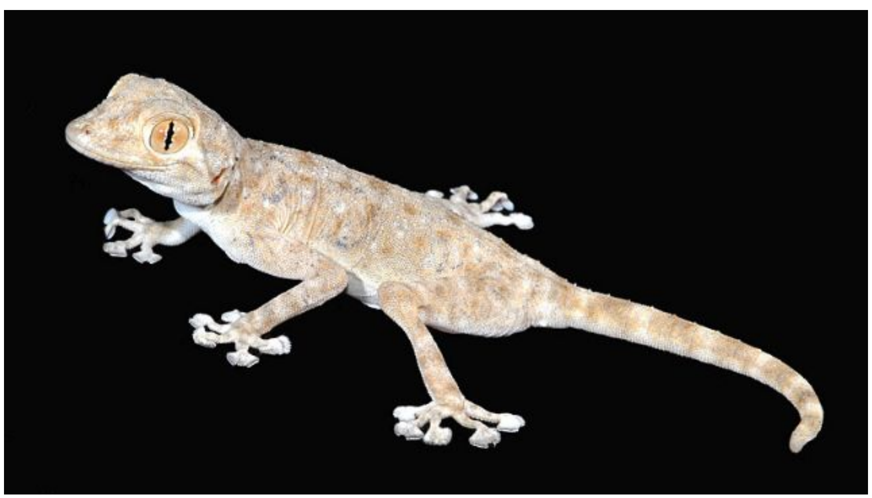
Photochemistry in a Capsule: Dynamics and Reactions

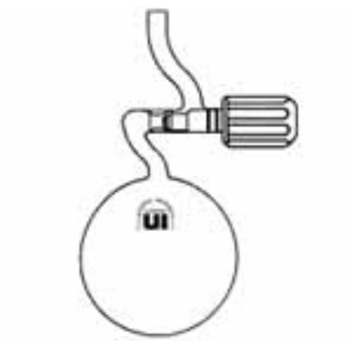
Controlling Photochemical Reactions With Confinement and Weak Intermolecular Forces

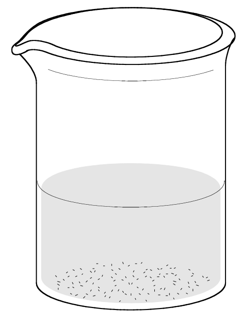
Confinement



Weak Forces

Medium Matters





Gas phase

Solution
(solvent + solute)

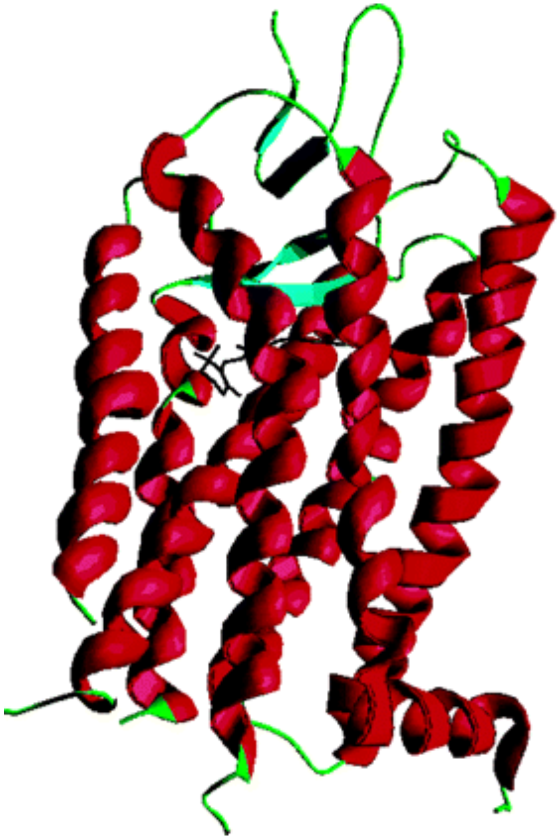
Rhodopsin

Increasing selectivity

How do biological media enforce selectivity?

By providing highly constrained and well defined nano sized reaction cavity.

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



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

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?

Bioinspired Green Supramolecular (Nano) Photochemistry

Container Chemistry

Objective: To carry out product selective photoreactions in water (or in solid state)

Problem: Organic compounds generally are either poorly soluble or insoluble in water

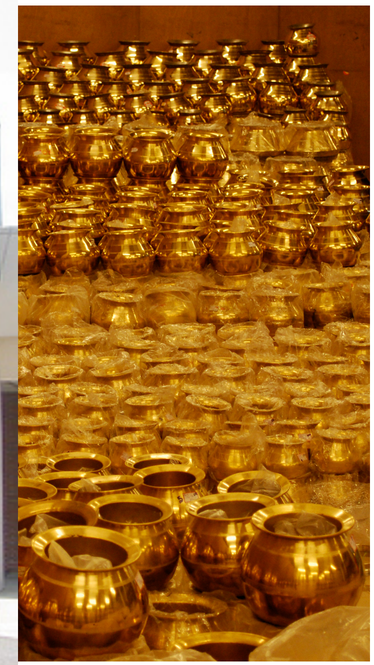
(Most organic compounds are liquid)

Solution: Use water soluble hosts to solubilize organic molecules

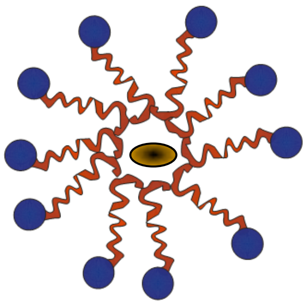
(Use solid hosts to trap liquid molecules)

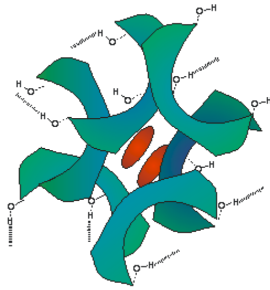
Use confining hosts to achieve product selectivity

