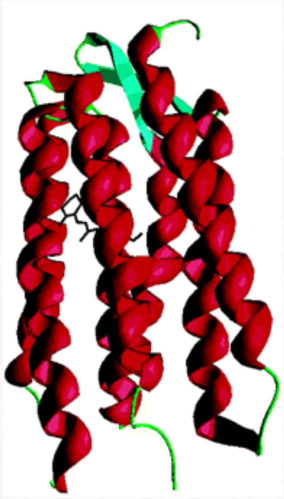
Increasing selectivity

How do biological media enforce selectivity?

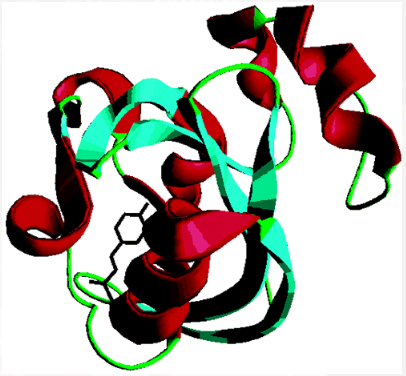
Highly selective geometric isomerization occurs within a protein medium



Rhodopsin



Bacteriorhodopsin



Photoactive yellow protein

Green fluorescent protein

How do a biological media enforce selectivity?

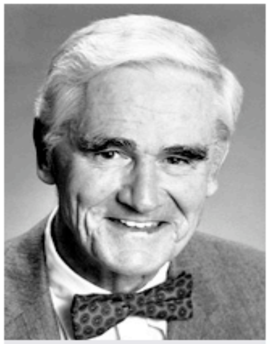
- by restricting the rotational and translational motions
- by pre-organizing the reactants
- by controlling the extent and the location of free space within a reaction cavity

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

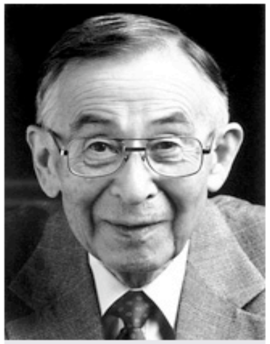
Jean-Marie Lehn

1/3 of the prize

France

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

b. 1939



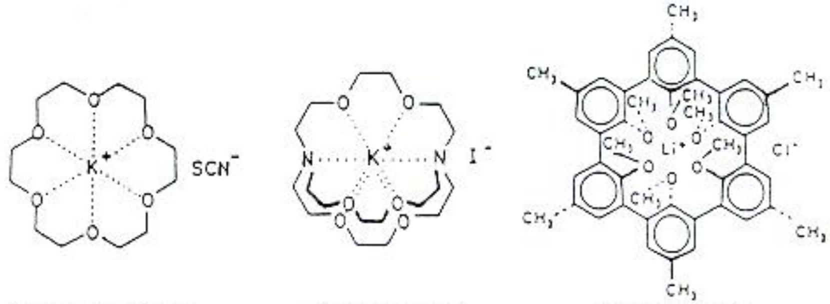
Charles J. Pedersen

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

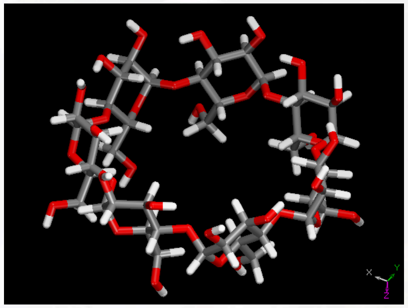
Supramolecular Photochemistry

R. Breslow

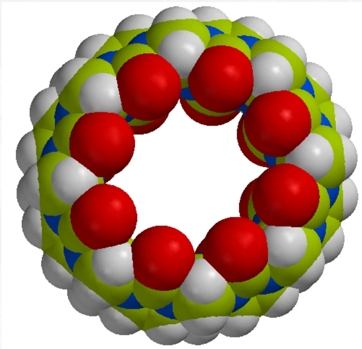
J. M. Lehn

N. J. Turro

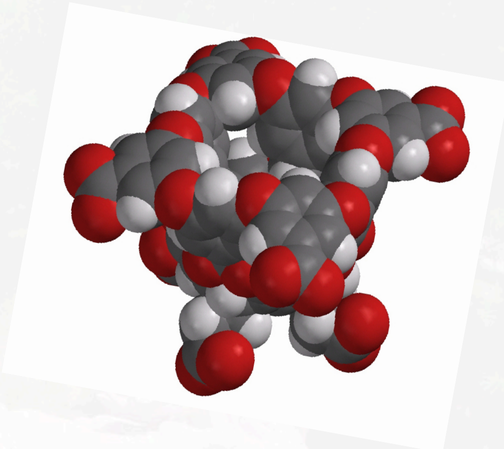
Supramolecular Hosts



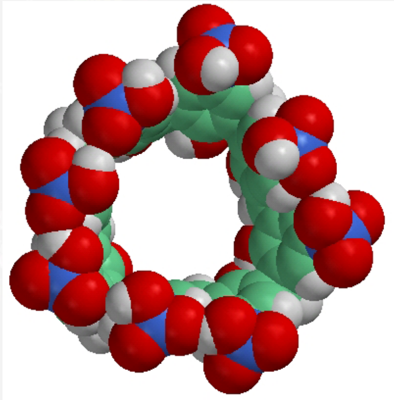
Cyclodextrins



Cucurbiturils

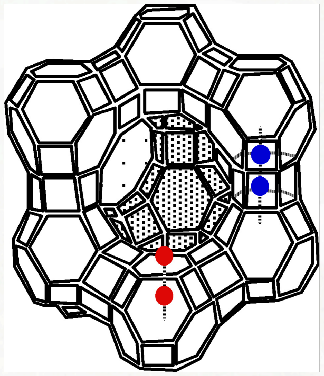


Octa acid(OA)

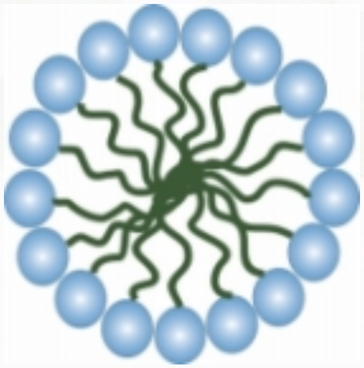


Calixarenes

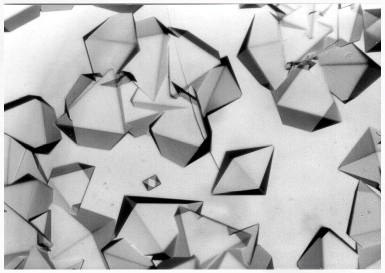
Dendrimers



Zeolites



Micelles

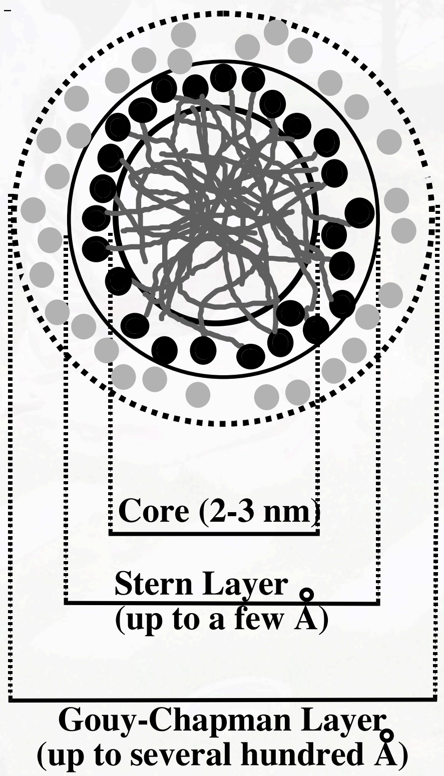


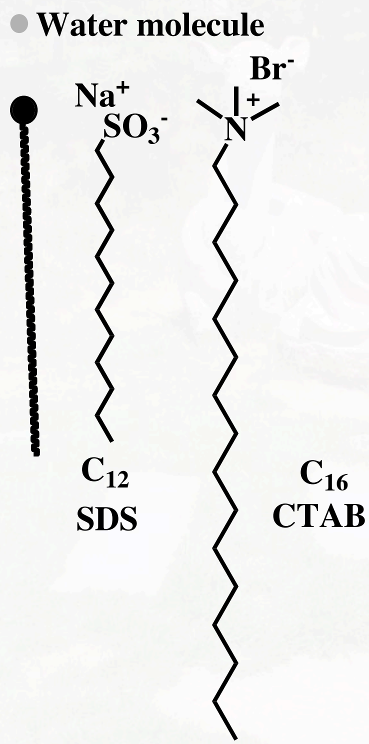
Crystals

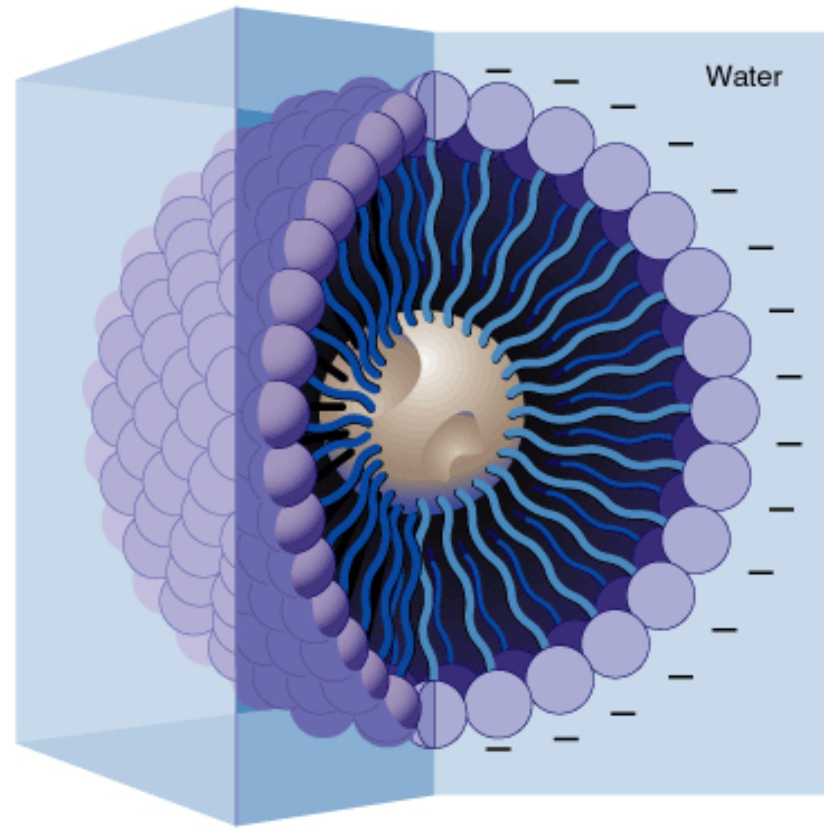
The guest@host paradigm

We'll be using this paradigm to discuss supramolecular systems

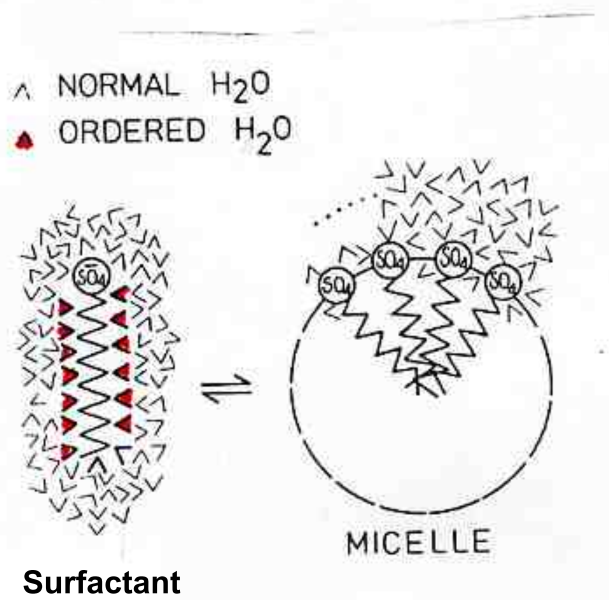
Cartoons of micelle structure







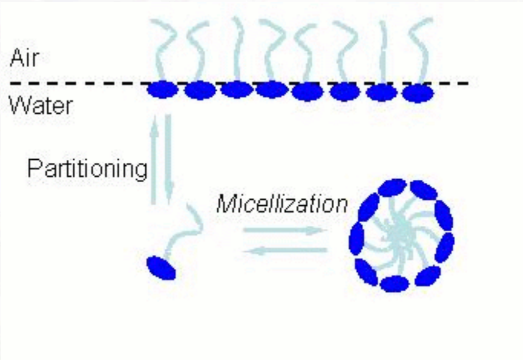
Why do micelles form at all?

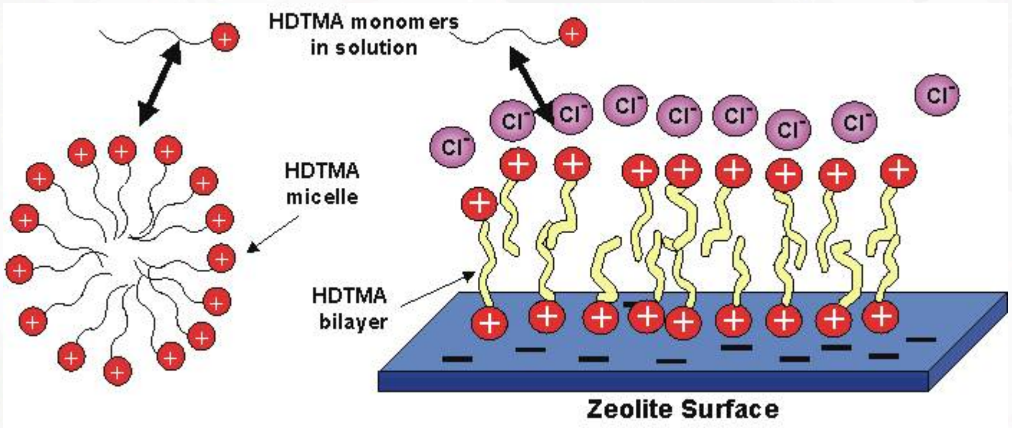


Cartoon of the hydrophobic effect: (1) water is more ordered about the surfactant monomer (left) than ordinary water causing an relative increase in water organization and a decrease;

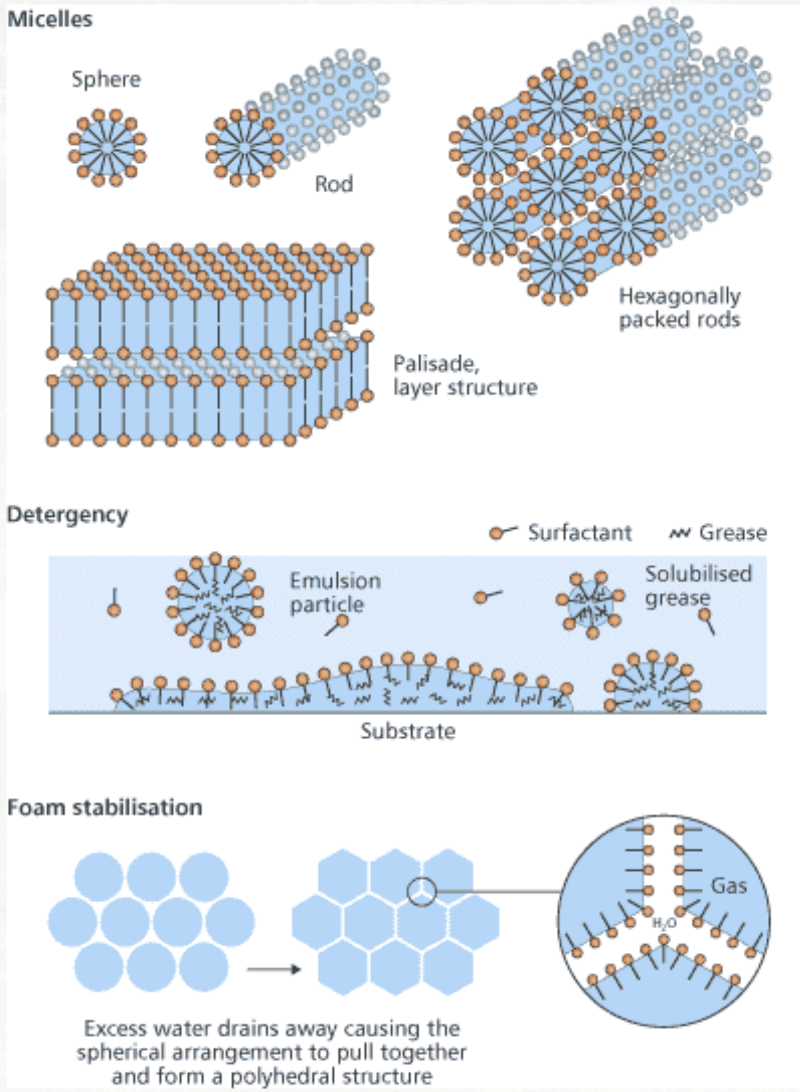
(2) Water is less ordered about the hydrophobic skin of the micelle causing a relative increase in entropy.

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

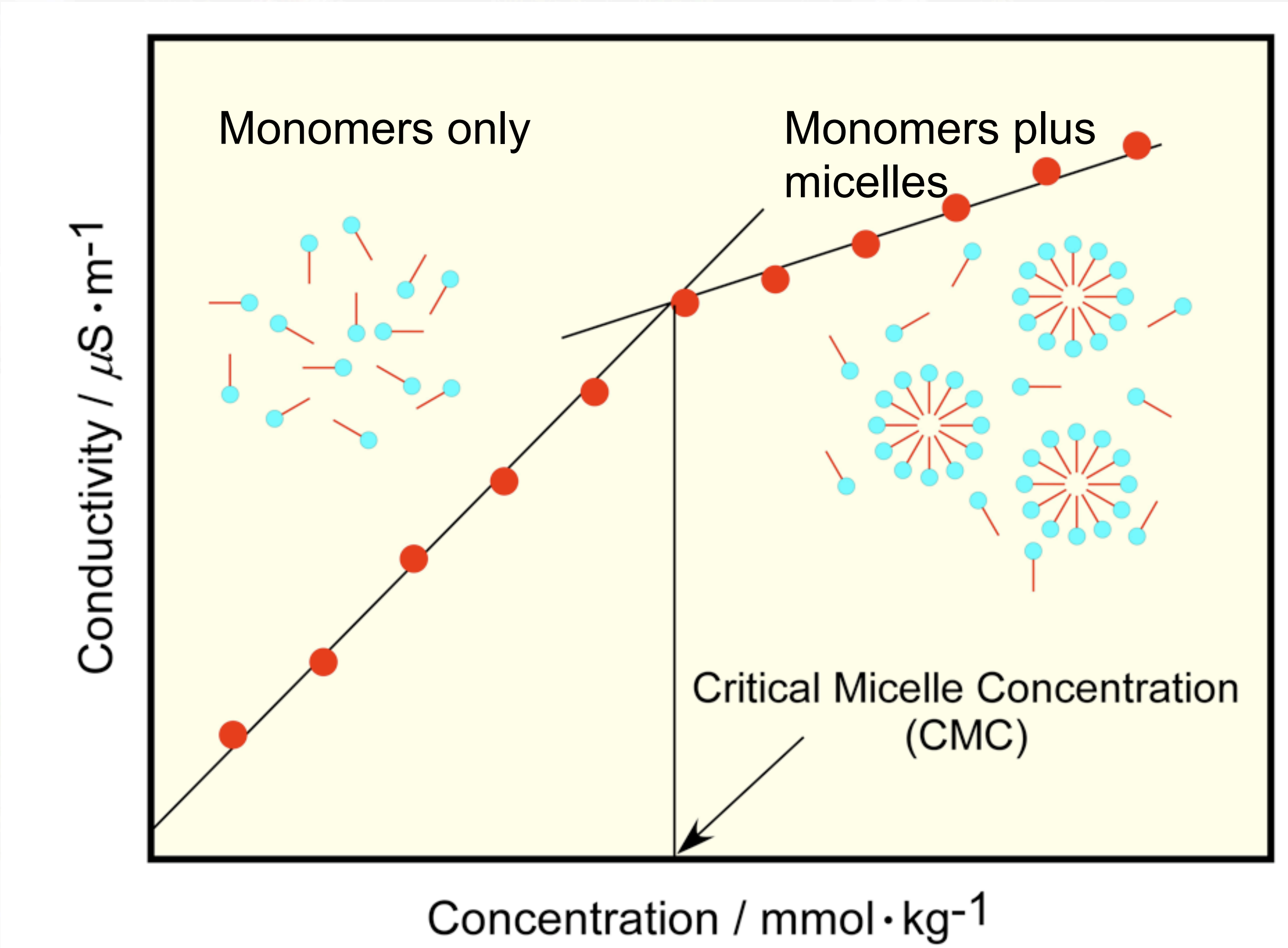




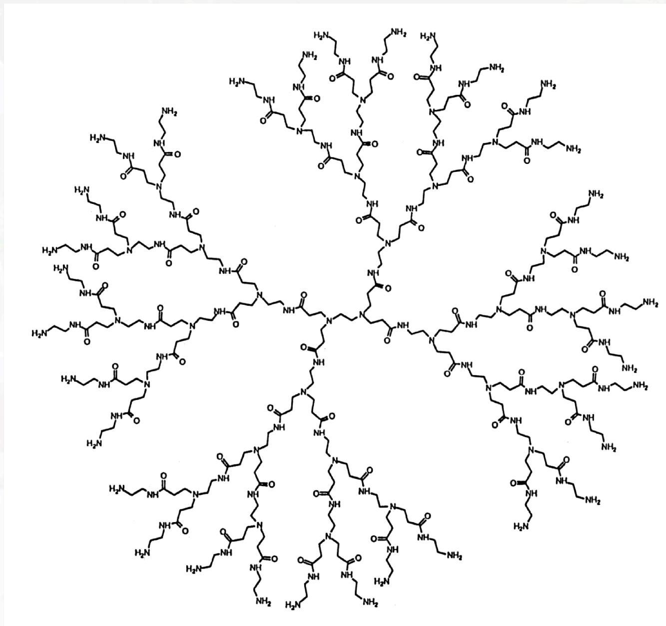
Structures formed from surfactants in aqueous solution



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

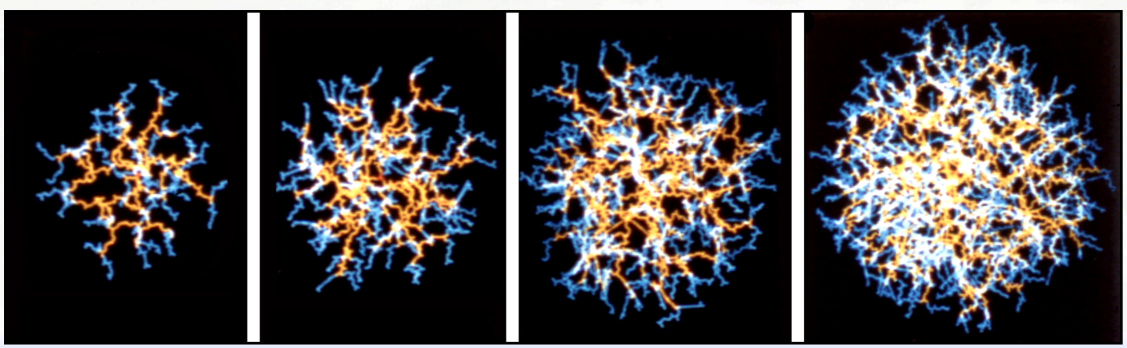


Dendrimers: covalent micelles

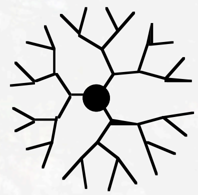


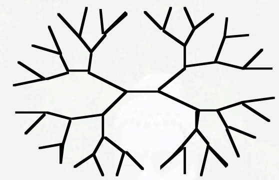
A dendrimer: a hyperbranched polymer

Generation increasing ➔

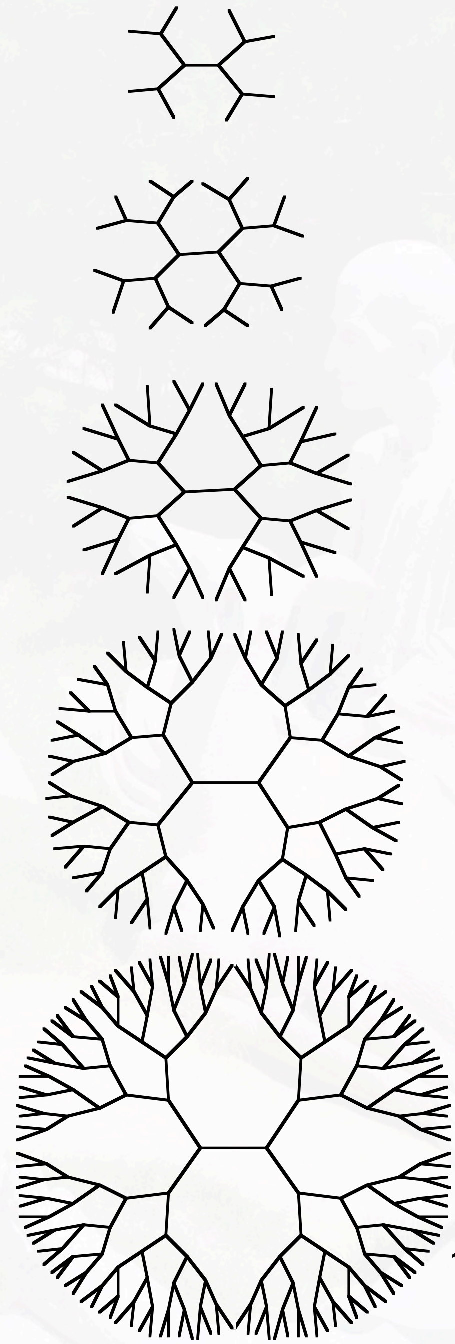


Generations of dendrimers

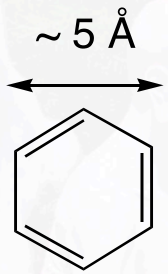


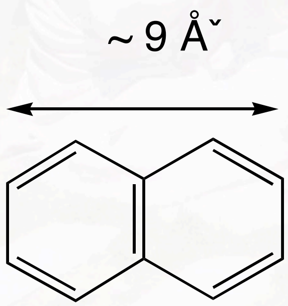


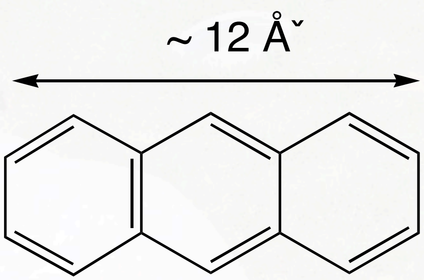
generation	surface groups	diameter (Å)	separation of the surface groups (Å)	surface groups
0.5	6	27.9	12.4	8
1.5	12	36.2	12.8	16
2.5	24	48.3	12.7	32
3.5	48	66.1	12.6	64
4.5	96	87.9	11.5	128
5.5	192	103.9	10.3	256
6.5	384	126.8	9.8	512
7.5	768	147.3	7.7	1024

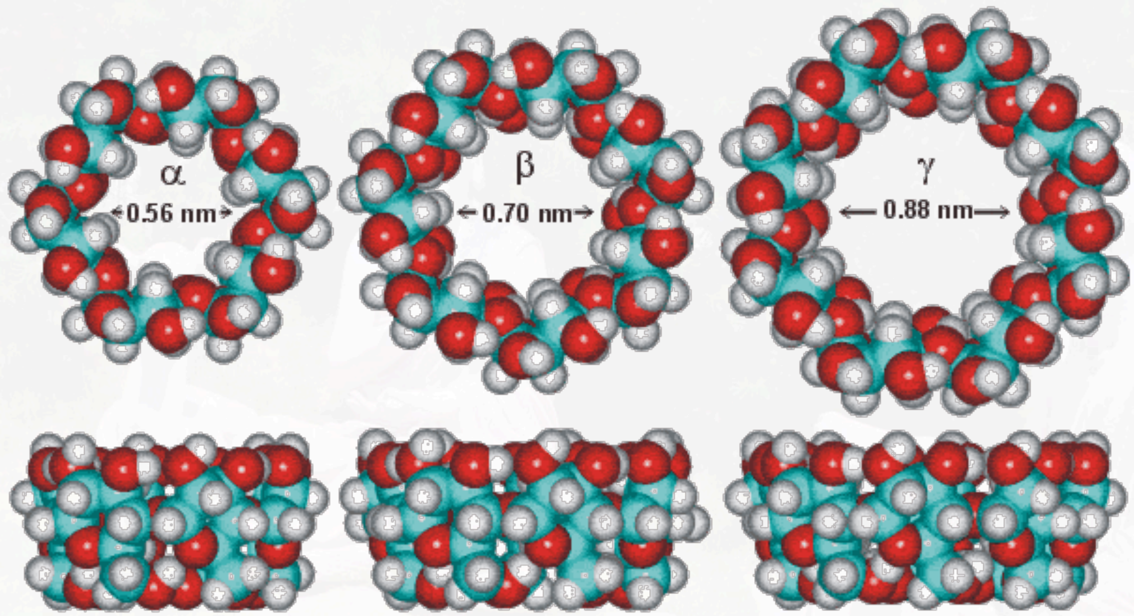


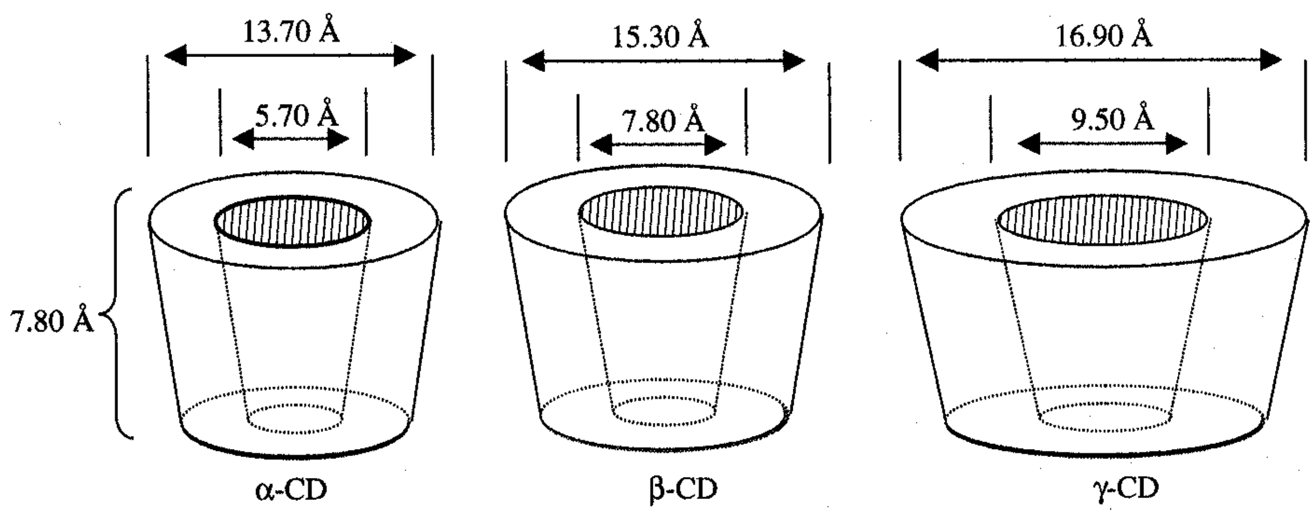
Water soluble organic hosts: Cyclodextrins



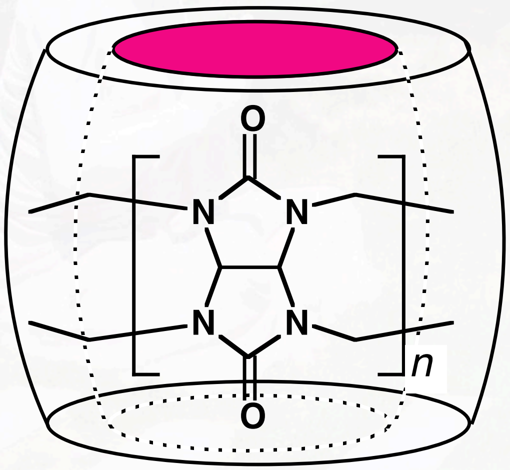








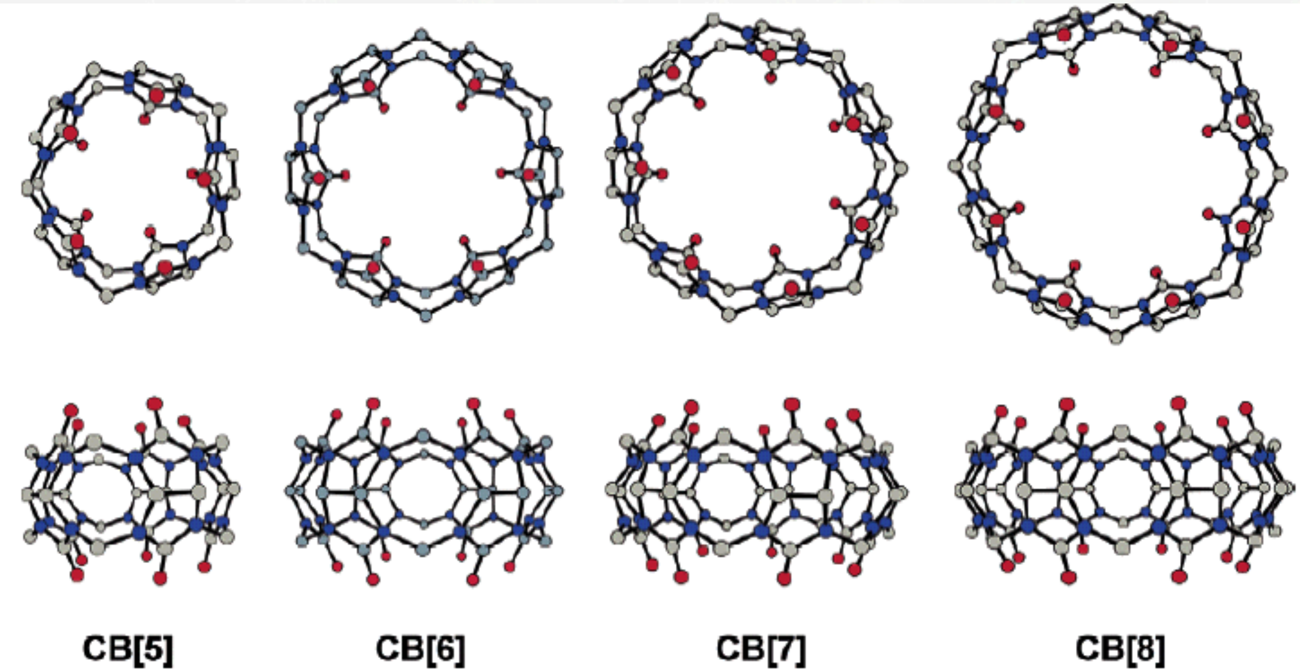
Water soluble organic hosts: Cucurbiturils



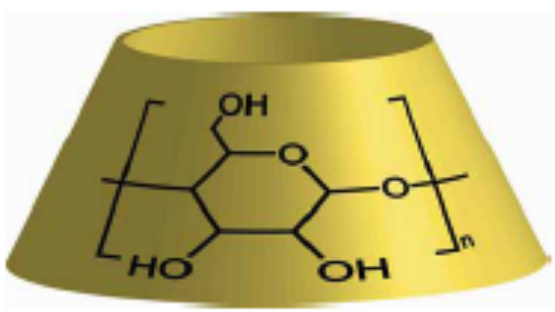
- Easily prepared by the condensation of glycoluril in acidic medium.