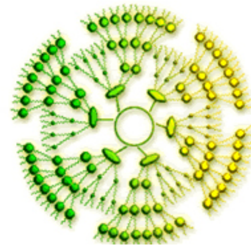
Common Containers

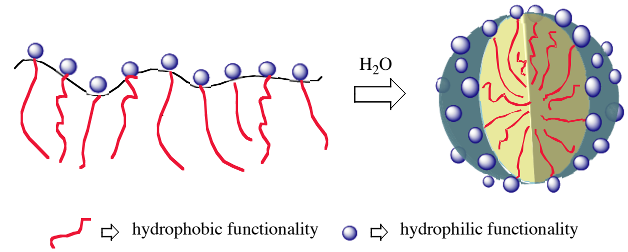


Supramolecular Containers

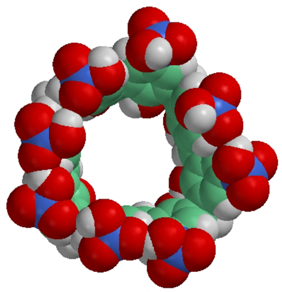

SDS / CTAC

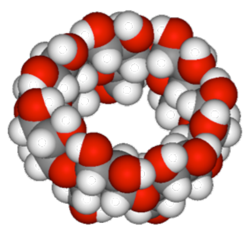

NaCh / NaDCh

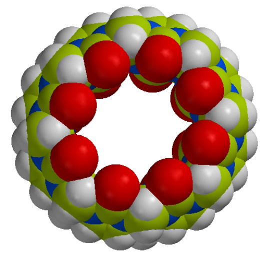

Dendrimers

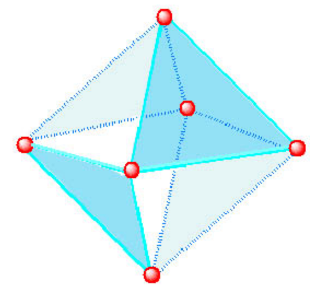


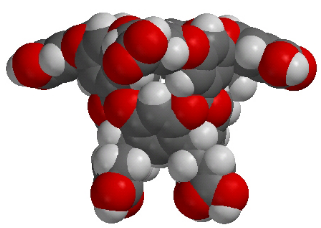
Water soluble polymer

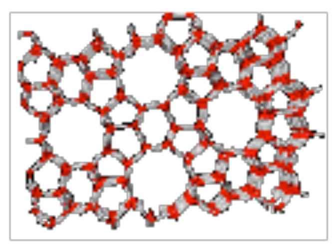

Calixarenes

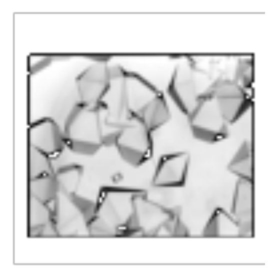

Cyclodextrins


Cucurbiturils

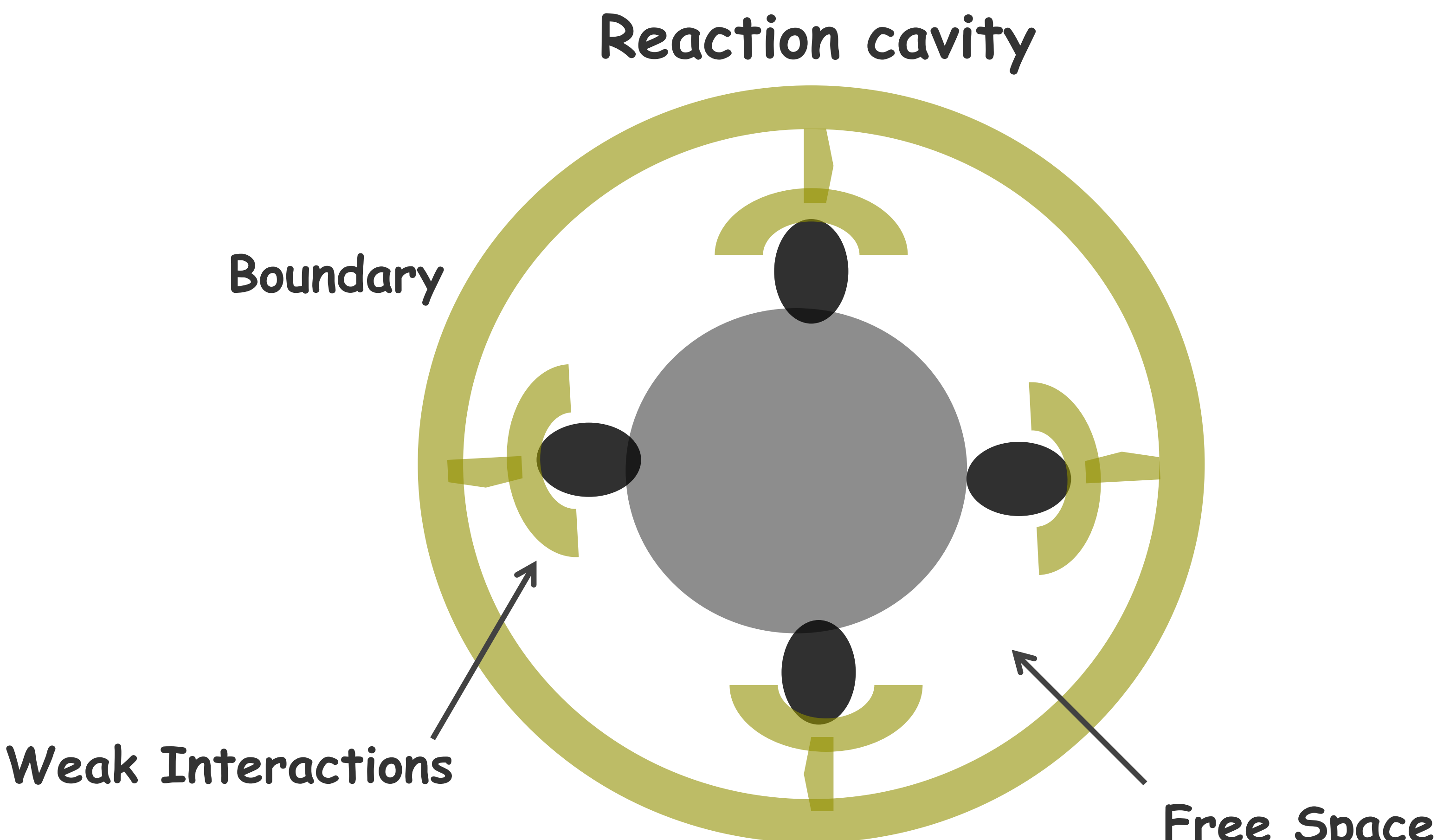

Pd nano cage


Octa acid


Zeolites

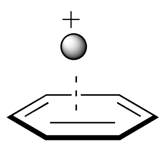

Crystals

Supramolecular Containers: General Features

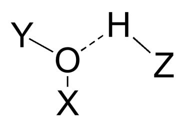


Relevant Weak Interactions in Supramolecular Chemistry

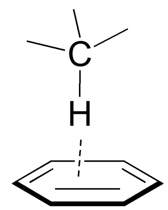
Examples of weak intermolecular interactions (typical energies vary from <1 kcal mol^{-1} to ~10 kcal mol^{-1})