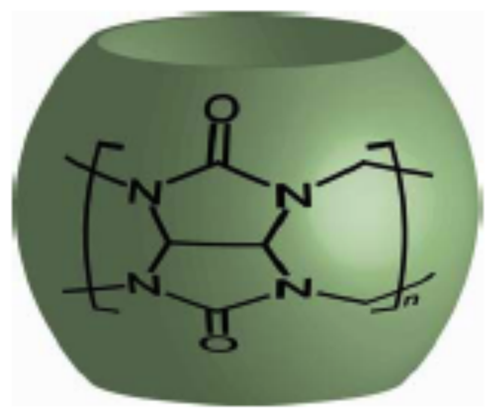
- Hexamer [CB6] known since early 1900's, first characterized in 1981.

- Kim and coworkers pioneered the synthesis and isolation of the higher CBs [*n* = 7, 8, 10] in 2000.

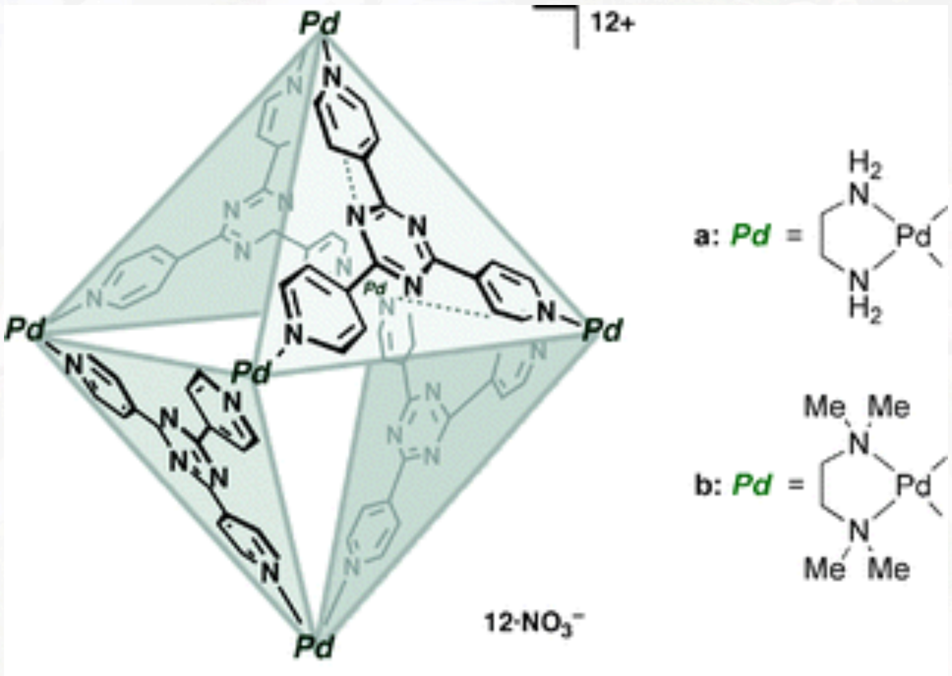


X-ray crystal structures of CB[n] (n = 5−8). Color codes: carbon, gray; nitrogen, blue; oxygen, red.





Water soluble inorganic host: Fujita's Pd host



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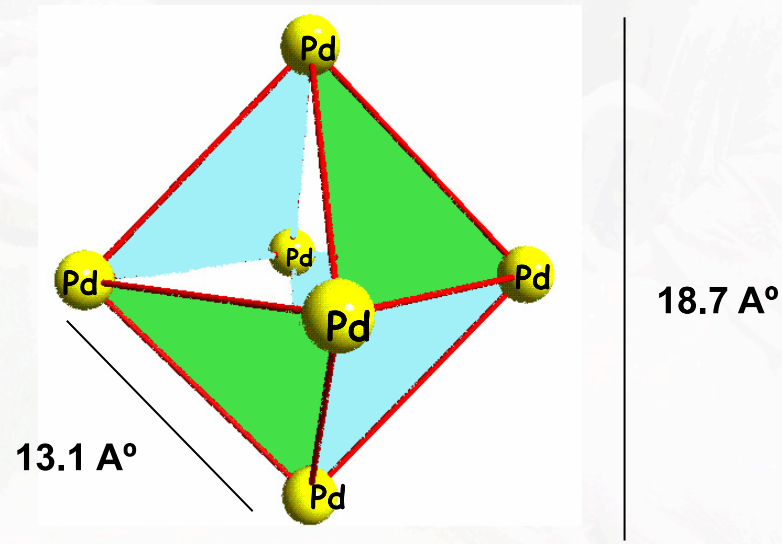
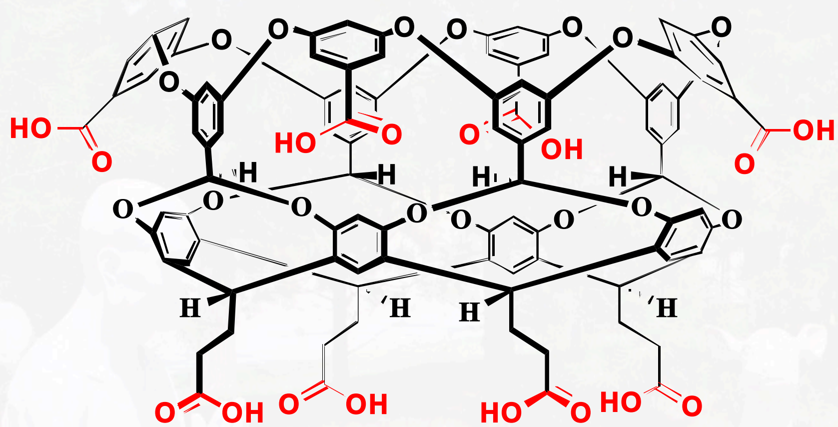
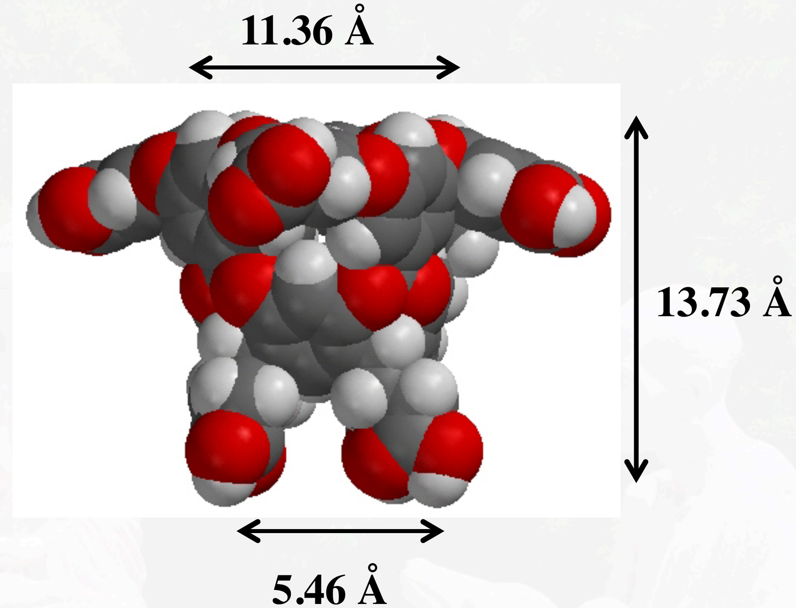
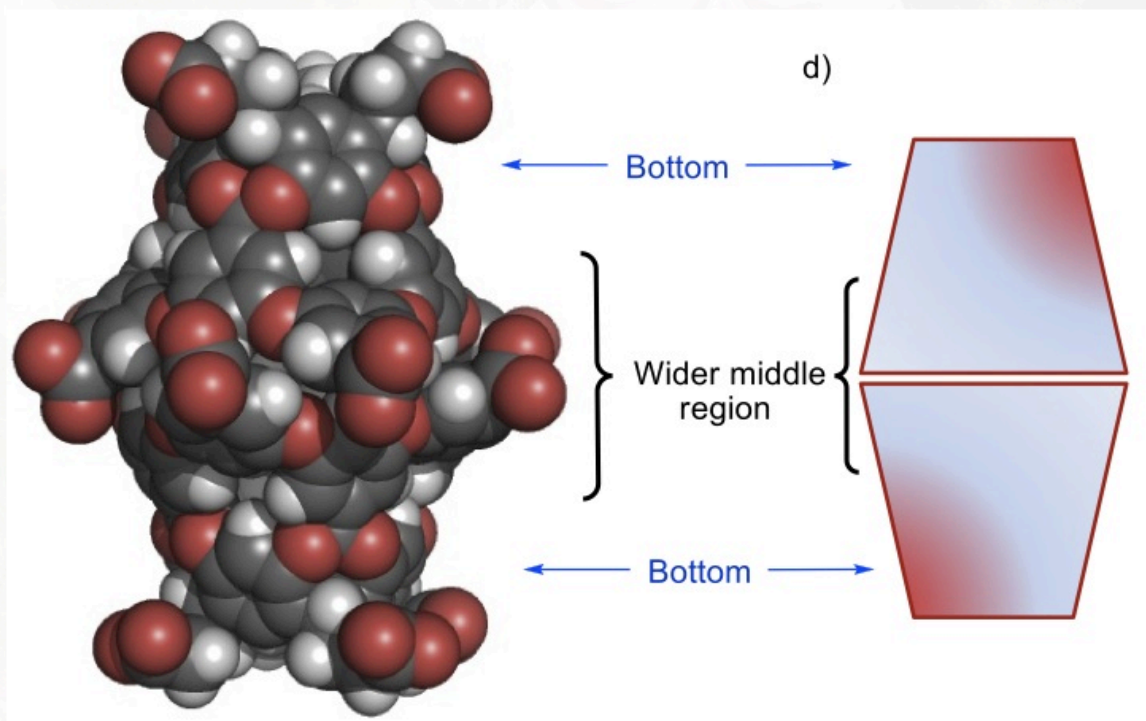
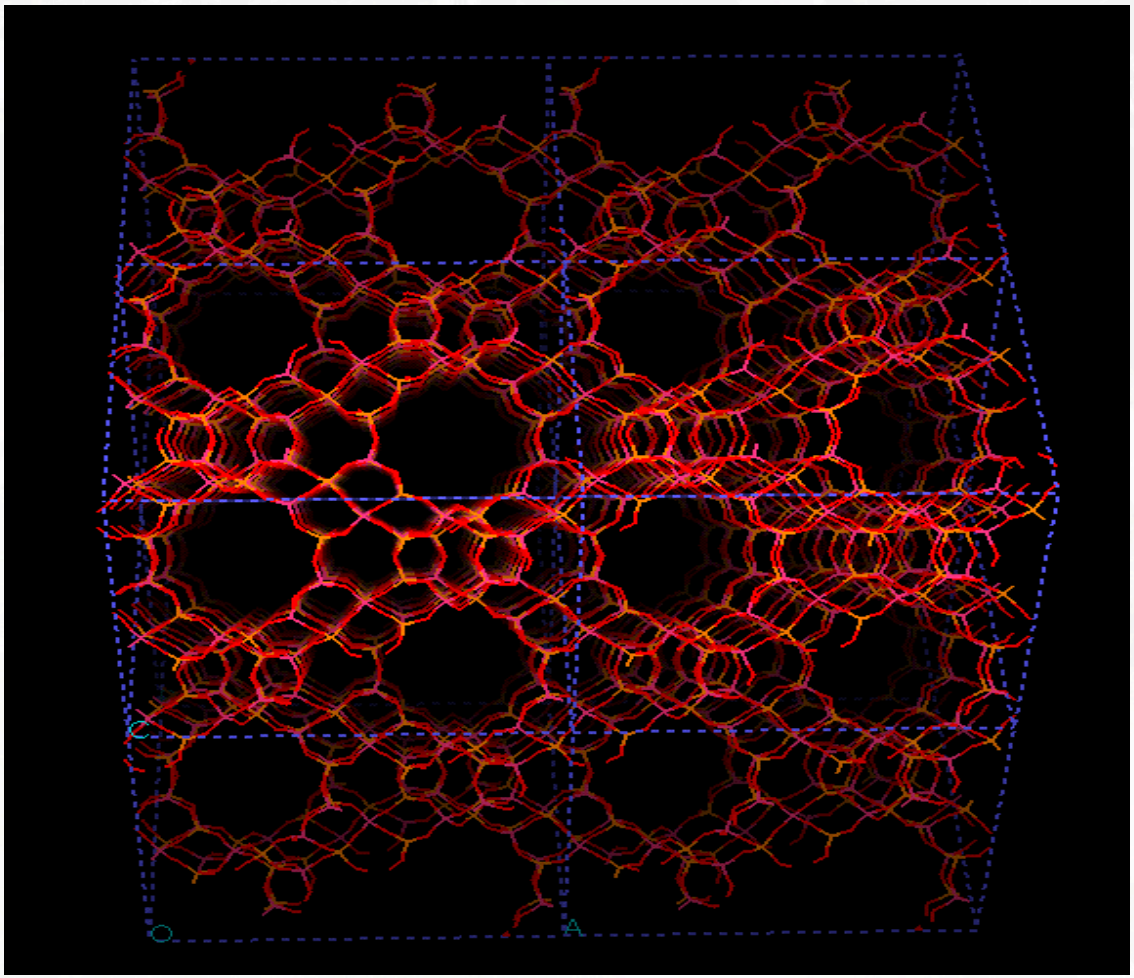





11.36 Å
13.73 Å
5.46 Å


d)
Bottom
Wider middle region
Bottom

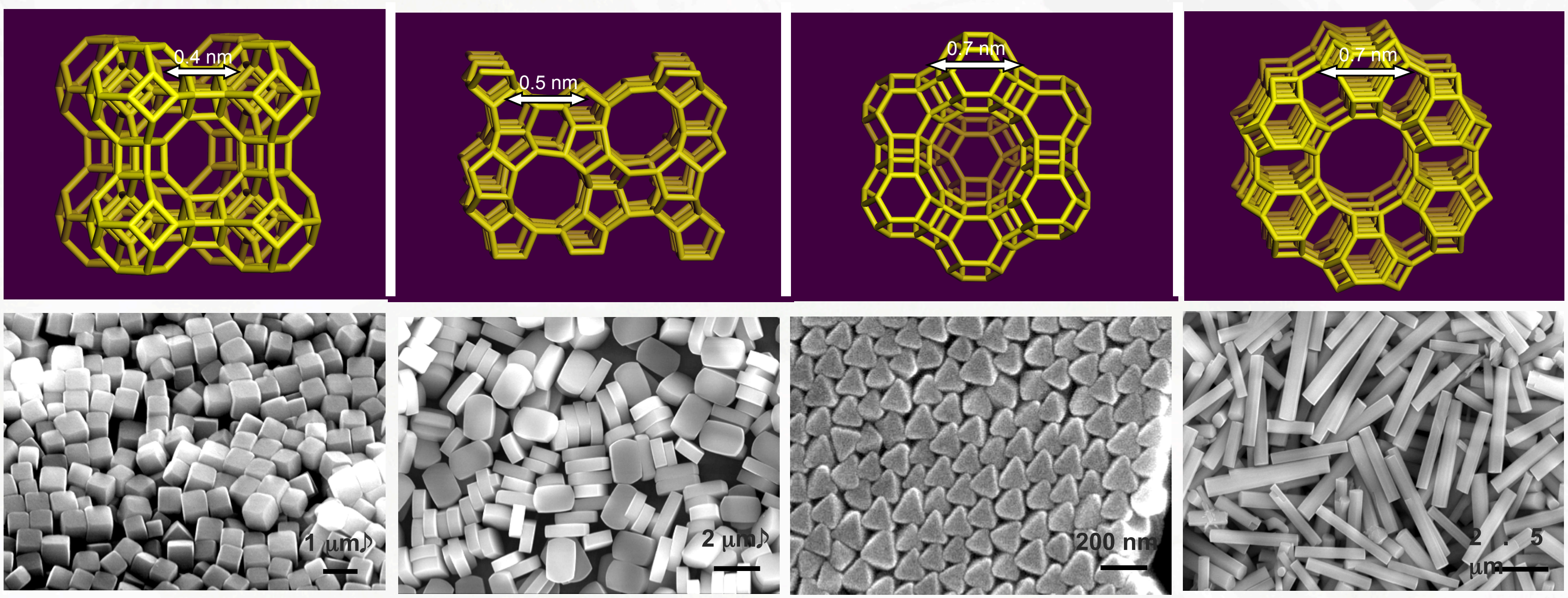
Porous Solids: Zeolites



Zeolites: Sythetic

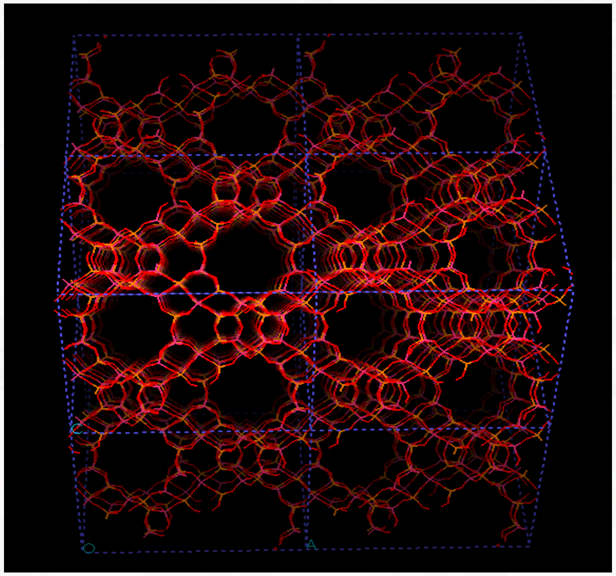
More than 65% of the earth's crust consists of 3D crystalline polyaluminosilicates (3D-CPAS): feldspar, zeolite, and ultramarine. Zeolite is a class of 3D-CPAS having nanochannels and nanocavities.

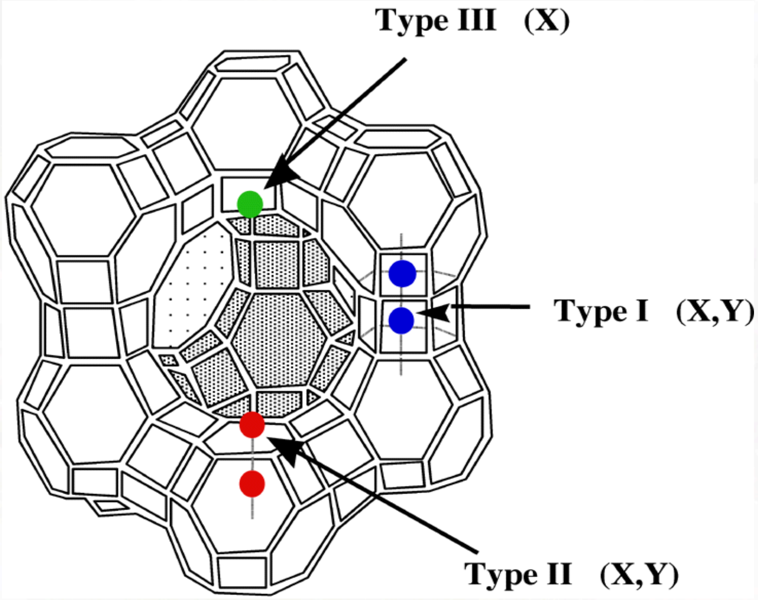
Zeolite-A **ZSM-5** **Zeolite-X or Y** **Zeolite-L**



Characteristics of Faujasites (Zeolites)

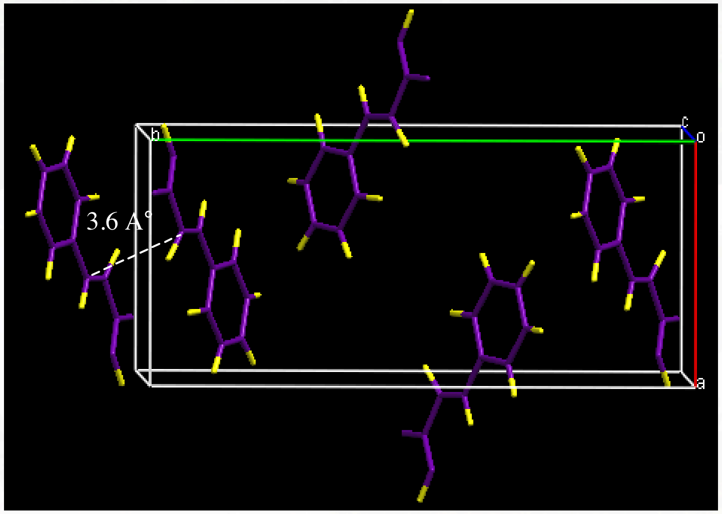
$M_x(AlO_2)_x\,(SiO_2)_y.ZH_2O$

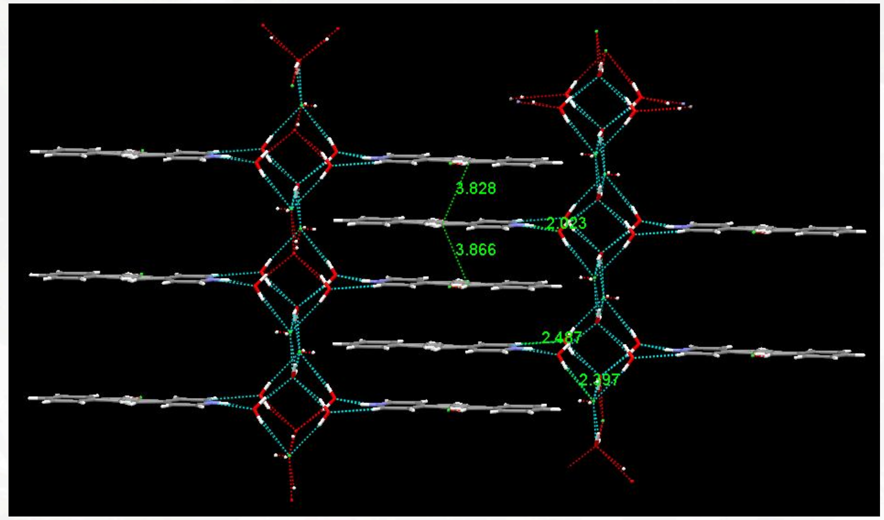


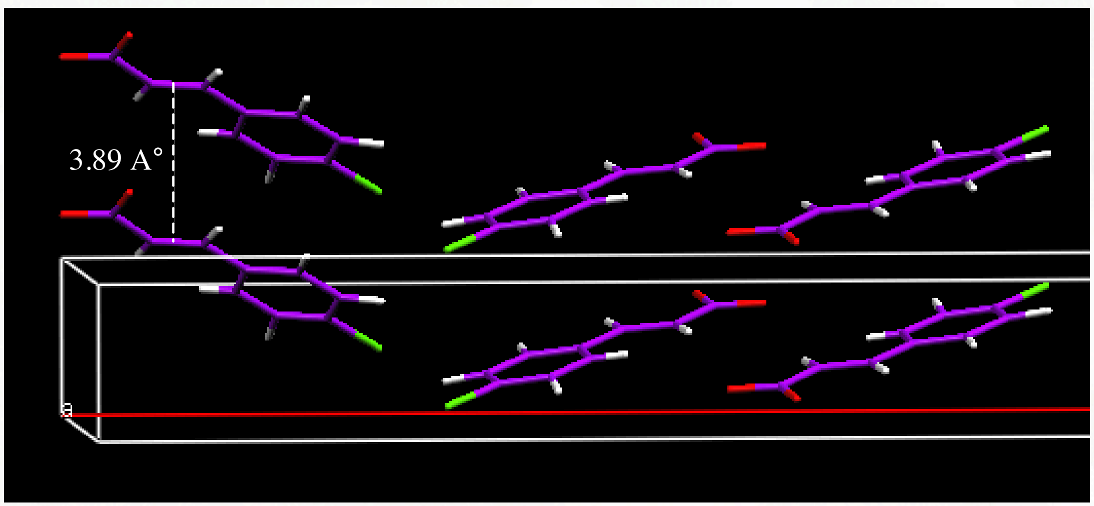


- Microporous solid
- Large surface area
- Well defined channels/cages
- Si/Al ratio = 2.4
- Type I - 4 cations /supercage
- Type II- 4 cations /supercage