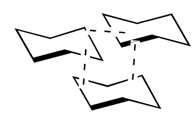
Cation---π bond



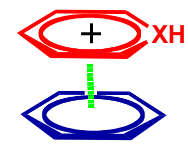
Hydrogen bond

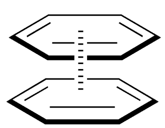


CH---π bond

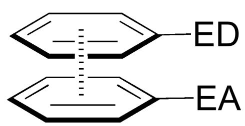


van der Waals bonds



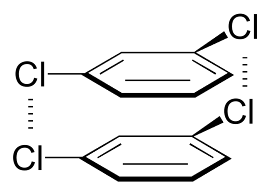


π–π bond

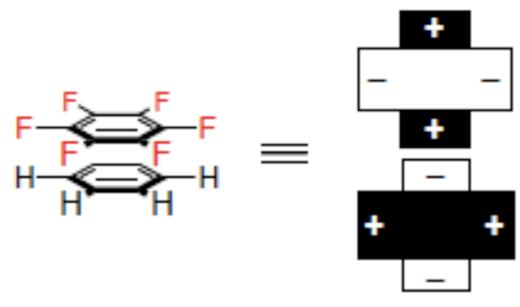


Charge transfer bond

ED = electron donor
EA = electron acceptor

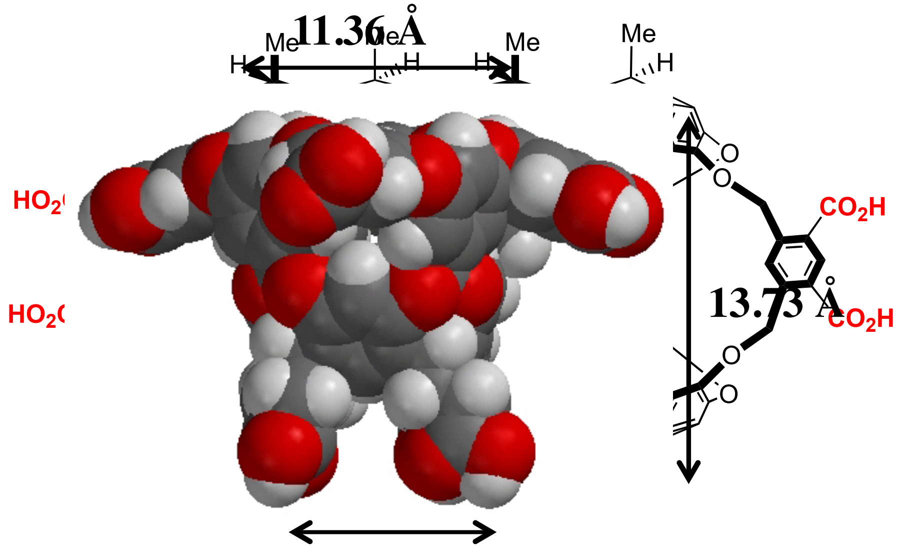


Chlorine---Chlorine

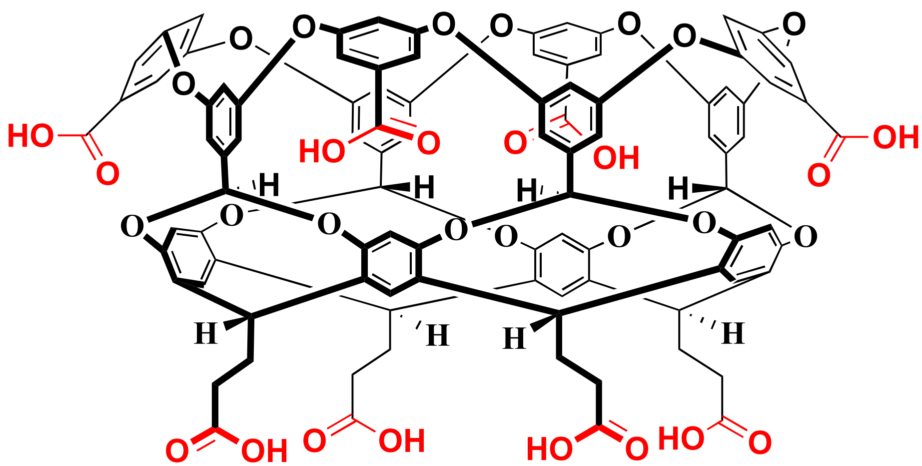


Quadrupole---Quadrupole

Octaacid as a Container

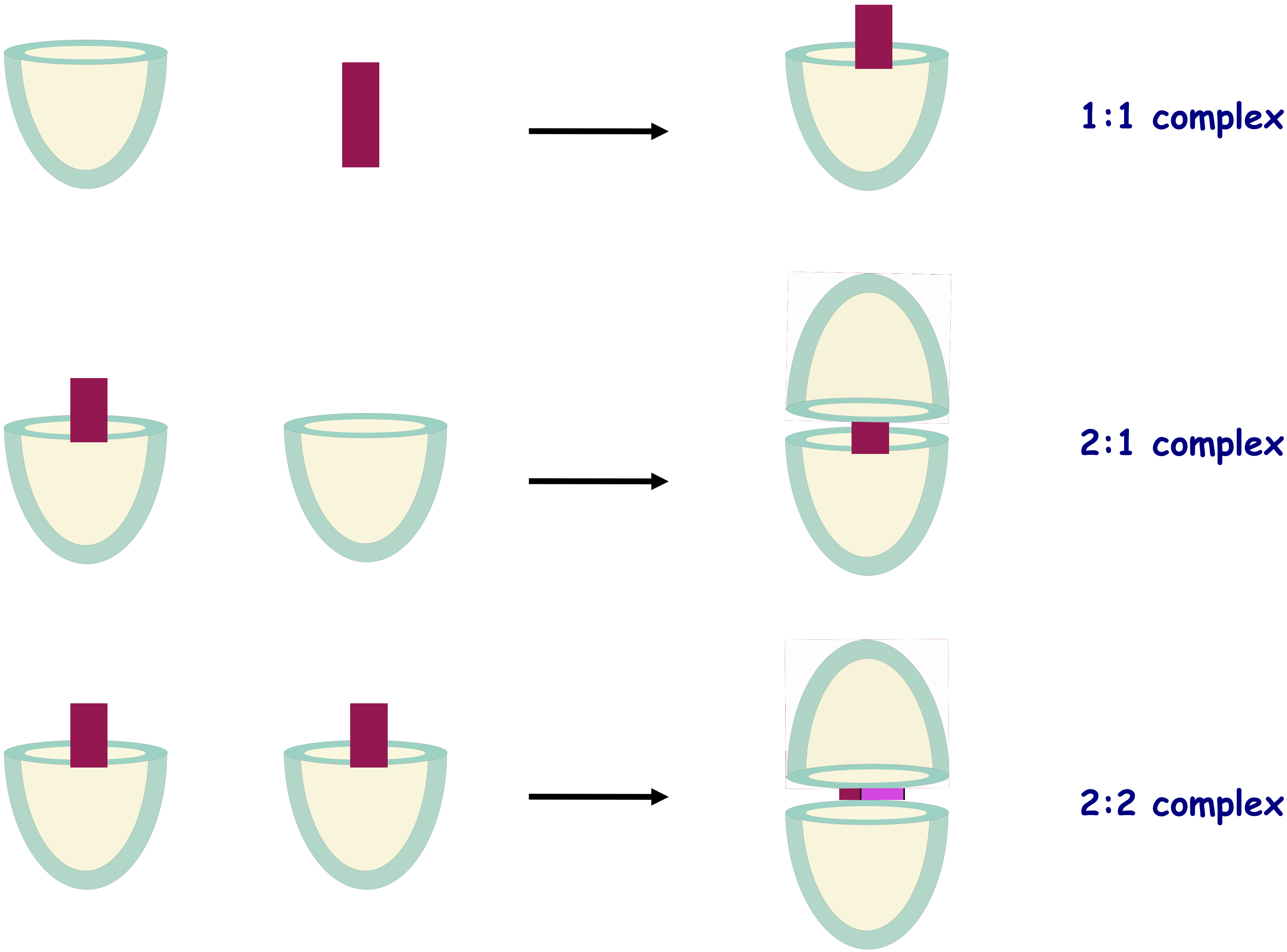


J. Yoon and D. J. Cram, *Chem. Comm.*, **1997**, 497

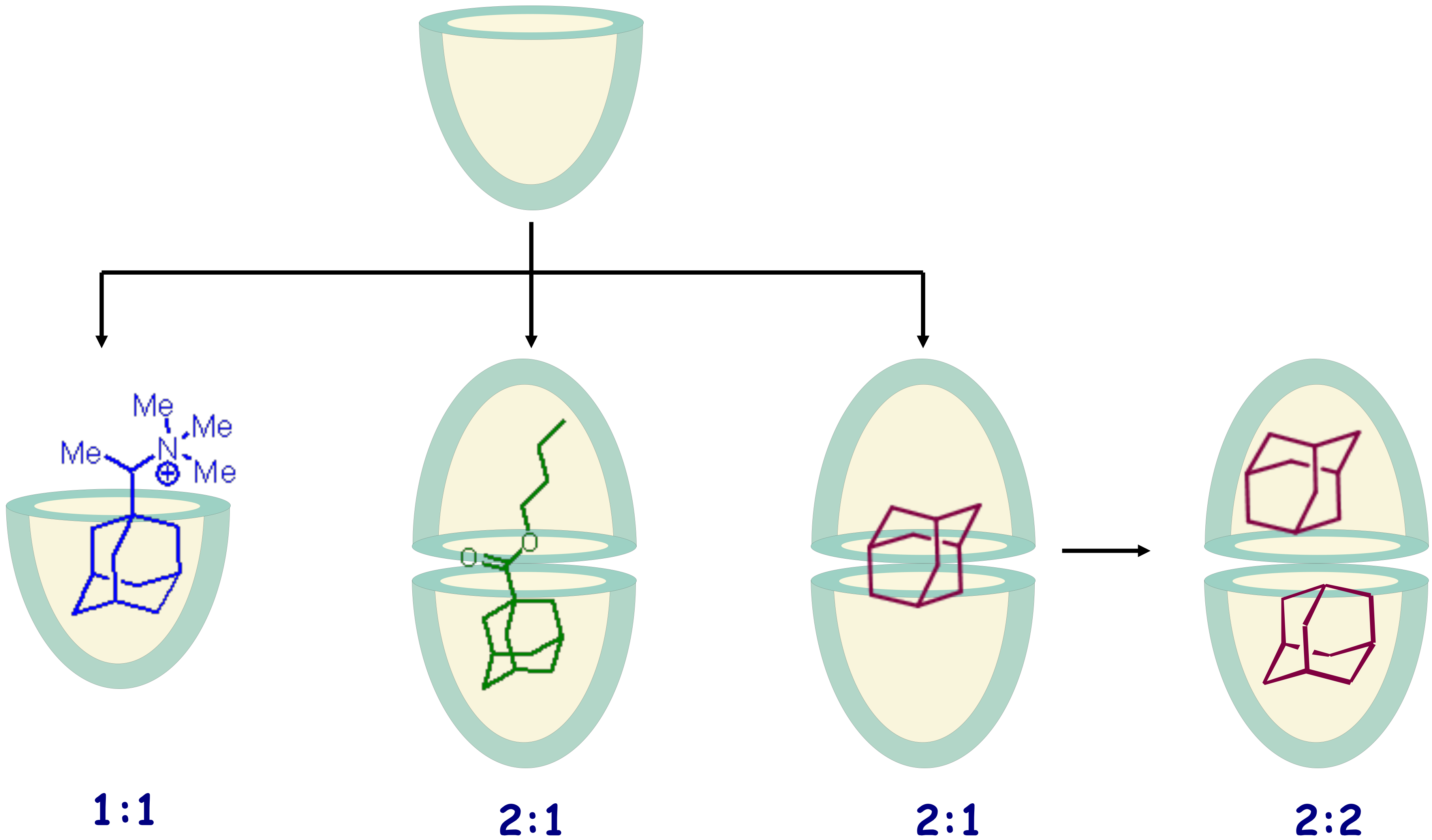


C. L. D. Gibb, and B. C. Gibb, *J. Am. Chem. Soc.*, **2004**, *126*, 11408.

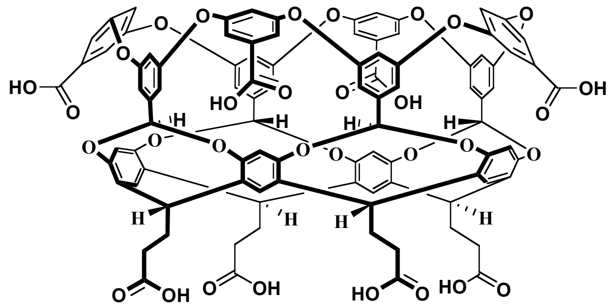
Complexation Modes

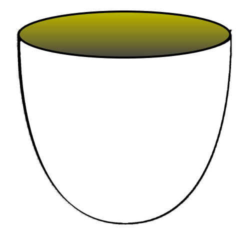


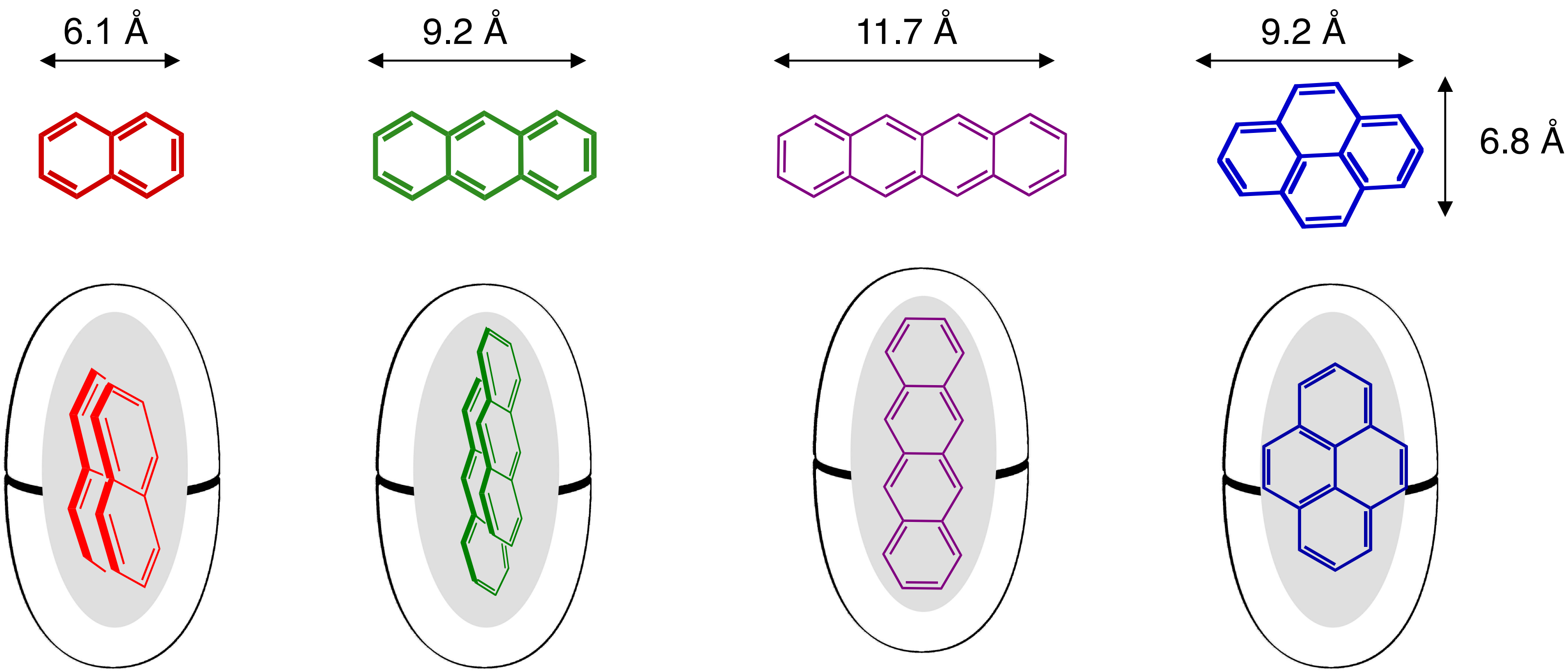
What type of and how many molecules may fit within a OA container?



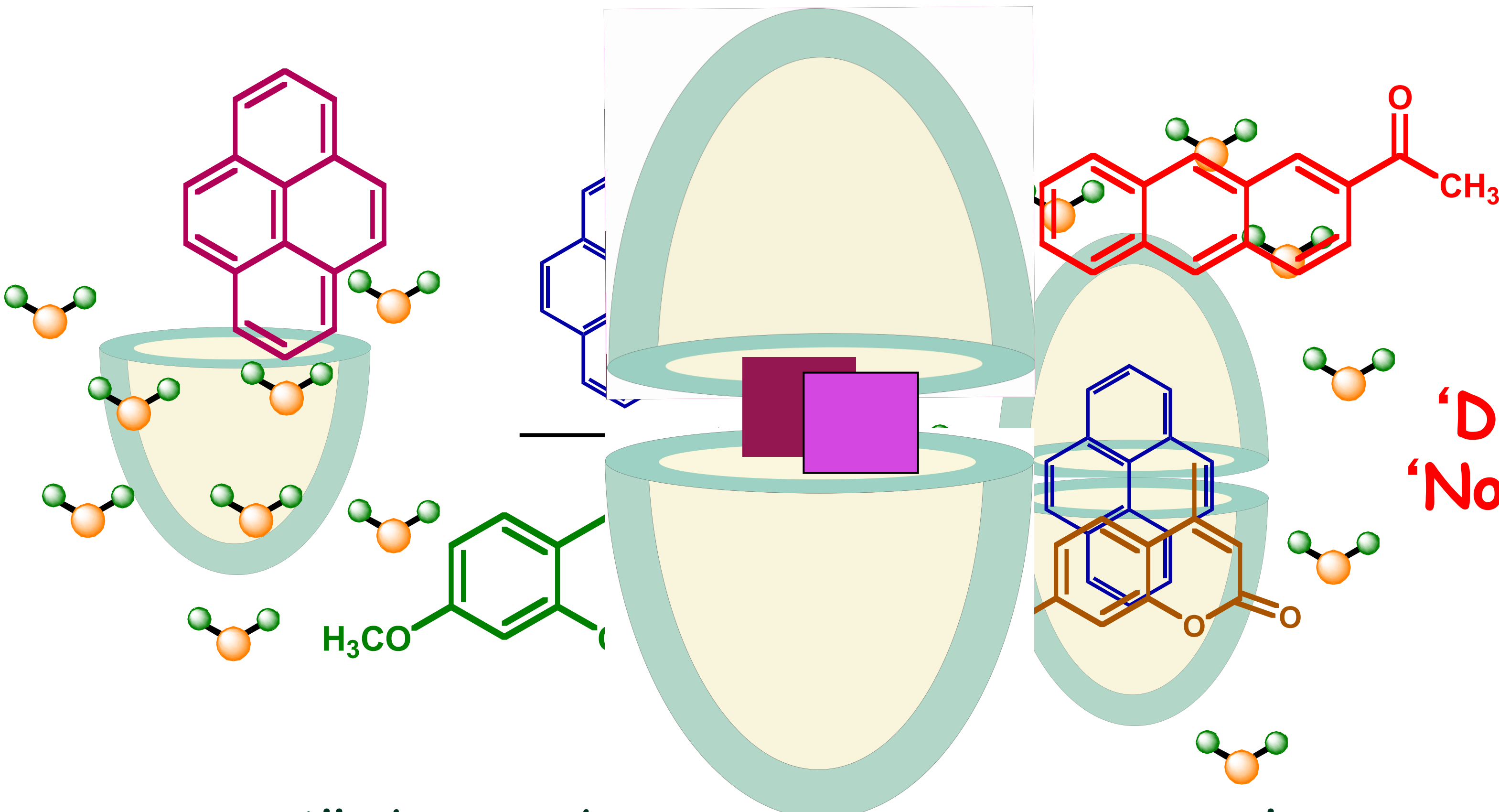
Encapsulation of aromatics within octa acid