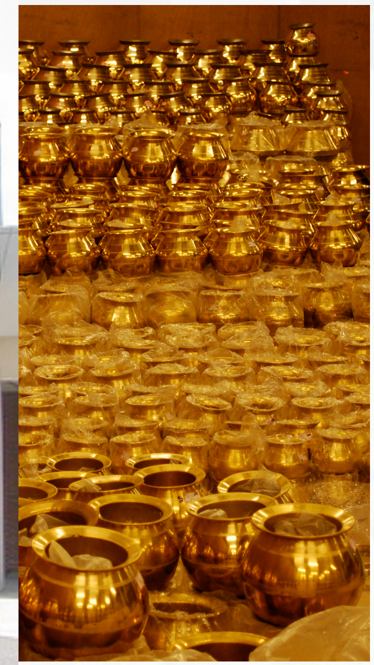
The crystal as a supramolecular entity







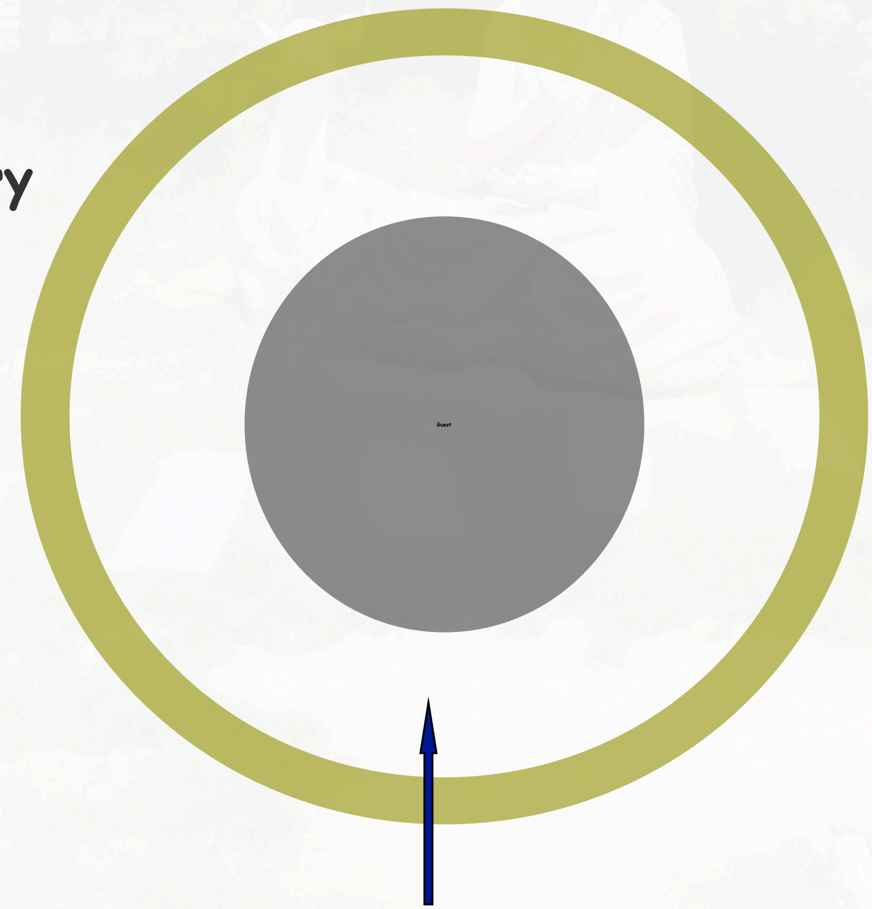
Common Containers



Supramolecular Containers

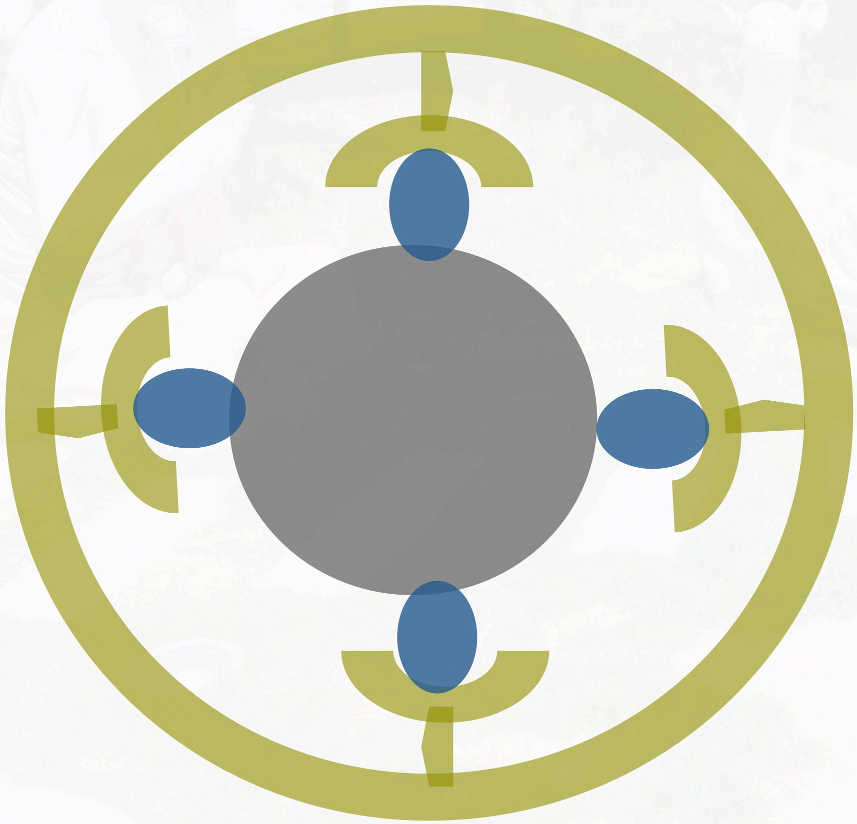
Reaction cavity

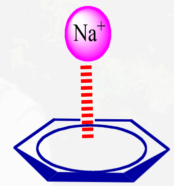
Boundary



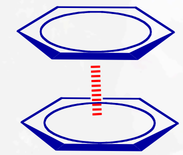
Free Space

Role of Weak Interactions

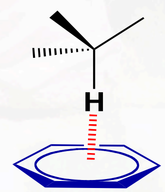




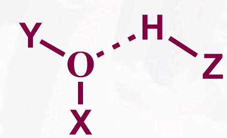
Cation---π



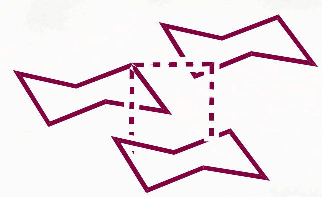
π---π



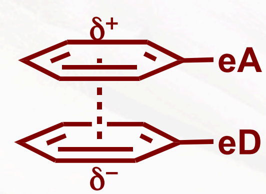
C–H---π



Hydrogen bond



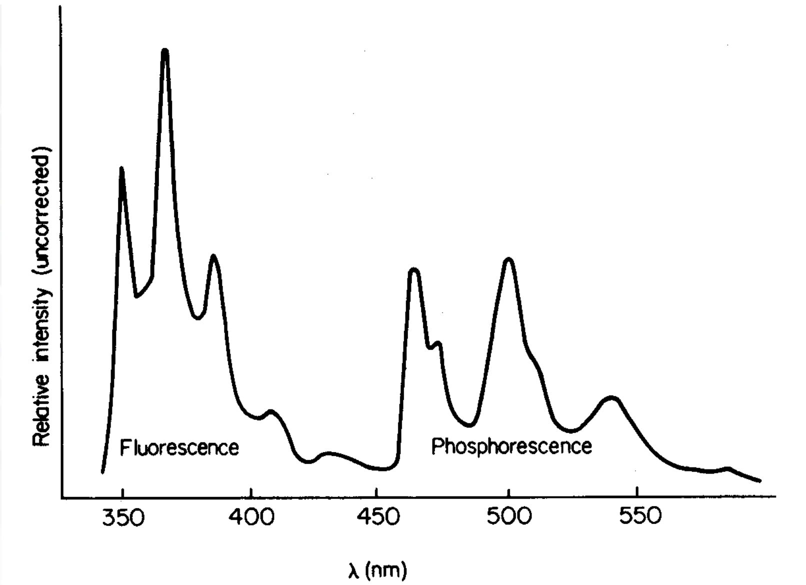
van der Waals

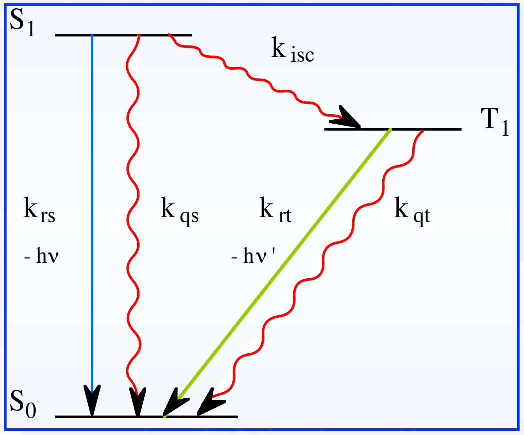


Charge transfer

Supramolecular Photophysics

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



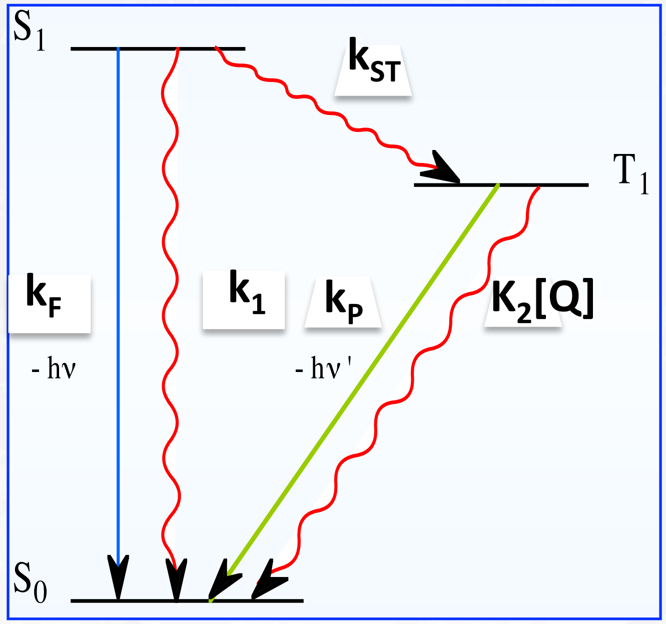


Fluorescence:

- 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



$$
\begin{tikzcd}
{}^*R(S_1) \arrow[r, "k_{ST}"] \arrow[d, "k_1"] & {}^*R(T_1) \arrow[r, "k_P"] \arrow[d, "k_2\,[Q]"] & S_0 + h\nu_P \\
\text{not } {}^*R(T_1) & \text{not } h\nu_P &
\end{tikzcd}
$$

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

$$^{*}R(S_1) \xrightarrow{k_{ST}} {}^{*}R(T_1)$$

$$^{*}R(S_1) \overset{k_1}{\nrightarrow} R(S_0)$$

Heavy atom effect mainly on k_{ST} so that $k_{ST} > k_1$

Make more triplets through the heavy atom effect

Stage 2

$$^{*}R(T_1) \xrightarrow{k_P} R(S_0) + h\nu_P$$

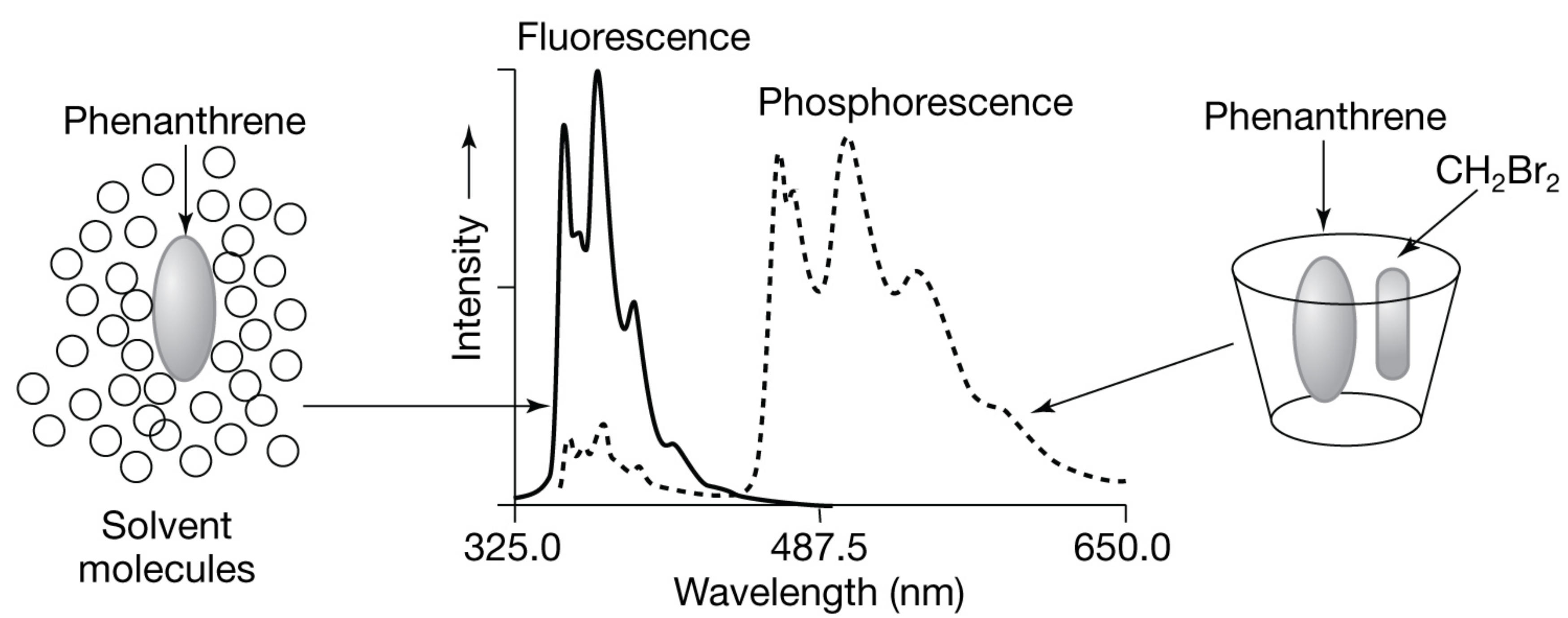
$$^{*}R(T_1) \overset{k_2[Q]}{\nrightarrow} R(S_0)$$

Heavy atom effect mainly on k_P so that $k_P > k_2[Q]$

Make triplets emit faster in competition with quenching processes

Cyclodextrins as hosts

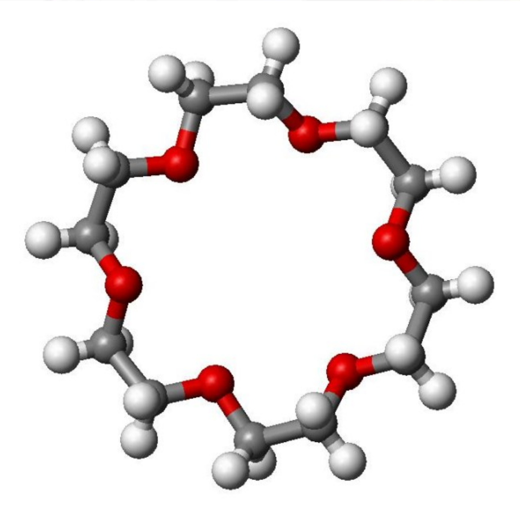
Phenanthrene@Cyclodextrin: effect of CH_2Br_2 as co-guest

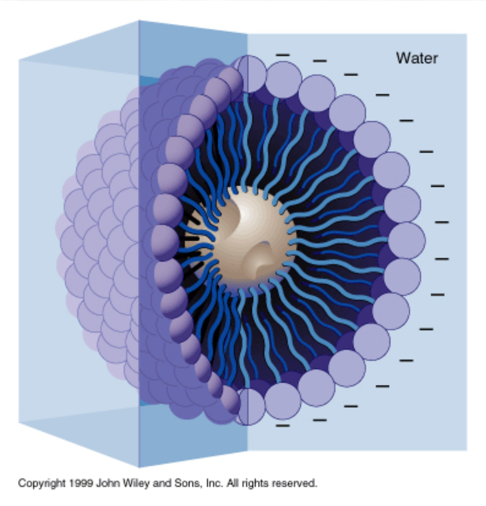


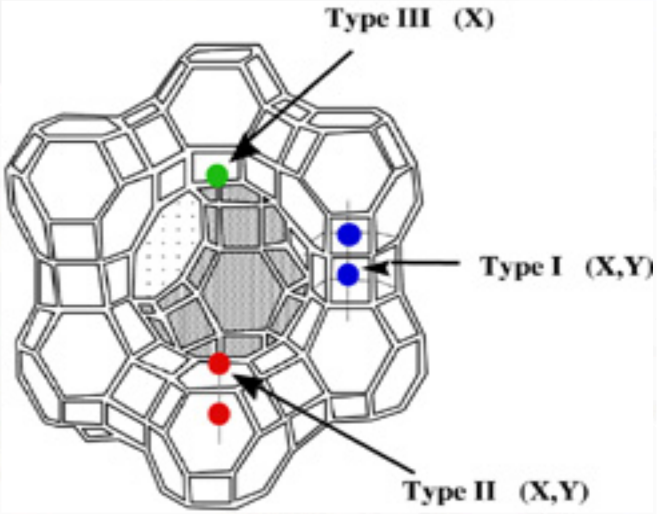
Induced Intersystem Crossing Depends on the SOC: Cations as the heavy atom pertuber

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 1.00×10^{-4} *F*)

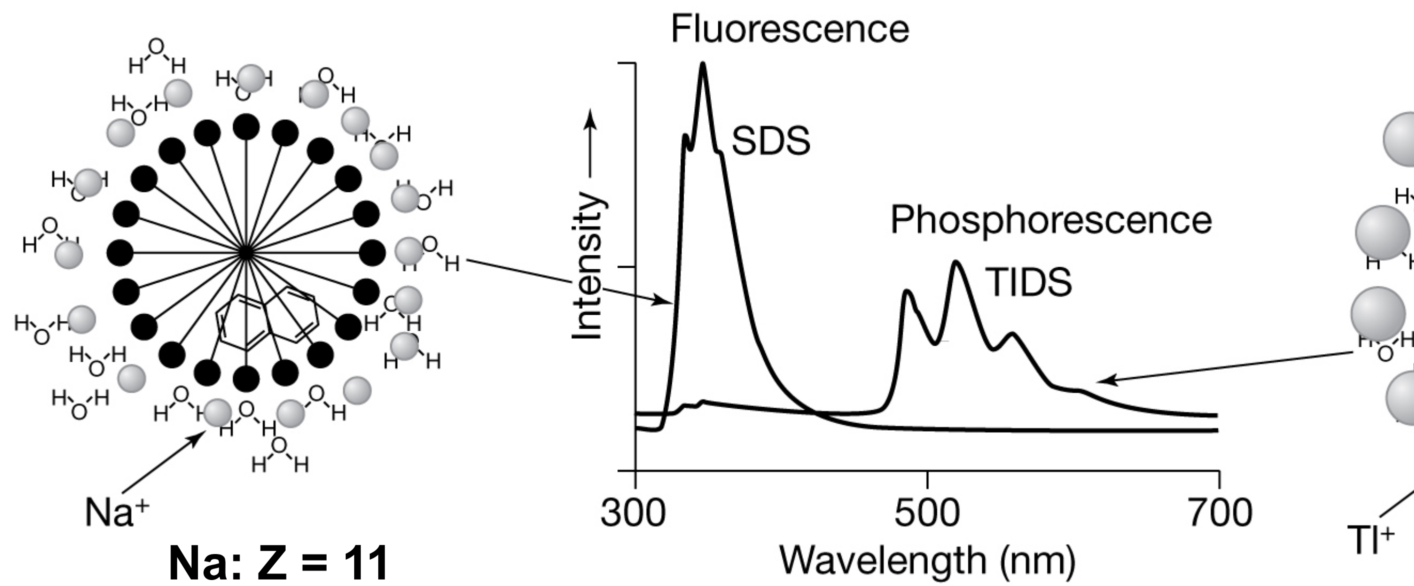
Salt added	$10^{-6}k_f$	$10^{-6}k_{nr}$	$10^2 k_p$[d]	k_{dt}[d]
None	3.1	25	8.7	0.37
NaCl	2.6	32	6.7	0.41
KCl	2.3	35	5.8	0.39
RbCl	1[e]	52	12.	0.50
CsCl	1[e]	670	81.	1.57

[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.

1

Micelles as hosts

Naphthalene@SDS micelle: effect of heavy atom counterions

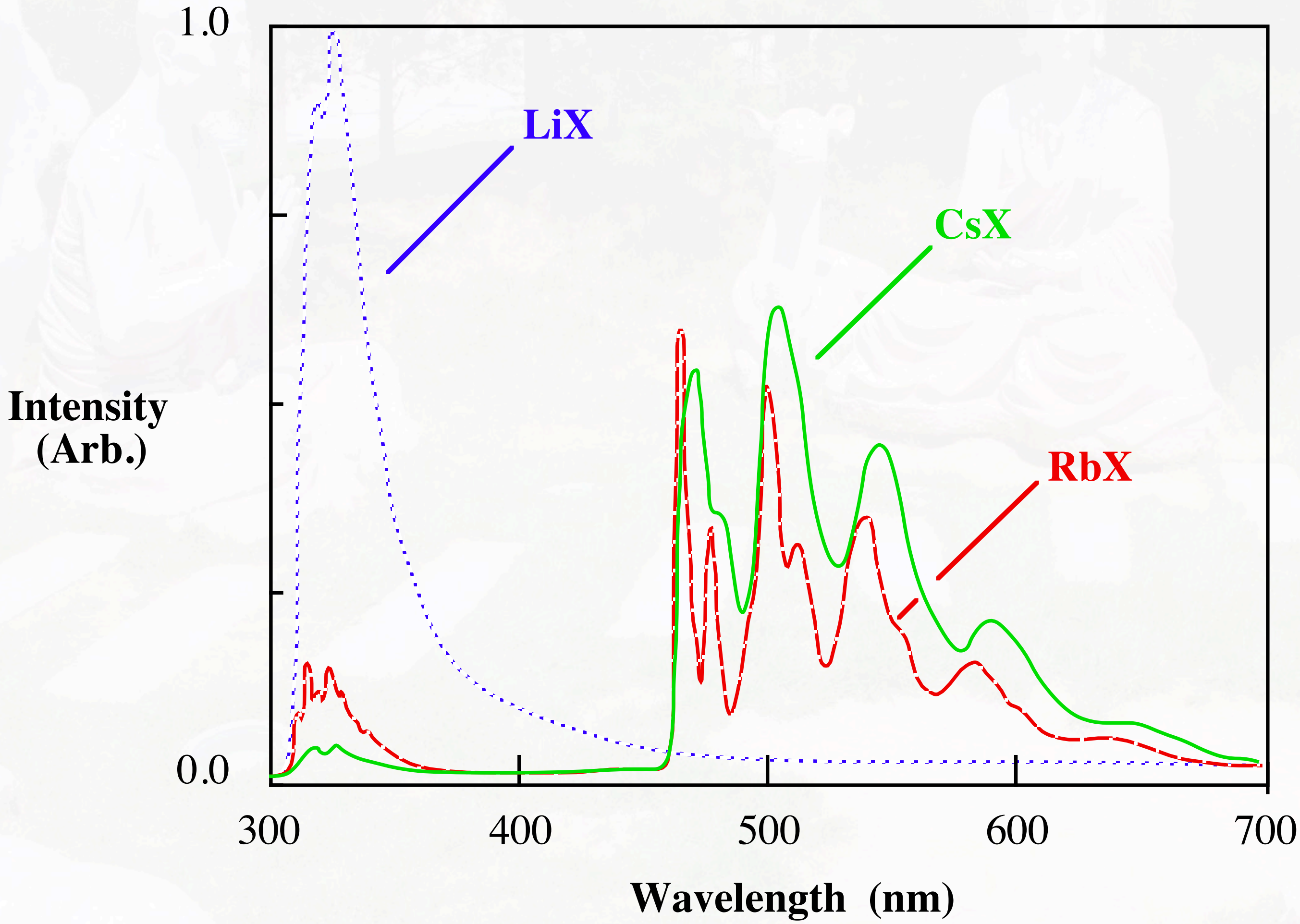


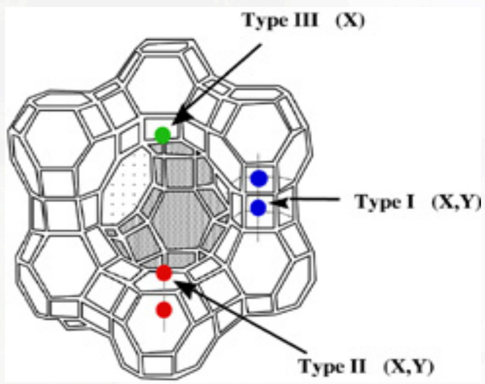
Na: Z = 11

Tl: Z = 81

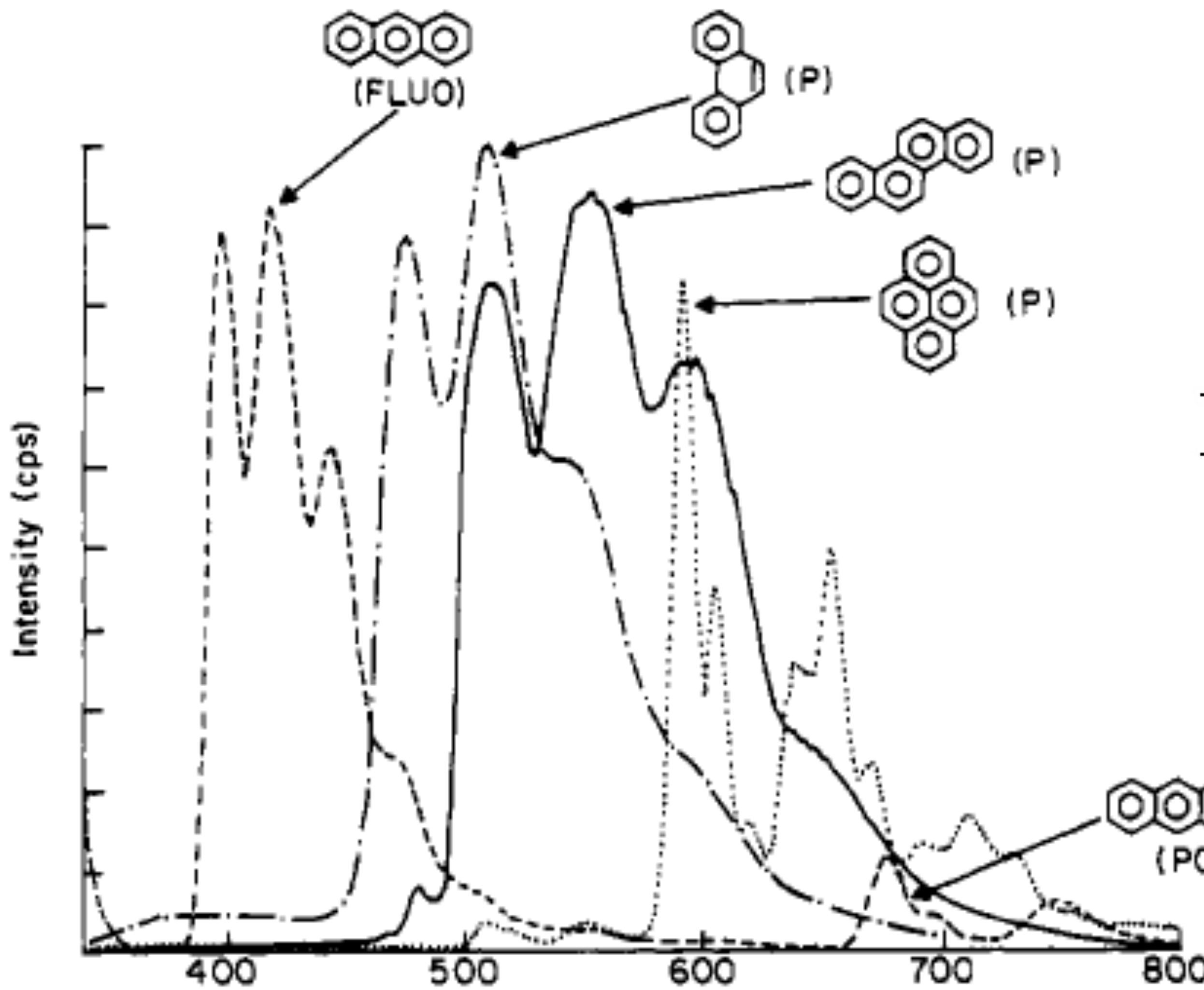
Heavy atom produces more triplets and the triplets produced phosphoresce at a faster rate

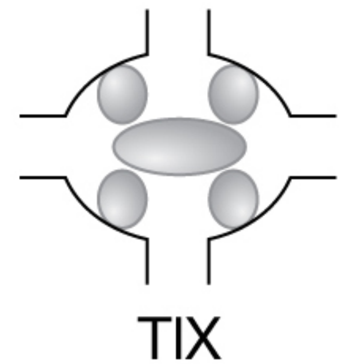
Emission Spectra of Naphthalene Included in MY Zeolites



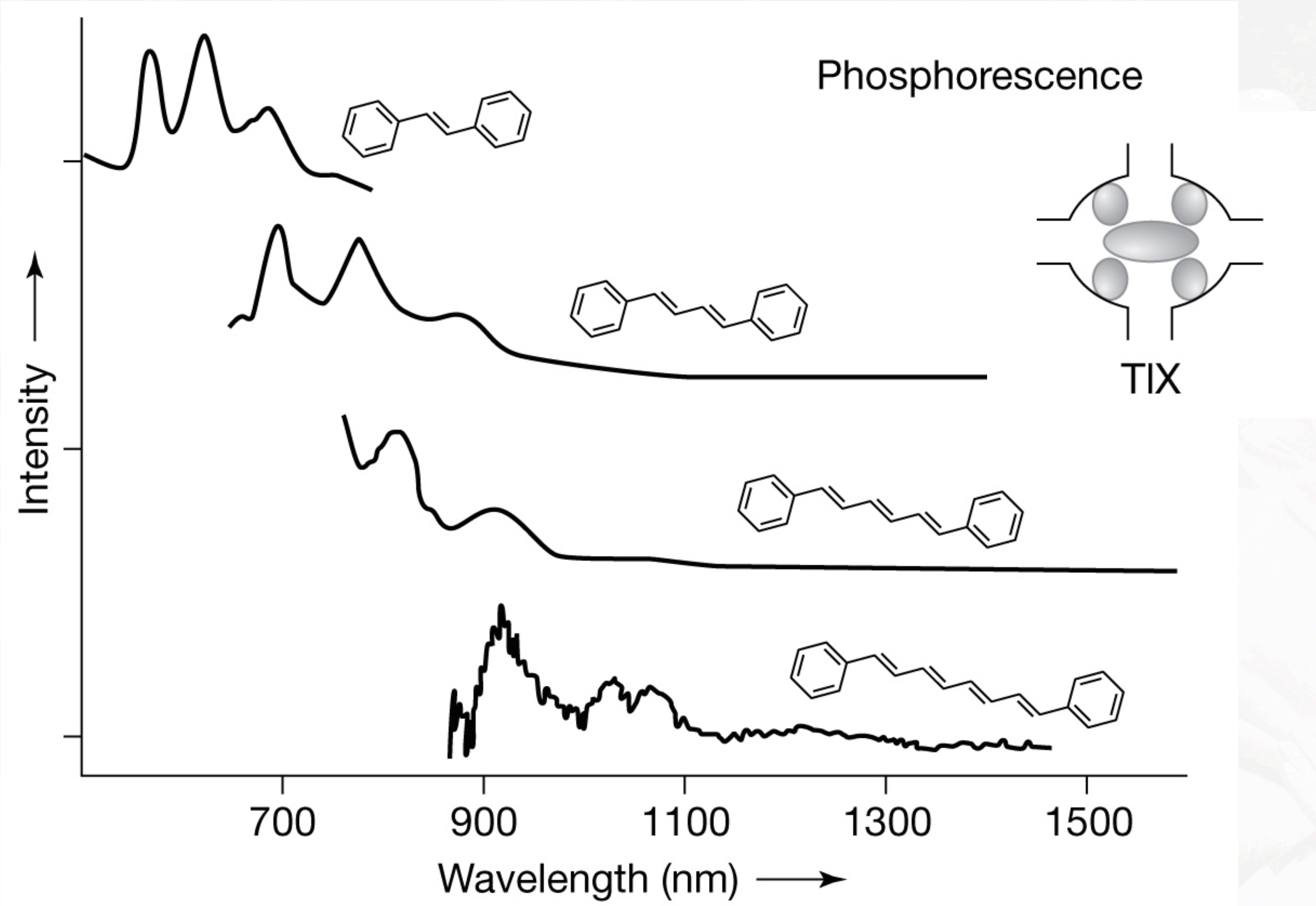


Room temperature phosphorescence



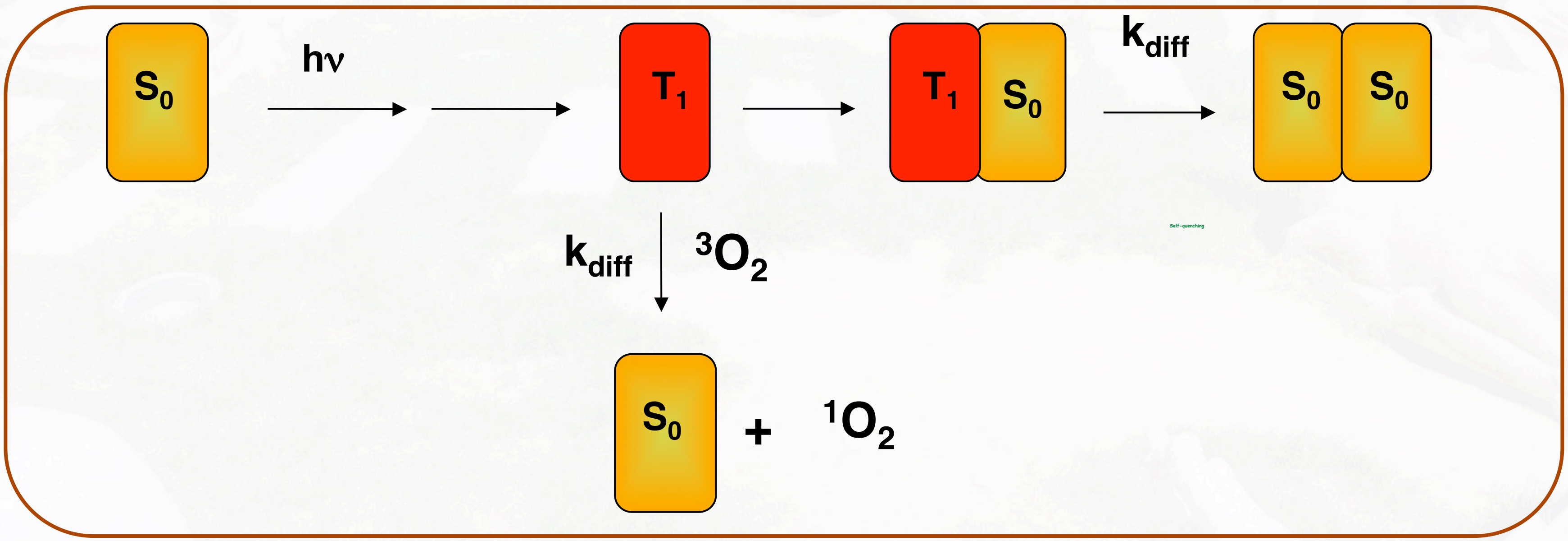


Phosphorescence from Diphenyl Polyenes

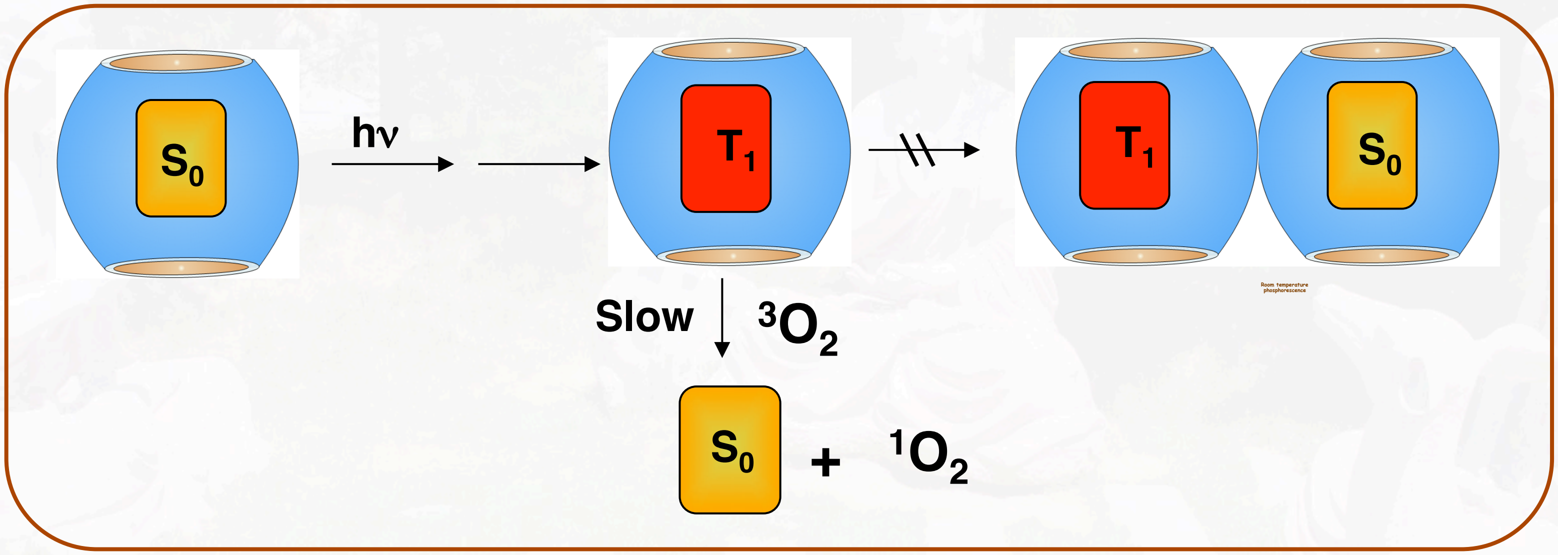


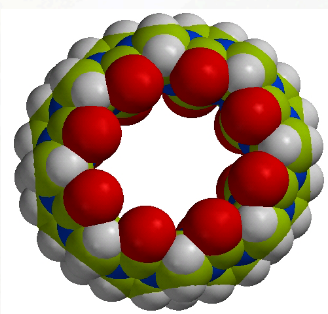
Diffusion controlled self-quenching and oxygen-quenching in solution

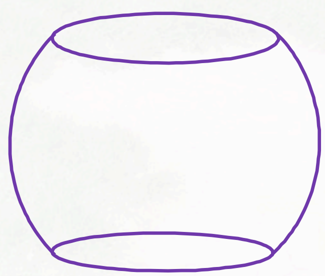
$$\begin{tikzcd}
{}^*R(S_1) \arrow[r, "k_{ST}"] \arrow[d, "k_1"] & {}^*R(T_1) \arrow[r, "k_P"] \arrow[d, "k_2\,[Q]"] & S_0 + h\nu_P \\
\text{not } {}^*R(T_1) & \text{not } h\nu_P &
\end{tikzcd}$$