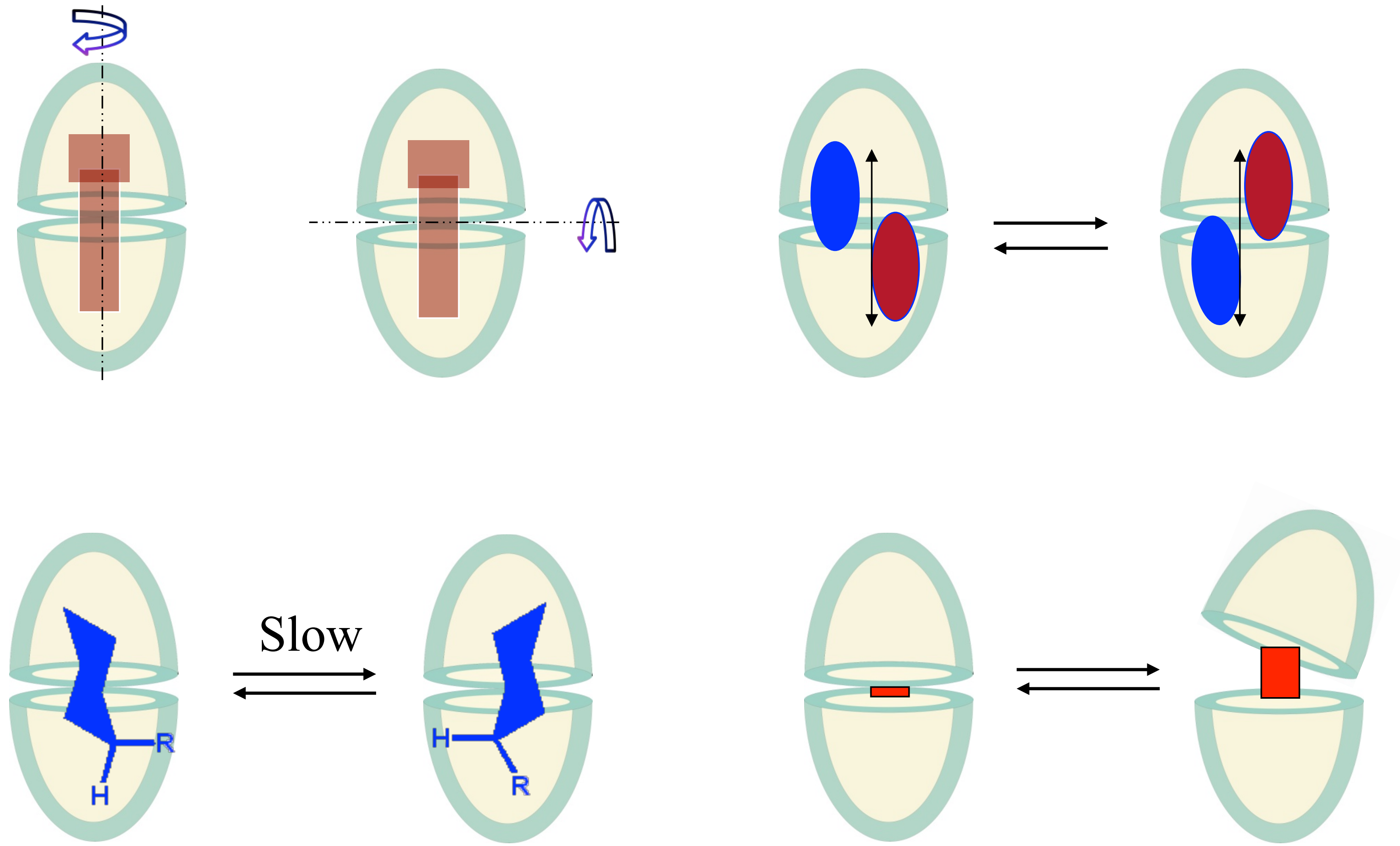
Probing the Micro-polarity of OA Capsule



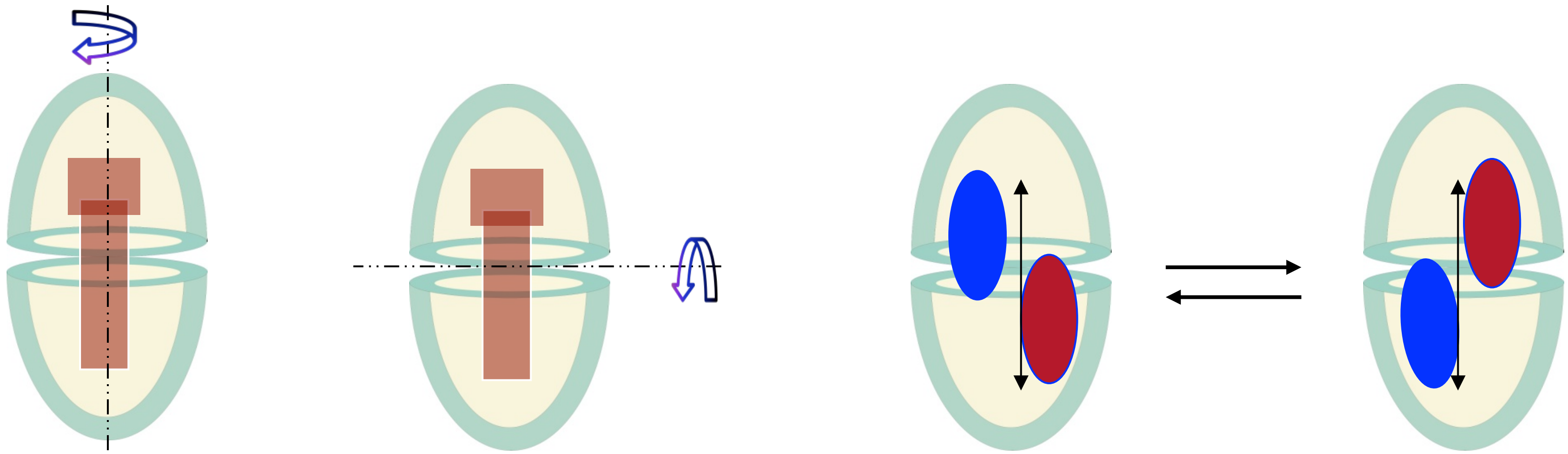
'Dry' and 'Non-polar'

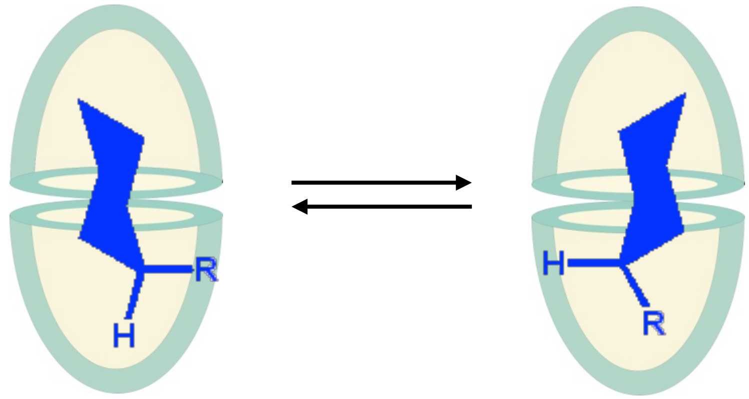
All above probes form 2:1 host-guest complexes.

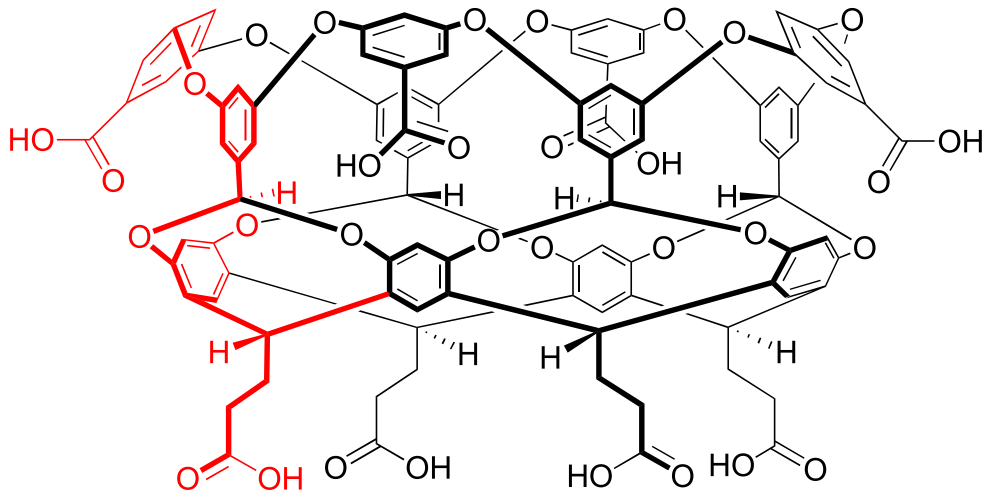
Dynamics of supramolecular assemblies

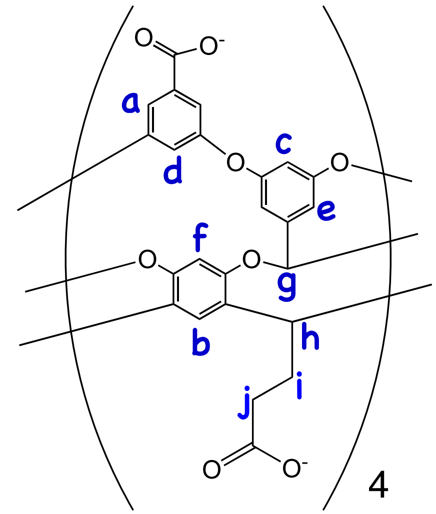


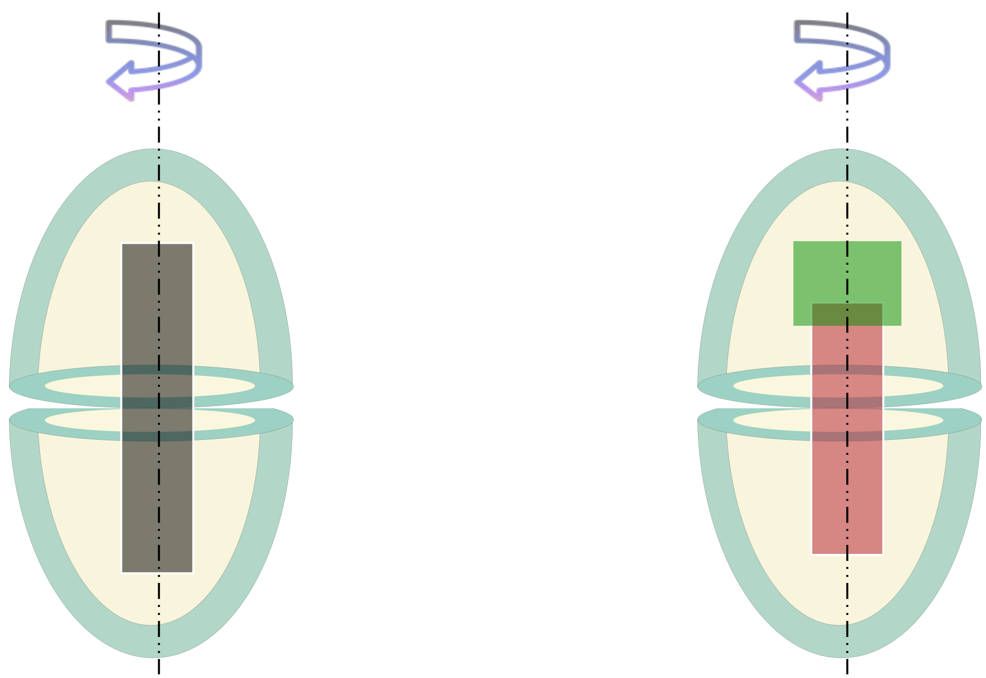
Dynamics of supramolecular assemblies

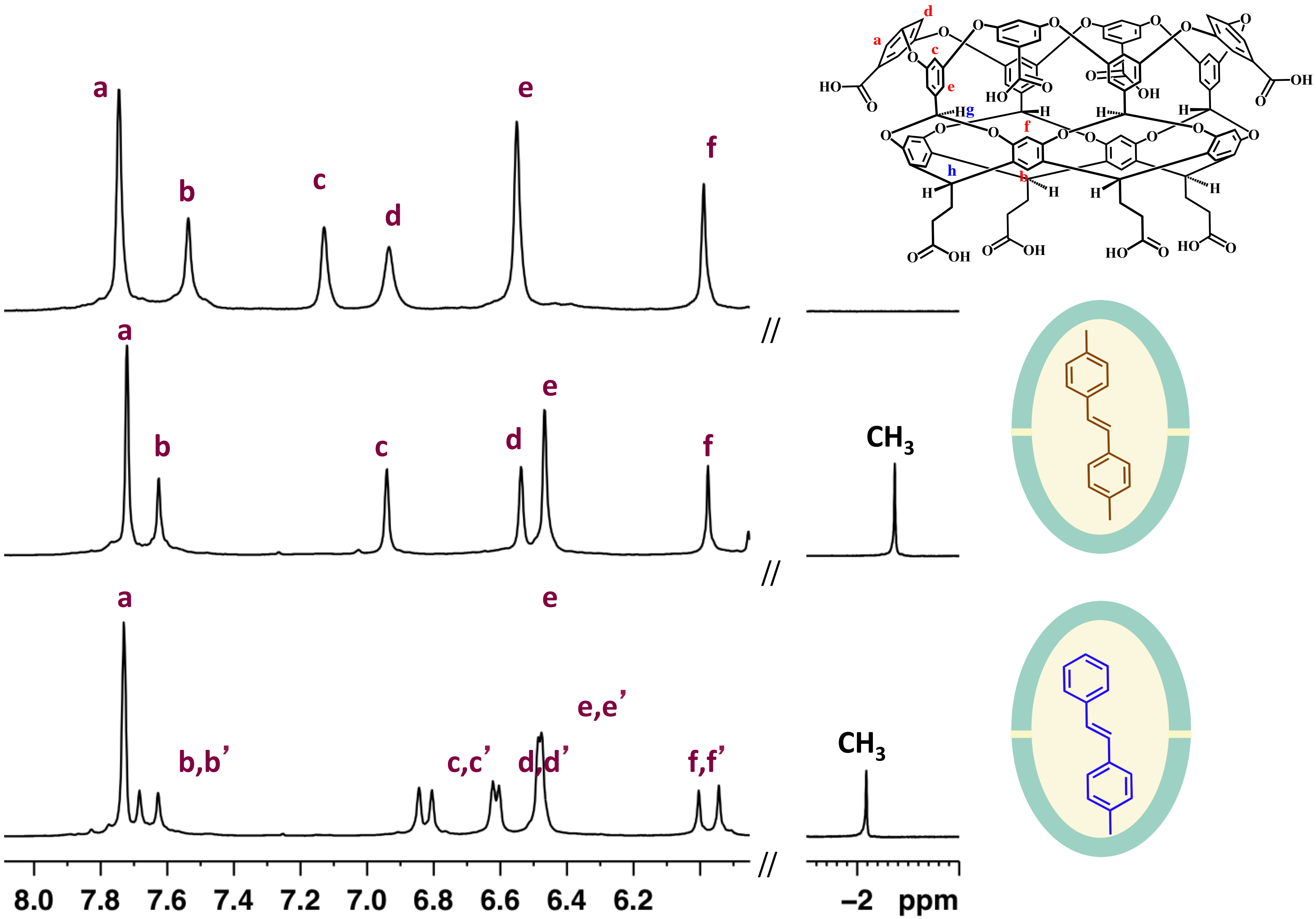


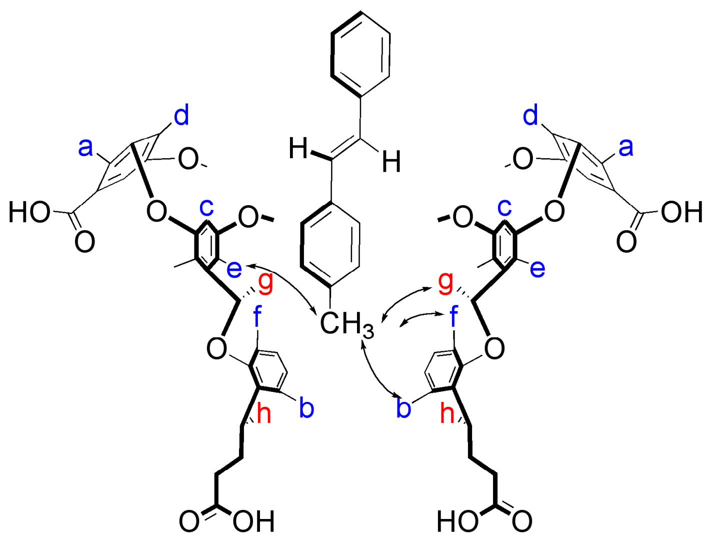


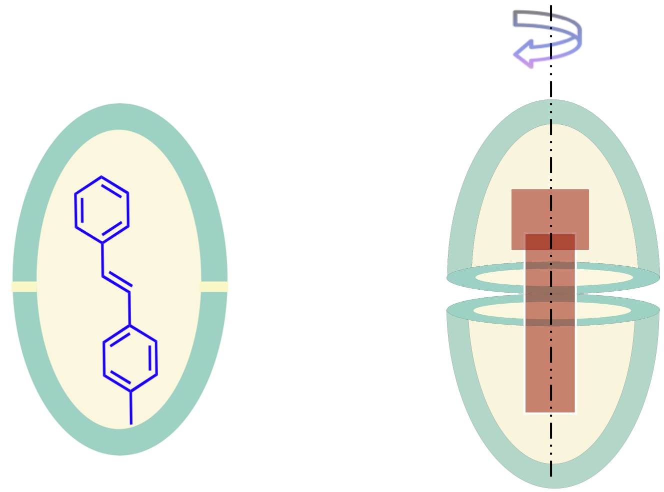

O
HO
OH
H

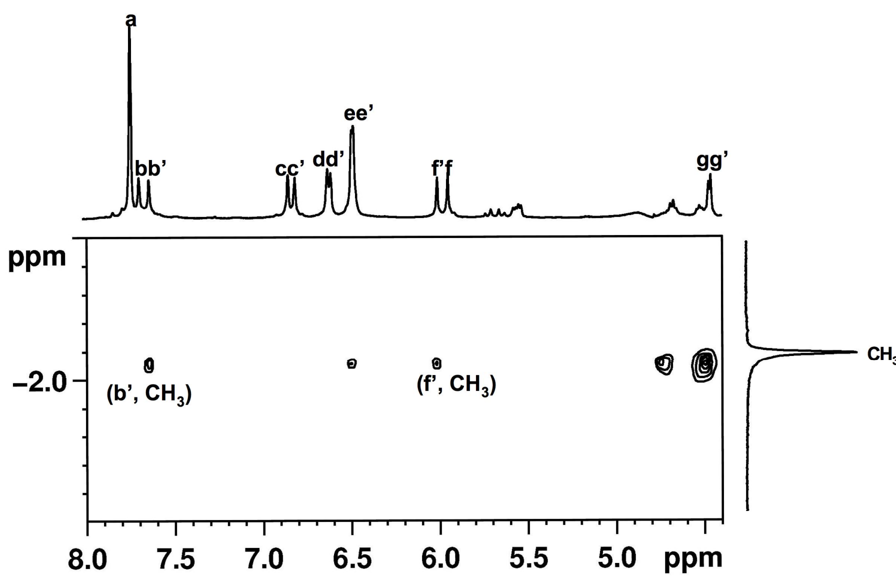

a
b
c
d
e
f
g
h
i
j
4



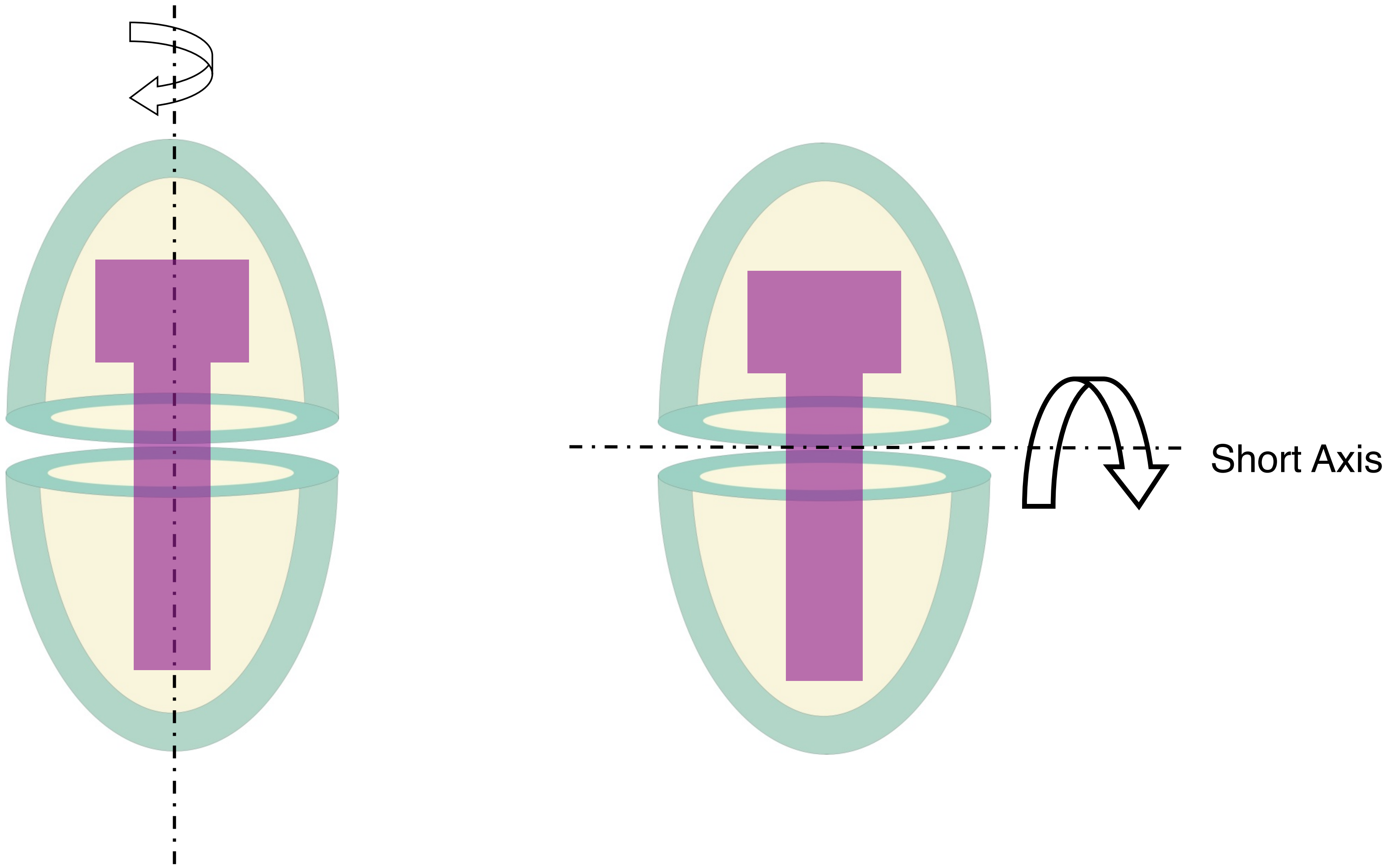

a
b
c
d
e
f
a
b
c
d
e
f
CH3