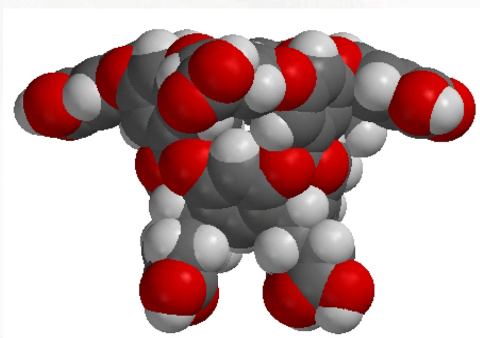


Prevention of self quenching and oxygen quenching with the help of containers

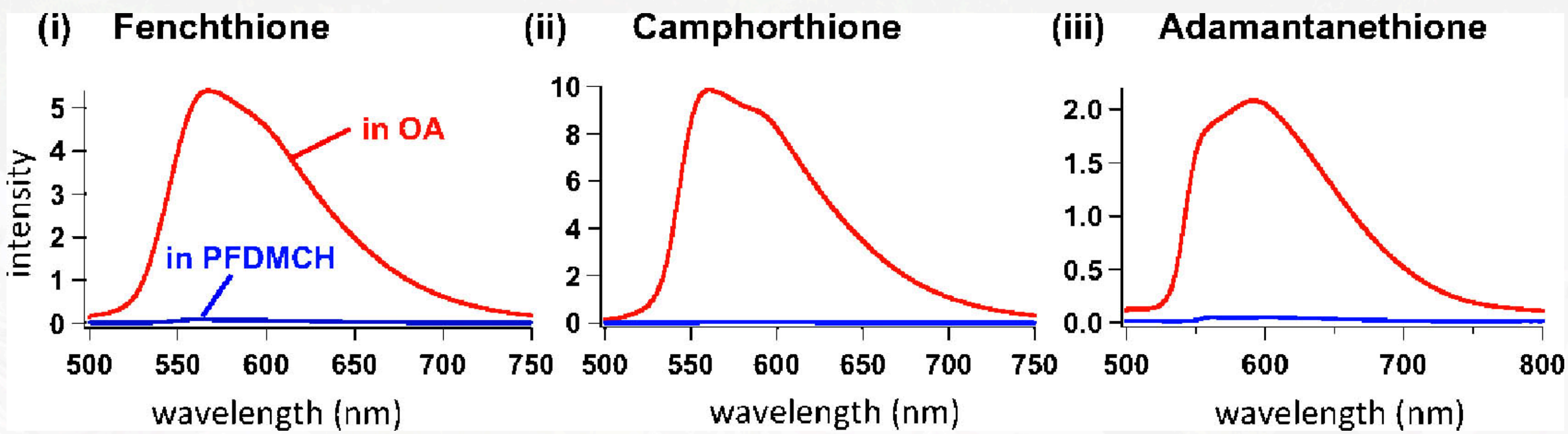


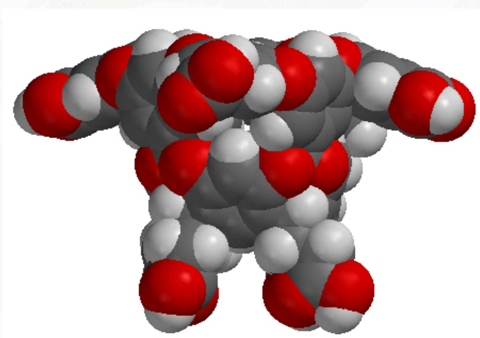


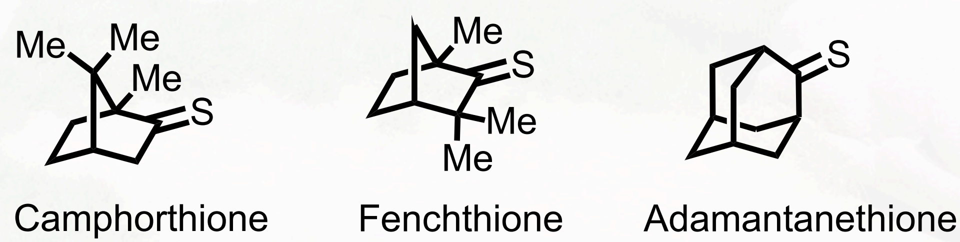


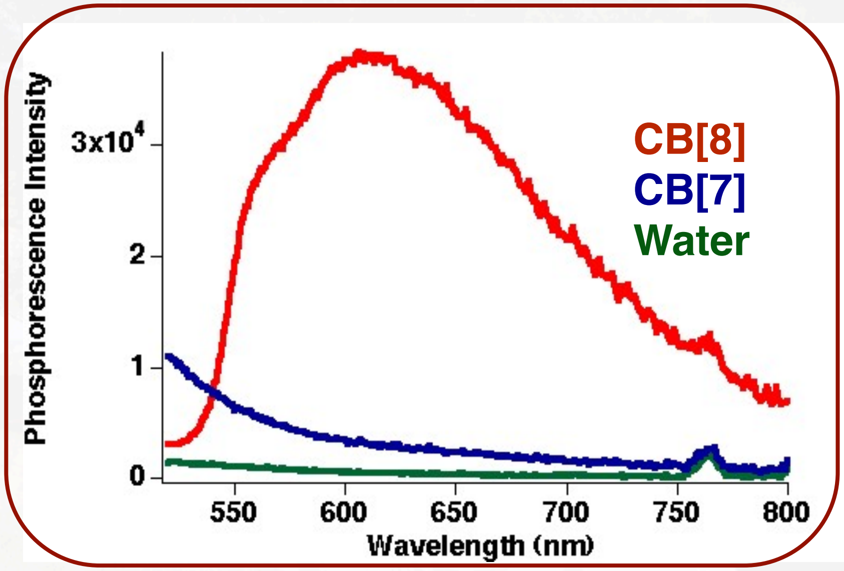


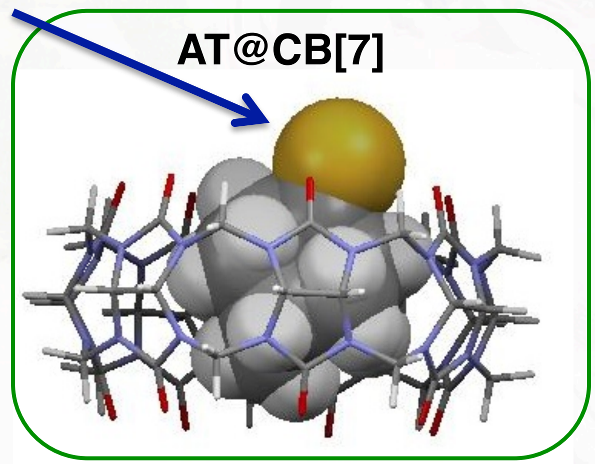
Room temperature phosphorescence from thioketones in solution







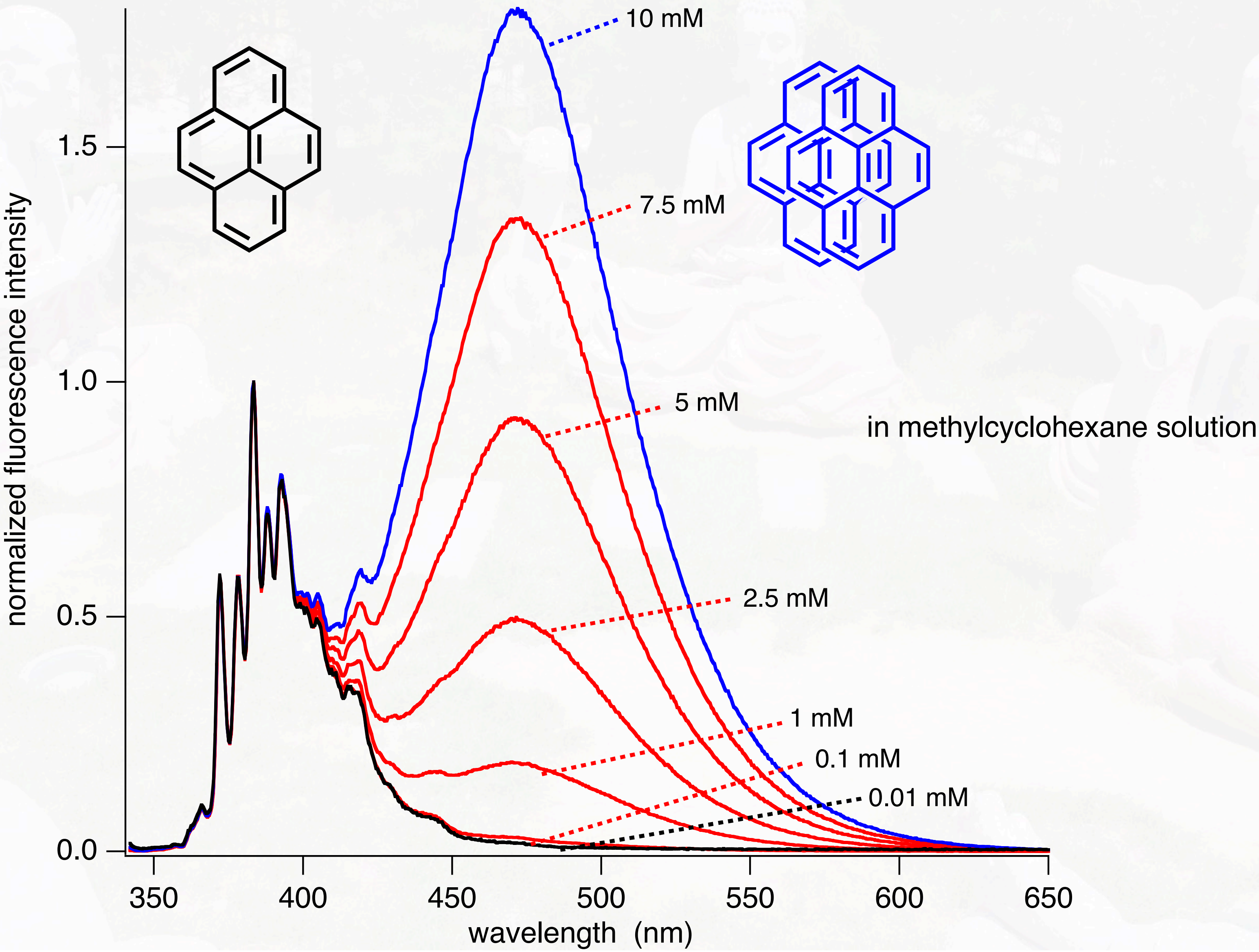




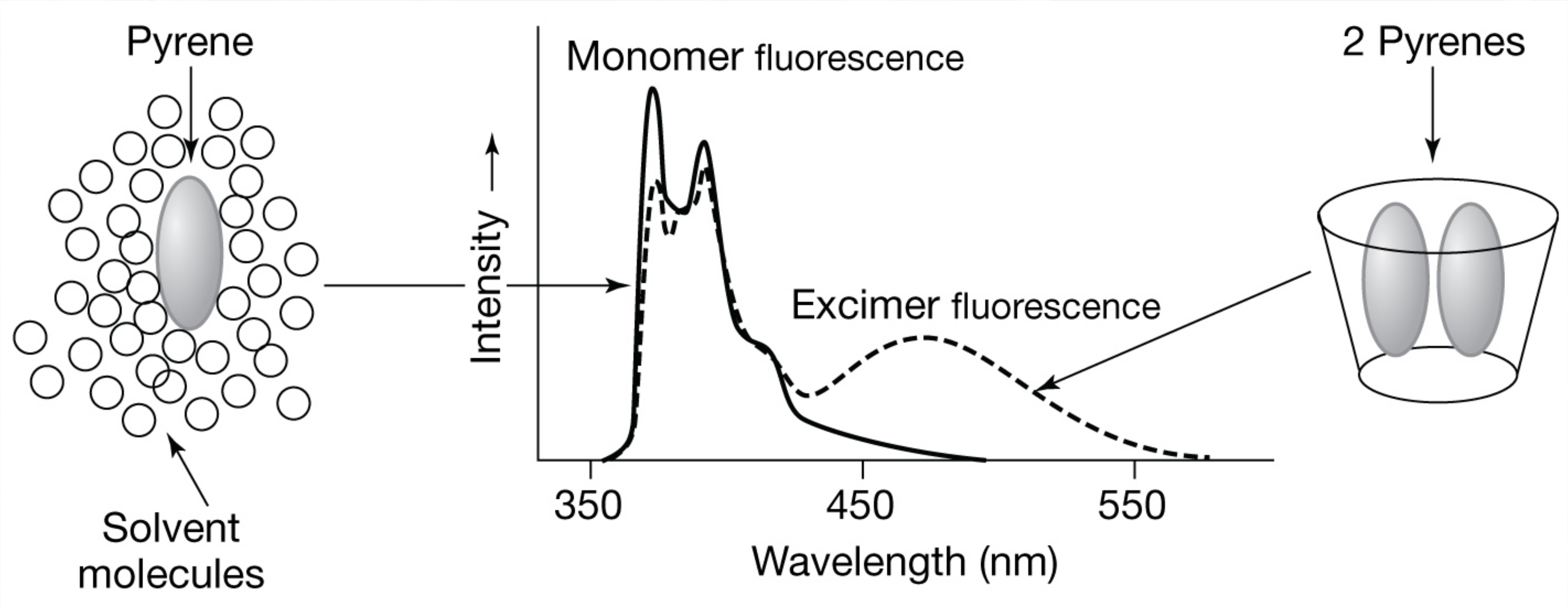
- No phosphorescence in spite of good binding within CB[7] (K= 4.85X 10^4 M^{-1})

- Exposure of C=S to water leads to this anomaly

Pyrene Excimer

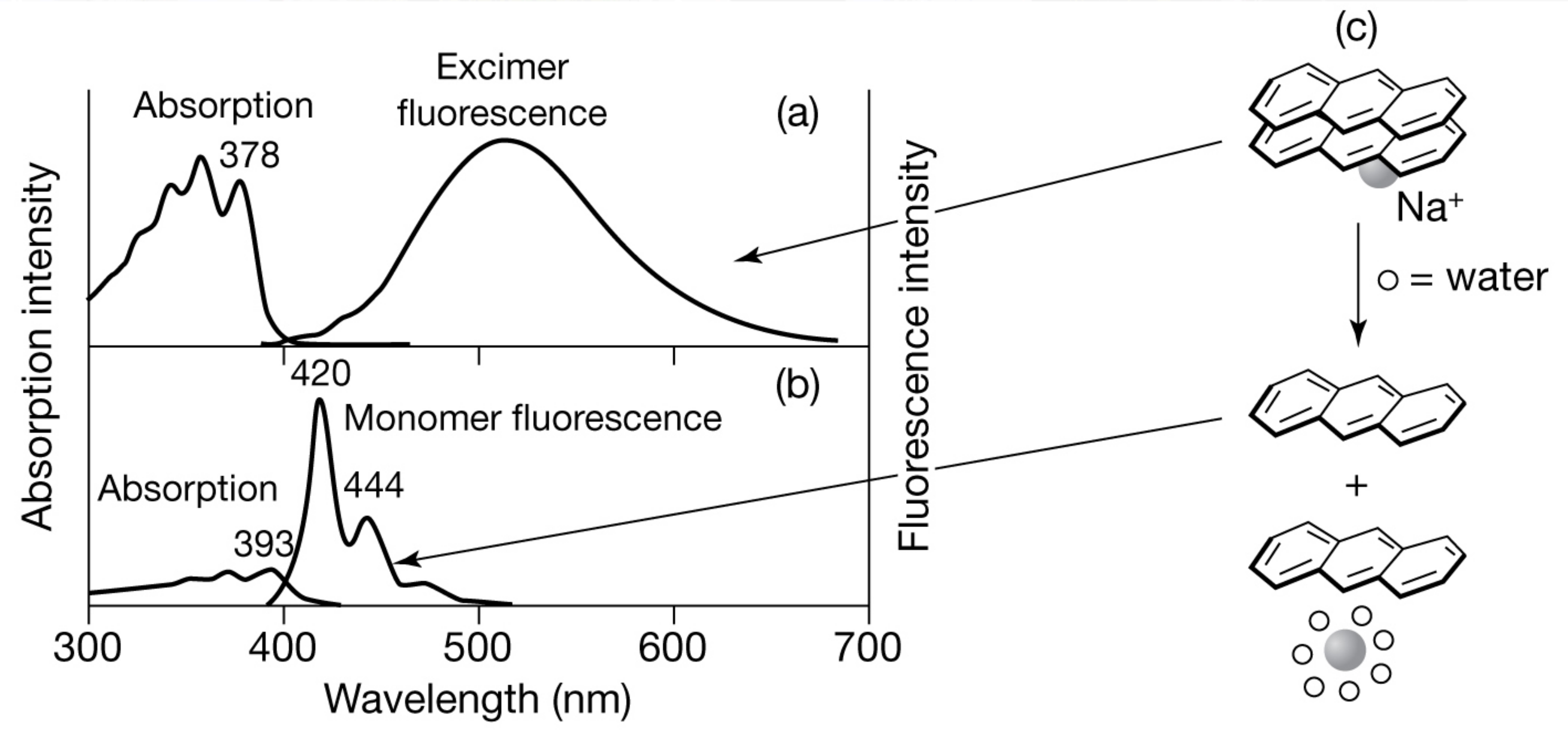


$(Py)_2$@Cyclodextrin: Enhanced excimer formation due to preorganization of two pyrenes in a cyclodextrin cavity