a
e
e,e'
b,b'
c,c'
d,d'
f,f'
CH3
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
−2
ppm

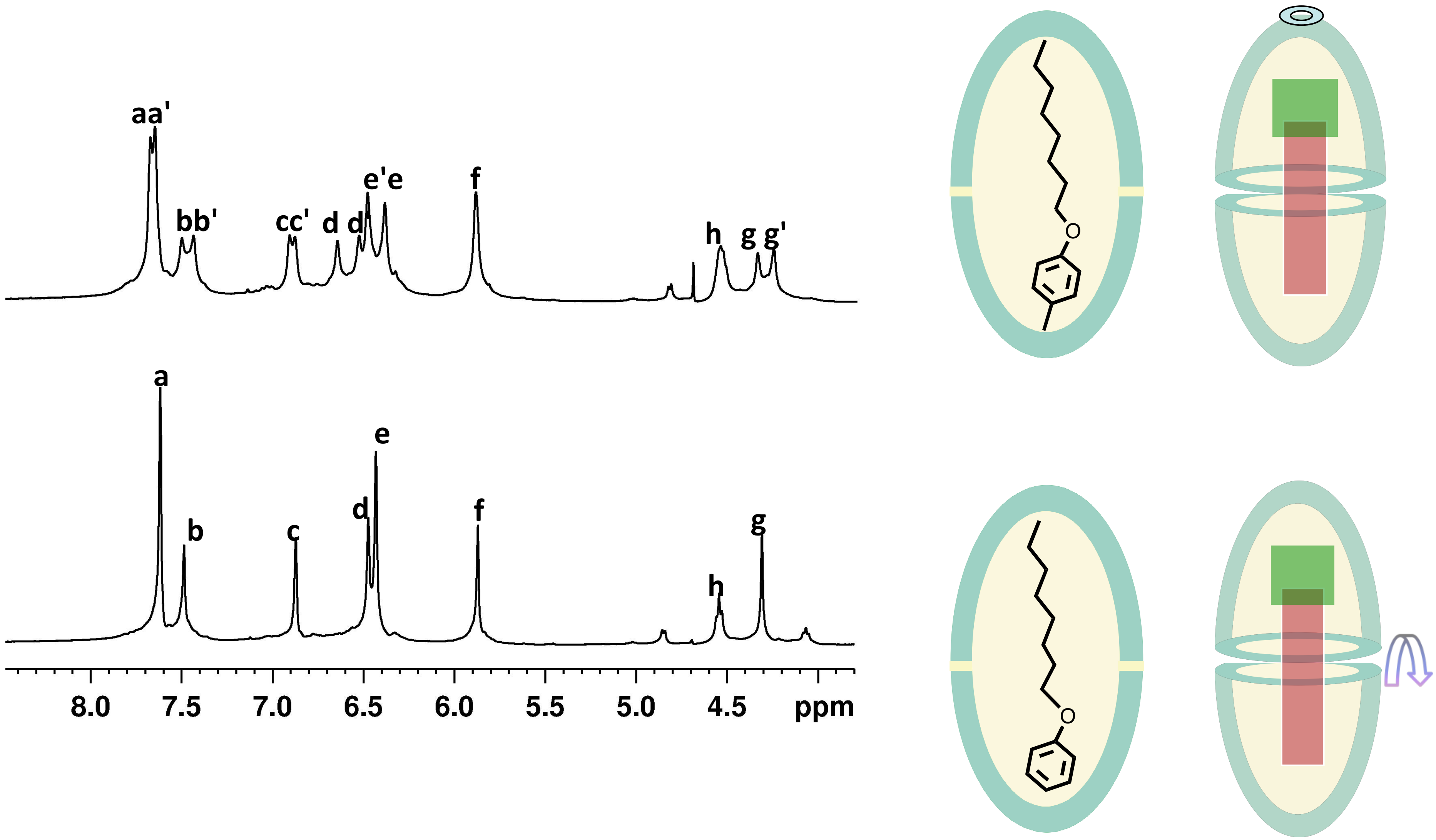

a
d
c
e
g
f
h
b
HO
O
OH
H
H
CH3




a
bb'
cc'
dd'
ee'
f'f
gg'
ppm
−2.0
(b', CH3)
(f', CH3)
CH3
8.0
7.5
7.0
6.5
6.0
5.5
5.0
ppm

NOSEY

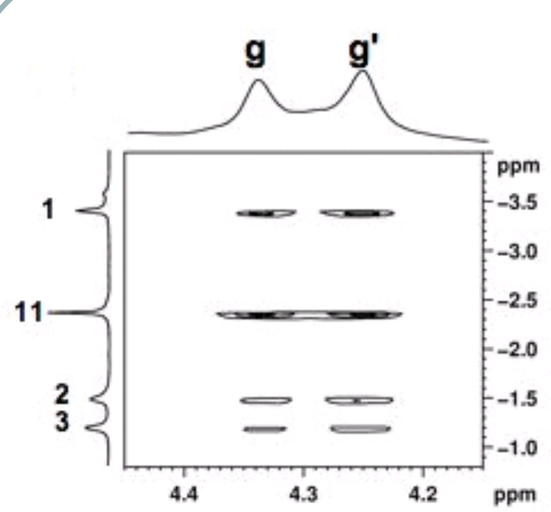

Short Axis



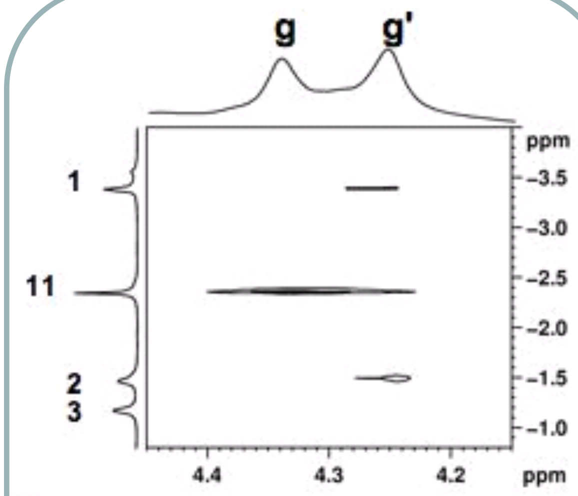
aa'
bb'
cc'
d
d
e'e
f
h
g
g'
a
b
c
d
e
f
h
g
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
ppm
O
O