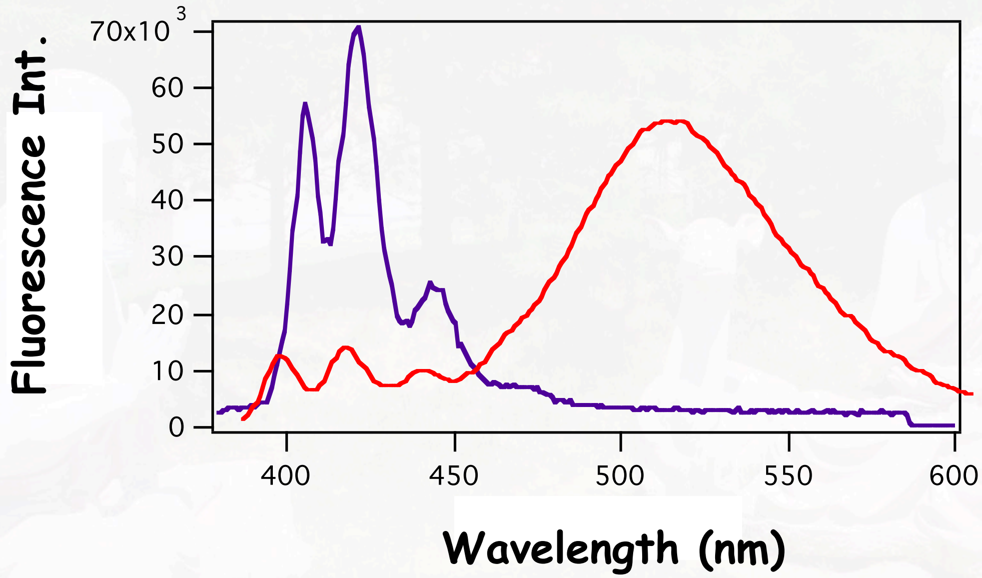


Zeolites as hosts

Anthracene@NaX: Cation controlled aggregation



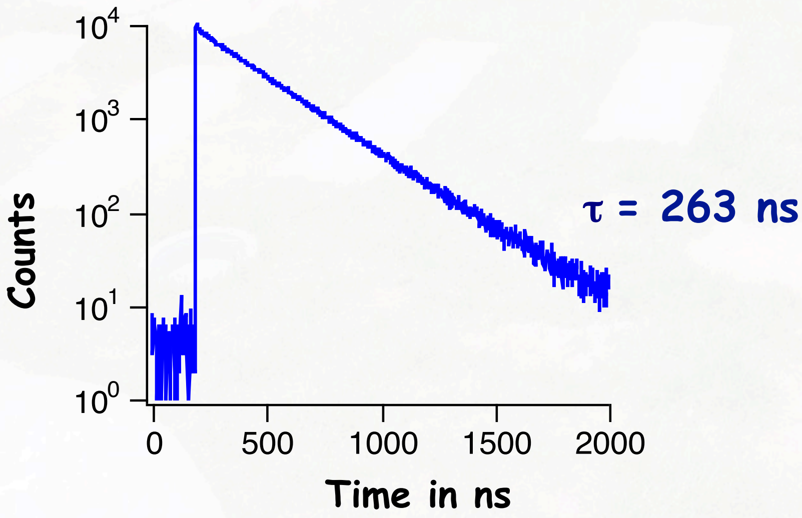
Photophysics of OA-Anthracene Complex

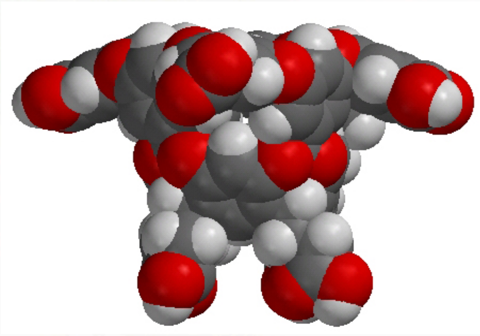


---- Anthracene in water

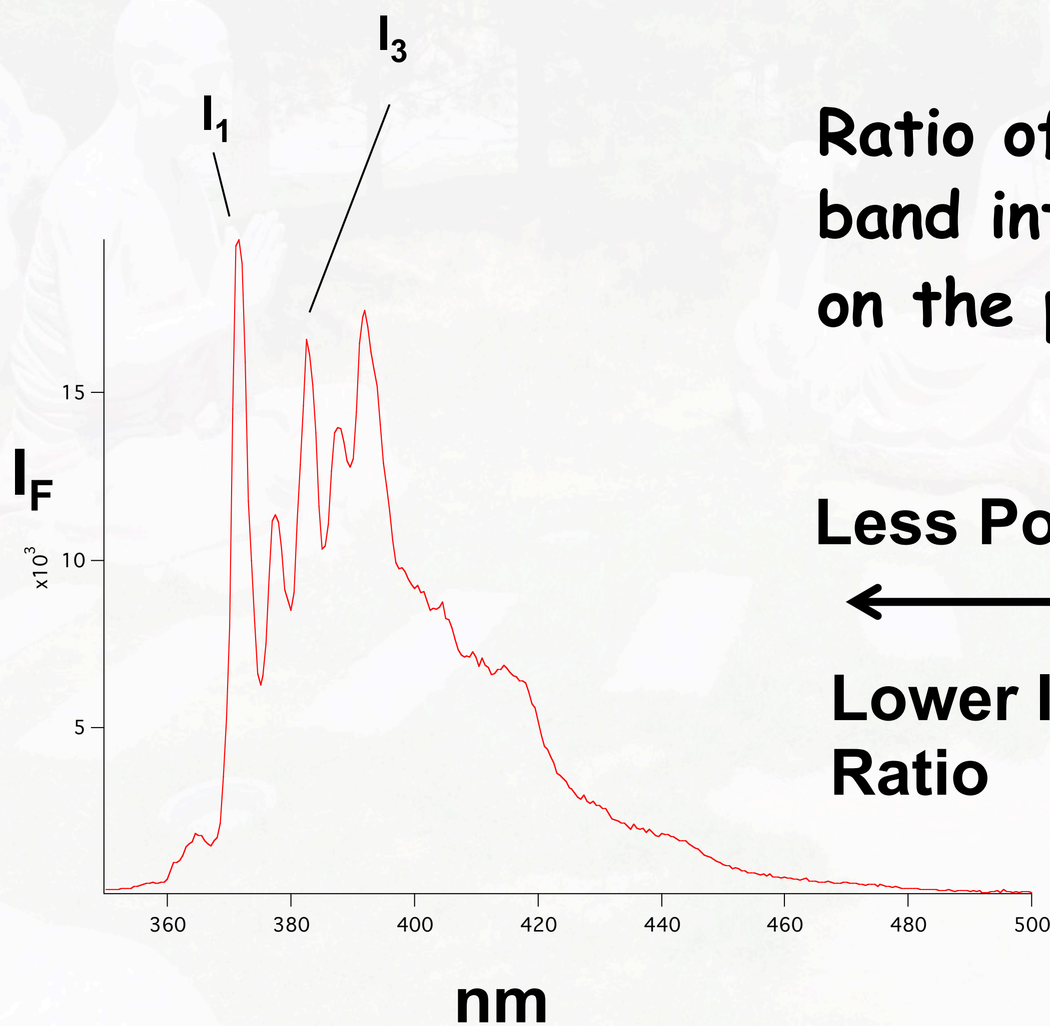
---- Anthracene in octa acid

Sandwich pair emission-
slow addition of host to
the guest in borate buffer





Fluorescence Response to Solvent Polarities



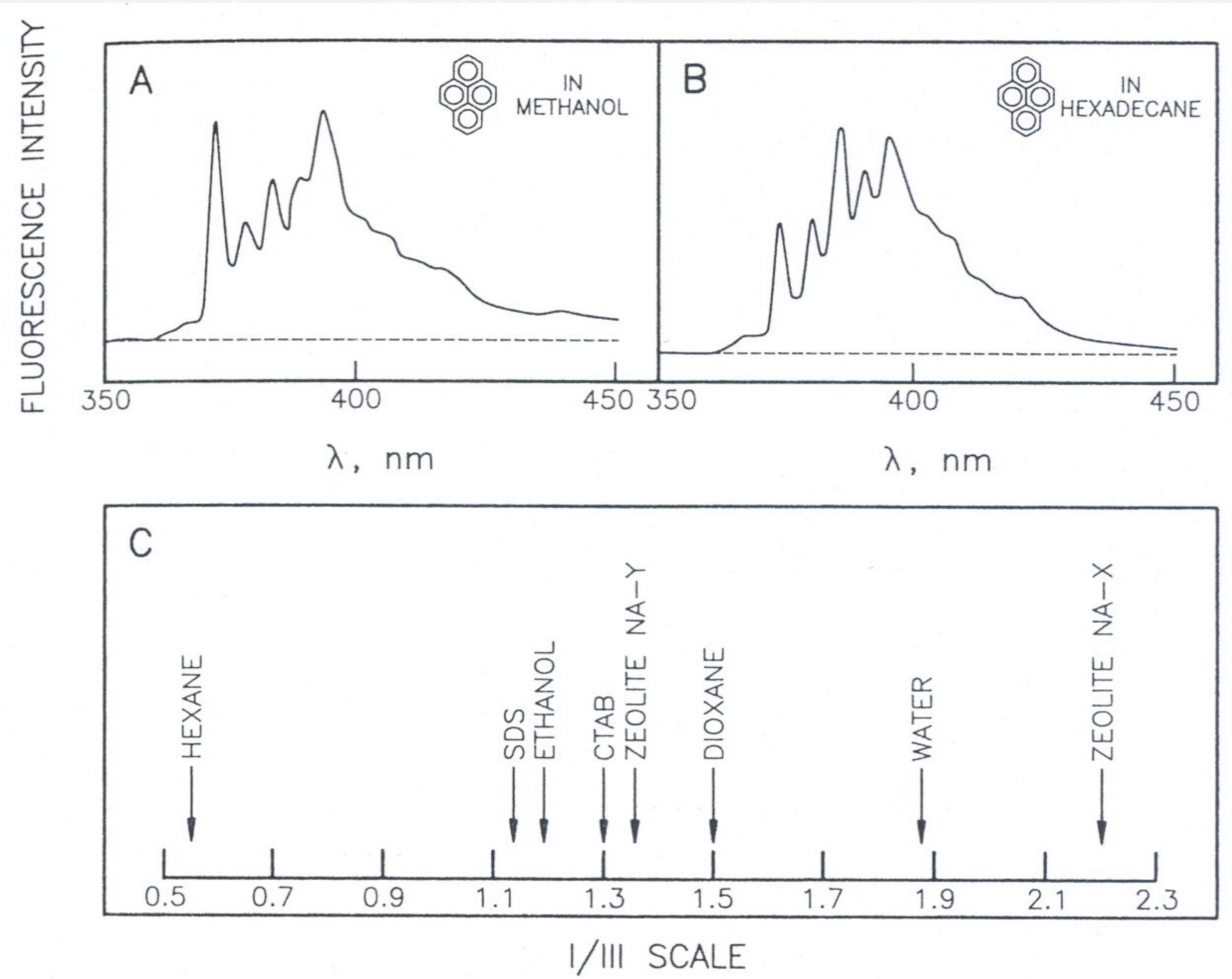
Ratio of 1st to 3rd vibrational band intensities is dependent on the polarity of the solvent.

Less Polar ⟷ **More Polar**

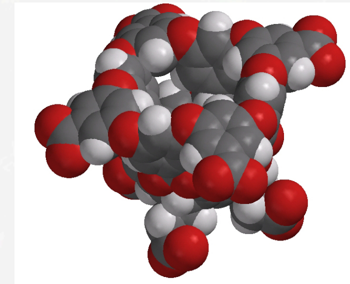
Lower I_1/I_3 Ratio

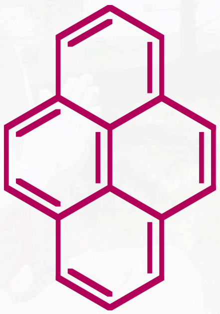
Higher I_1/I_3 Ratio

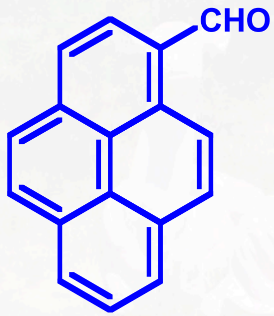
Pyrene as a polarity probe

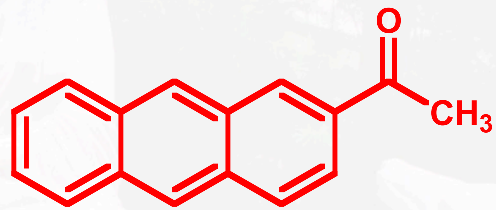


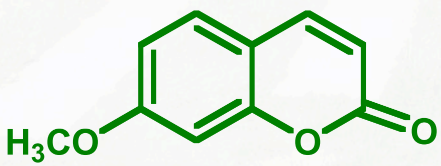
Octa acid's interior micropolarity probed

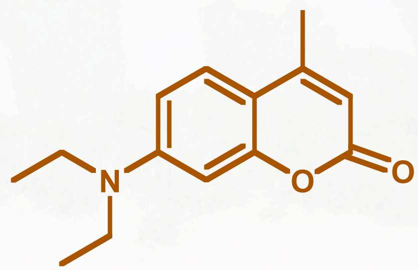






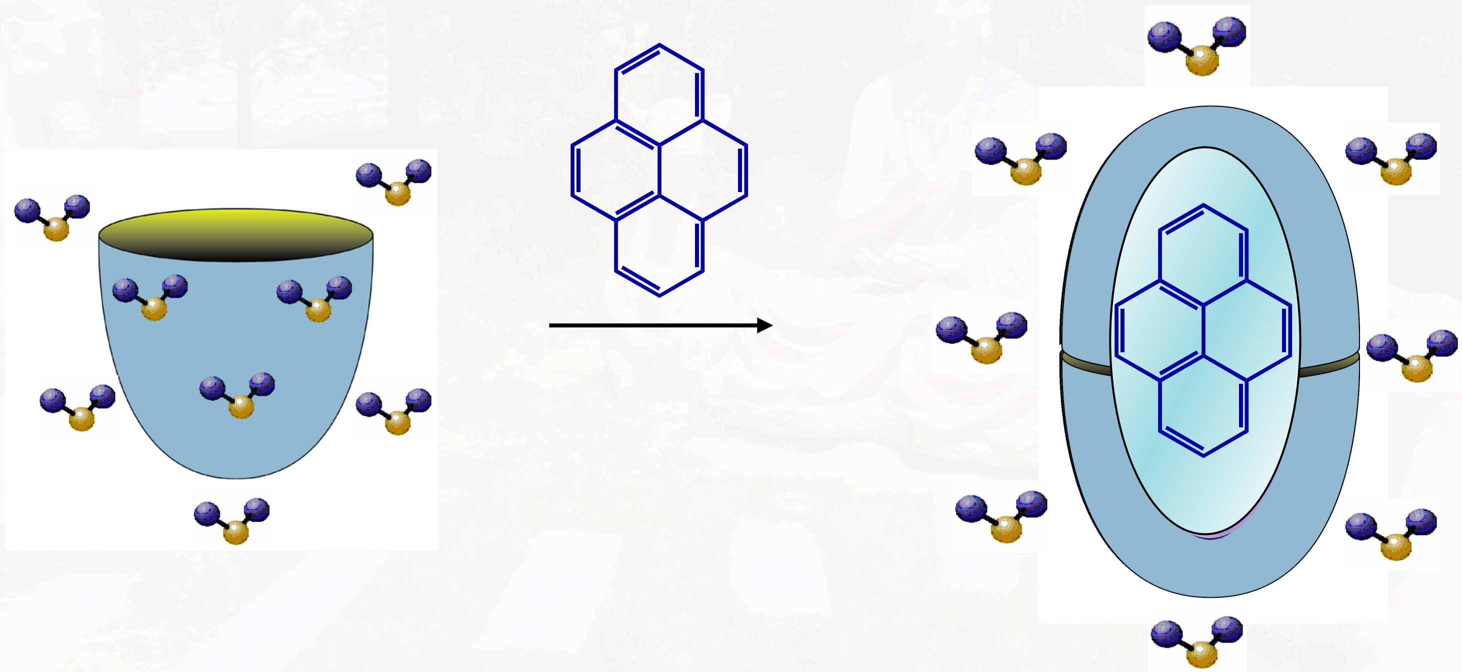






All above probes form 2:1 host-guest complexes.

Interior of octa acid is benzene-like



'Dry' and 'Non-polar'