Dynamics of guest molecules within OA: NOESY studies

Variation of Mixing time

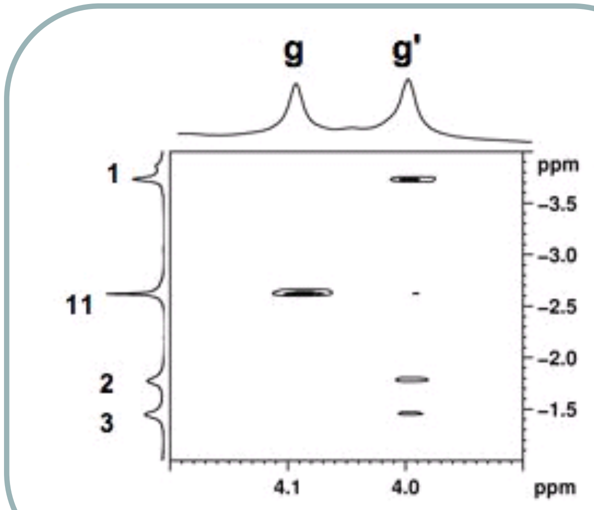


300 ms, 25 °C

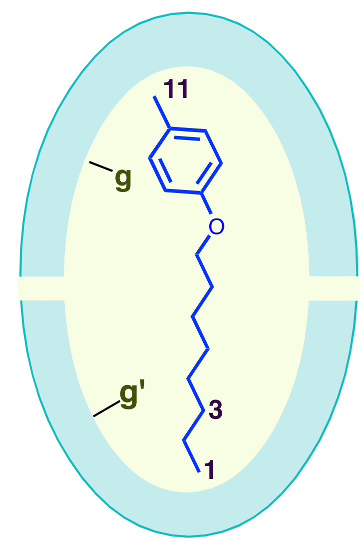


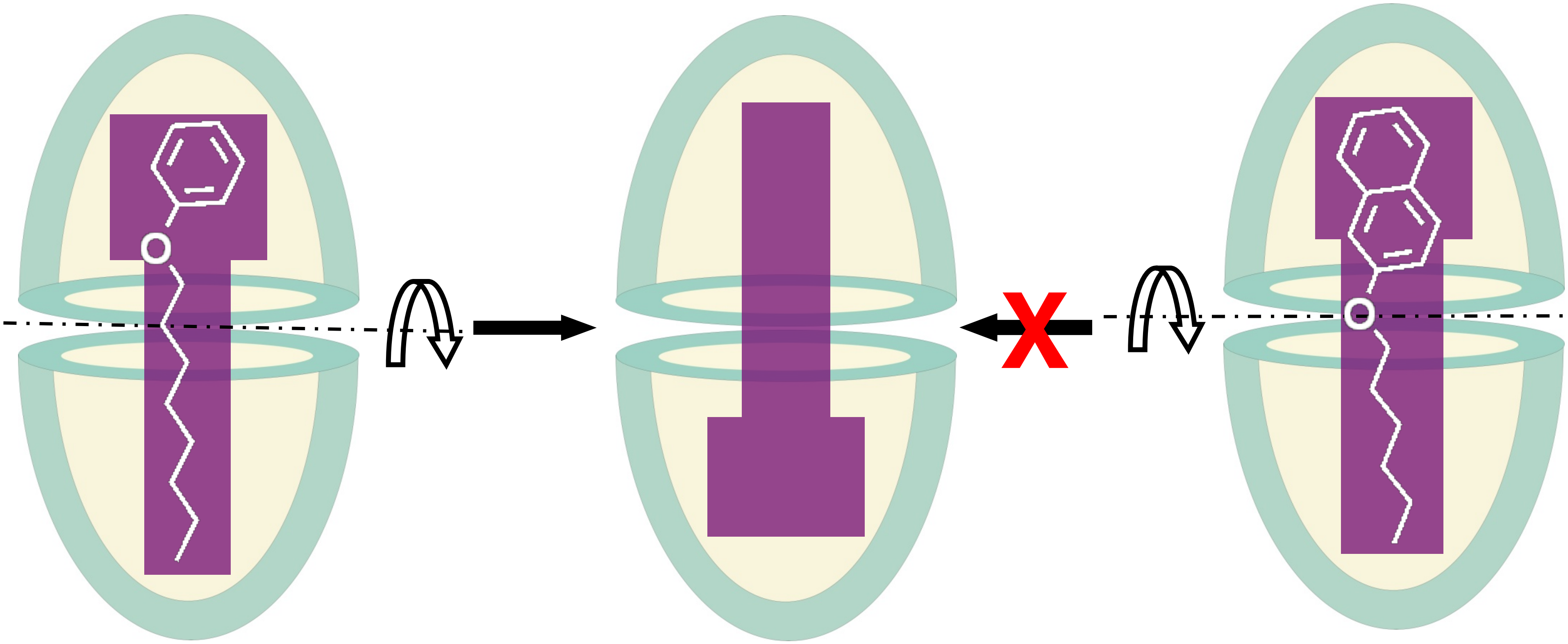
50 ms, 25 °C

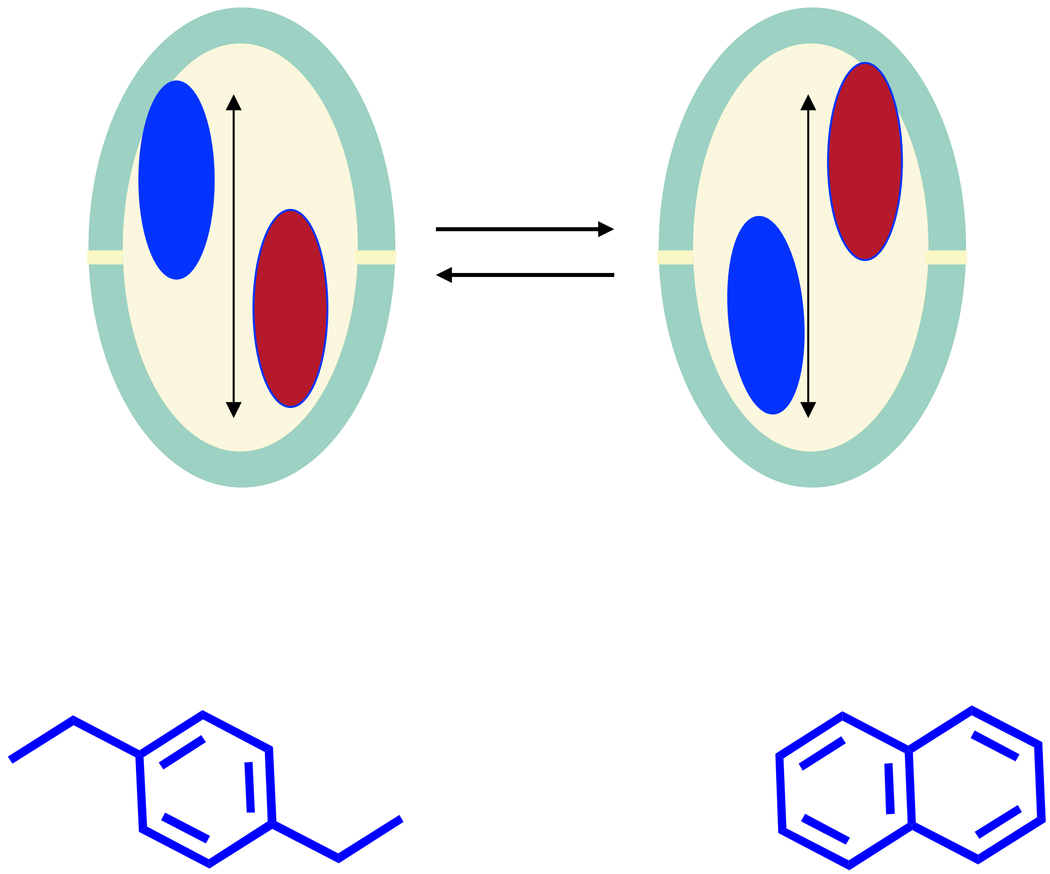
Variation of Temperature



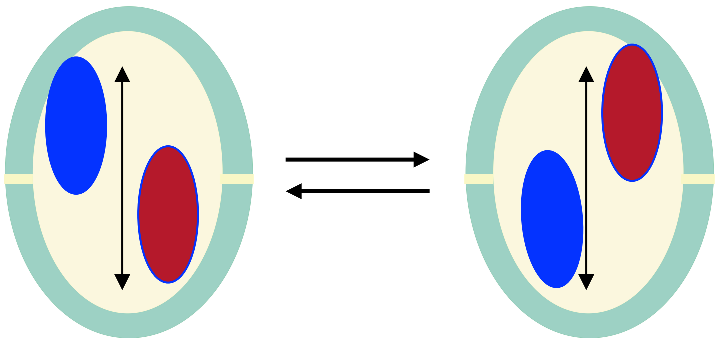
300 ms, 5 °C

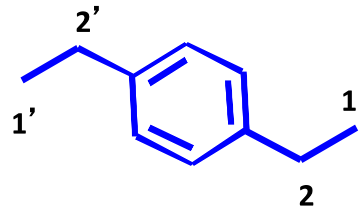


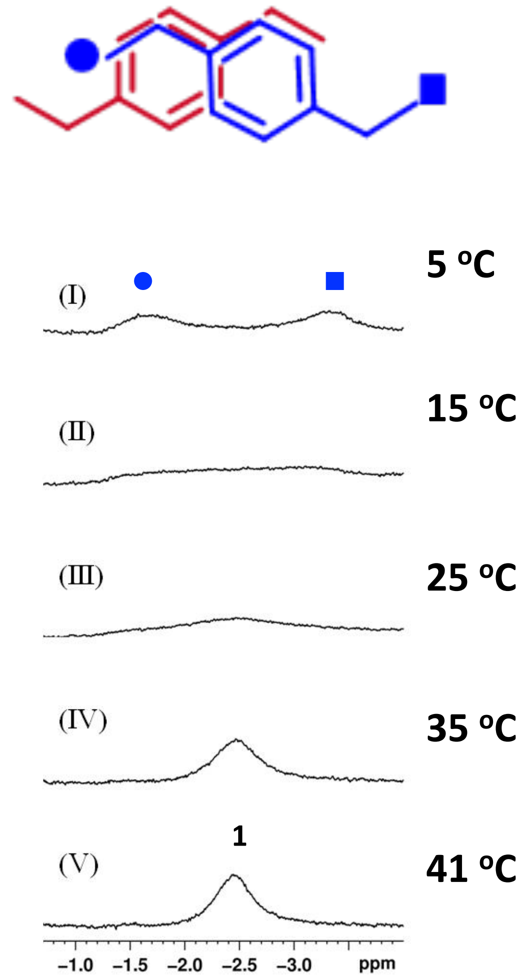


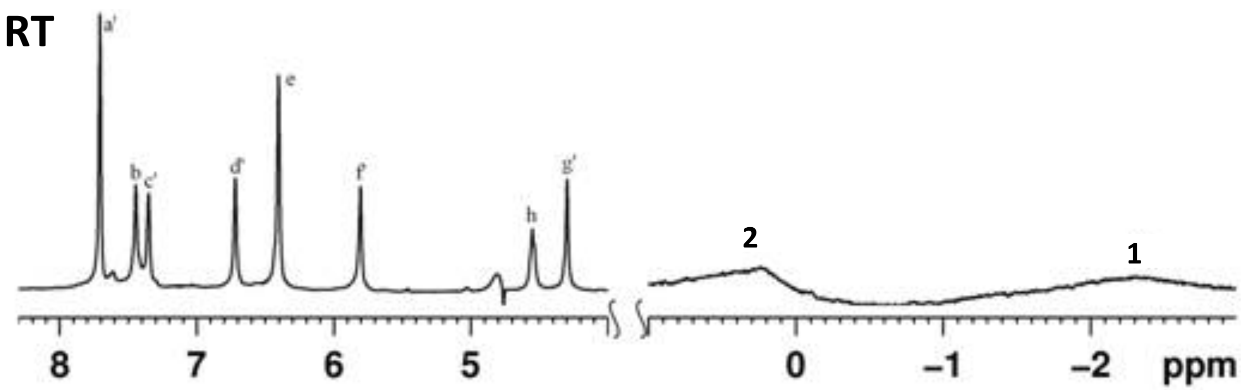


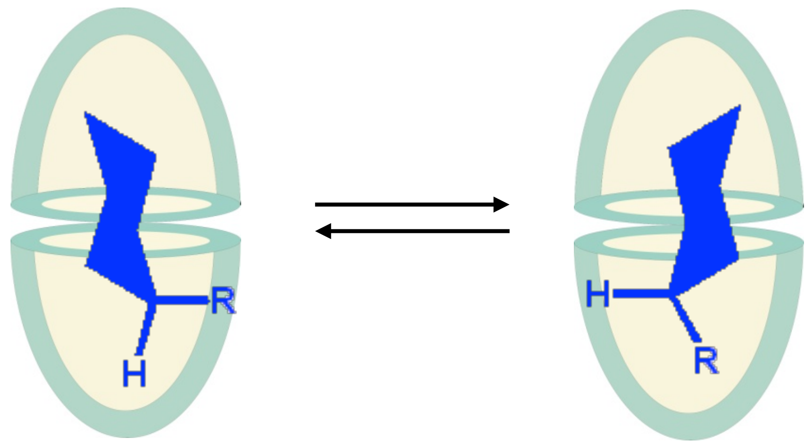
Slithering Motion of a Guest Within a Capsular Assembly

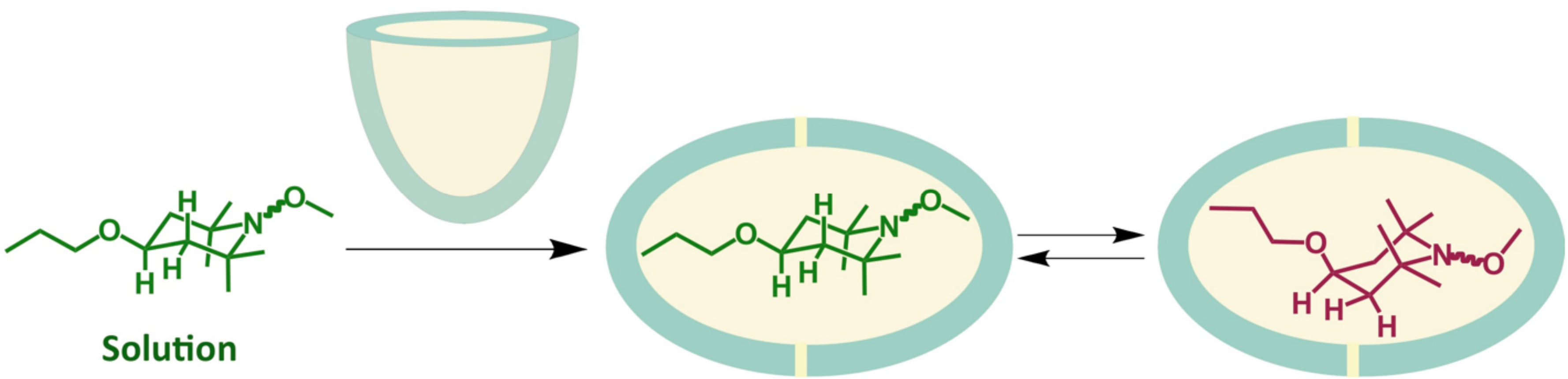


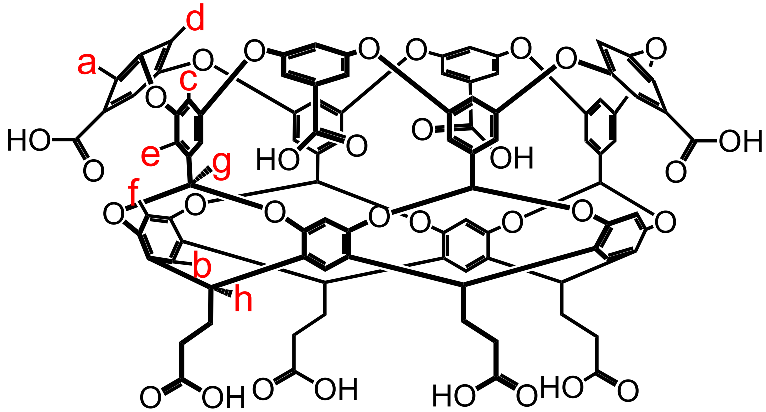


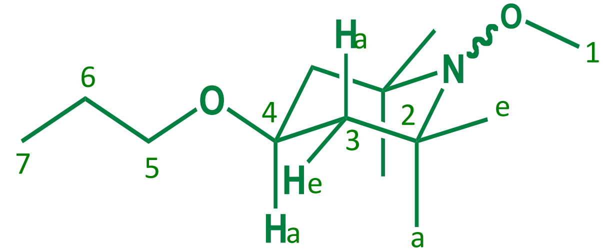


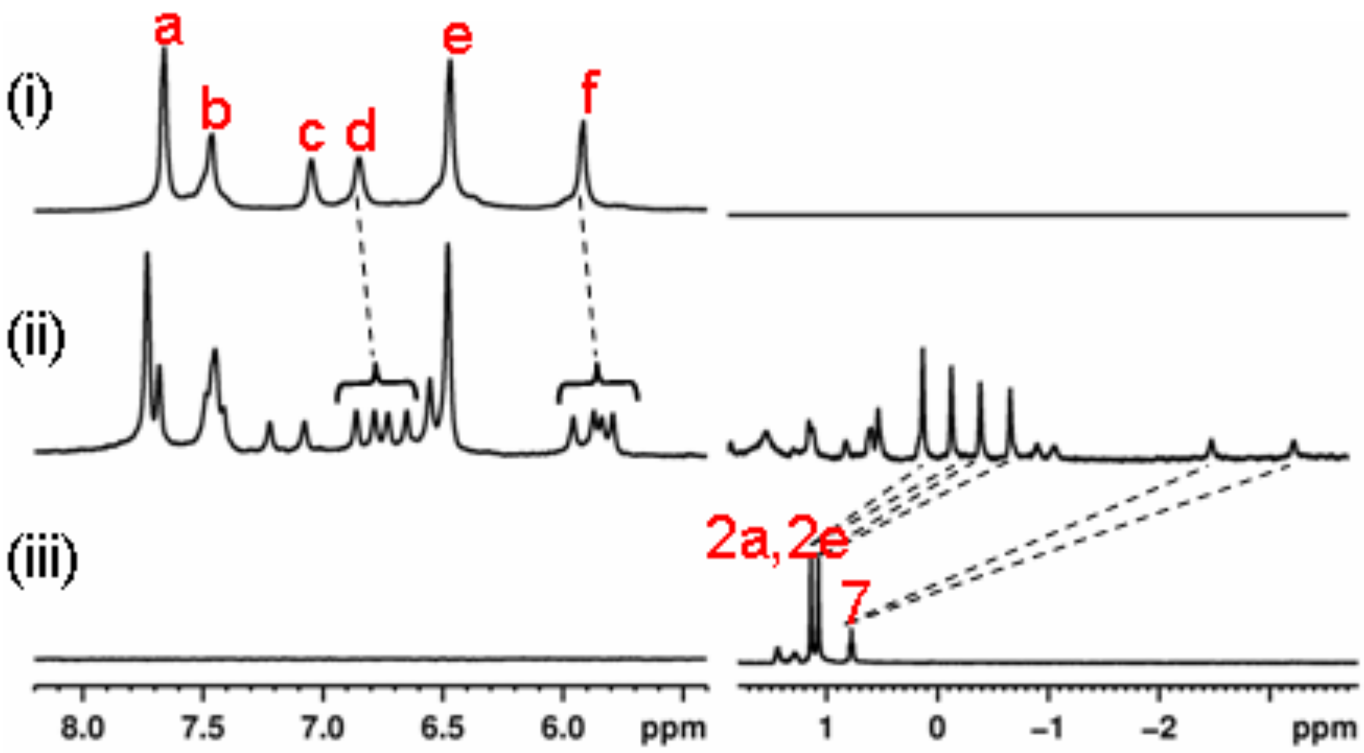


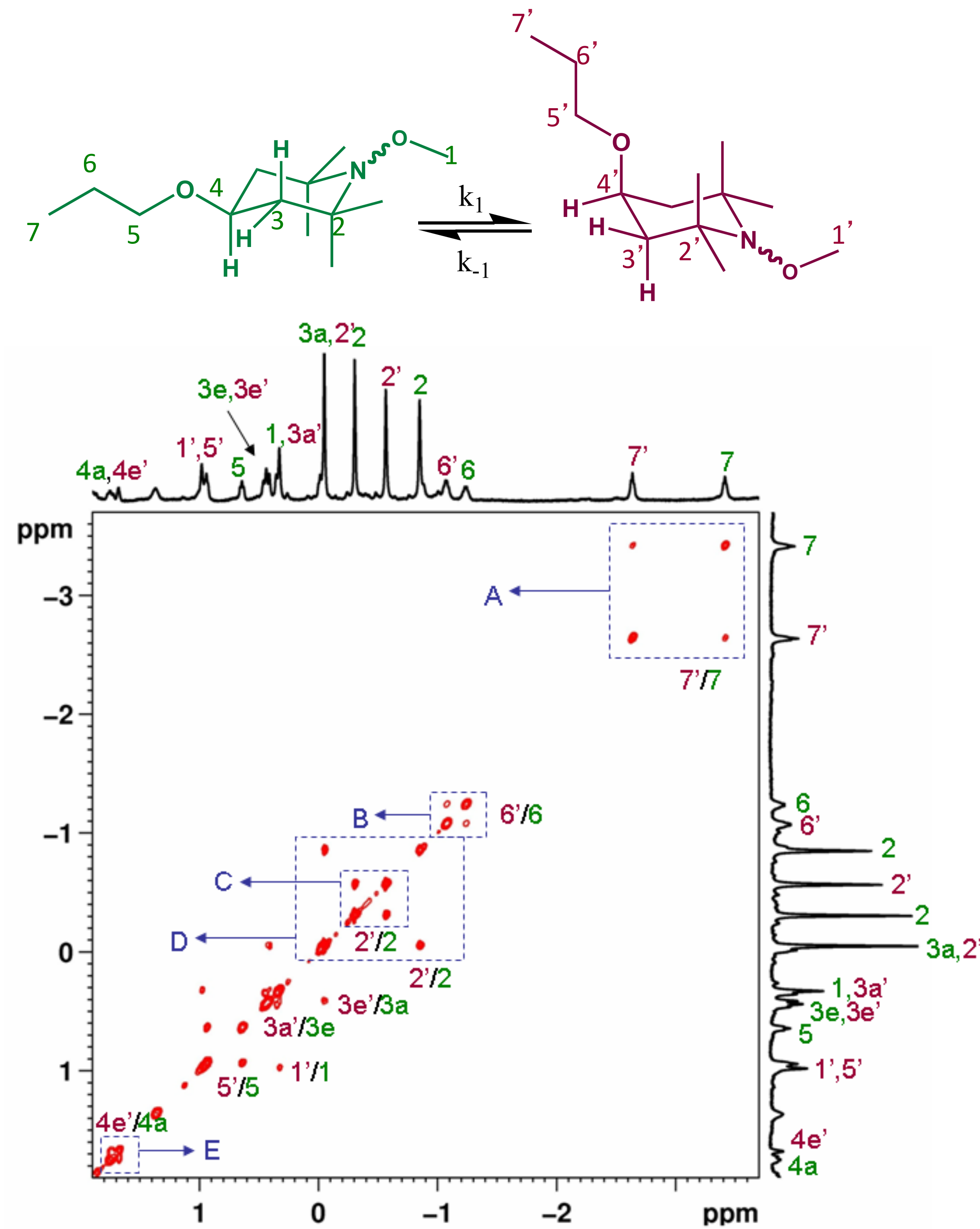

H
R
H
R


Solution

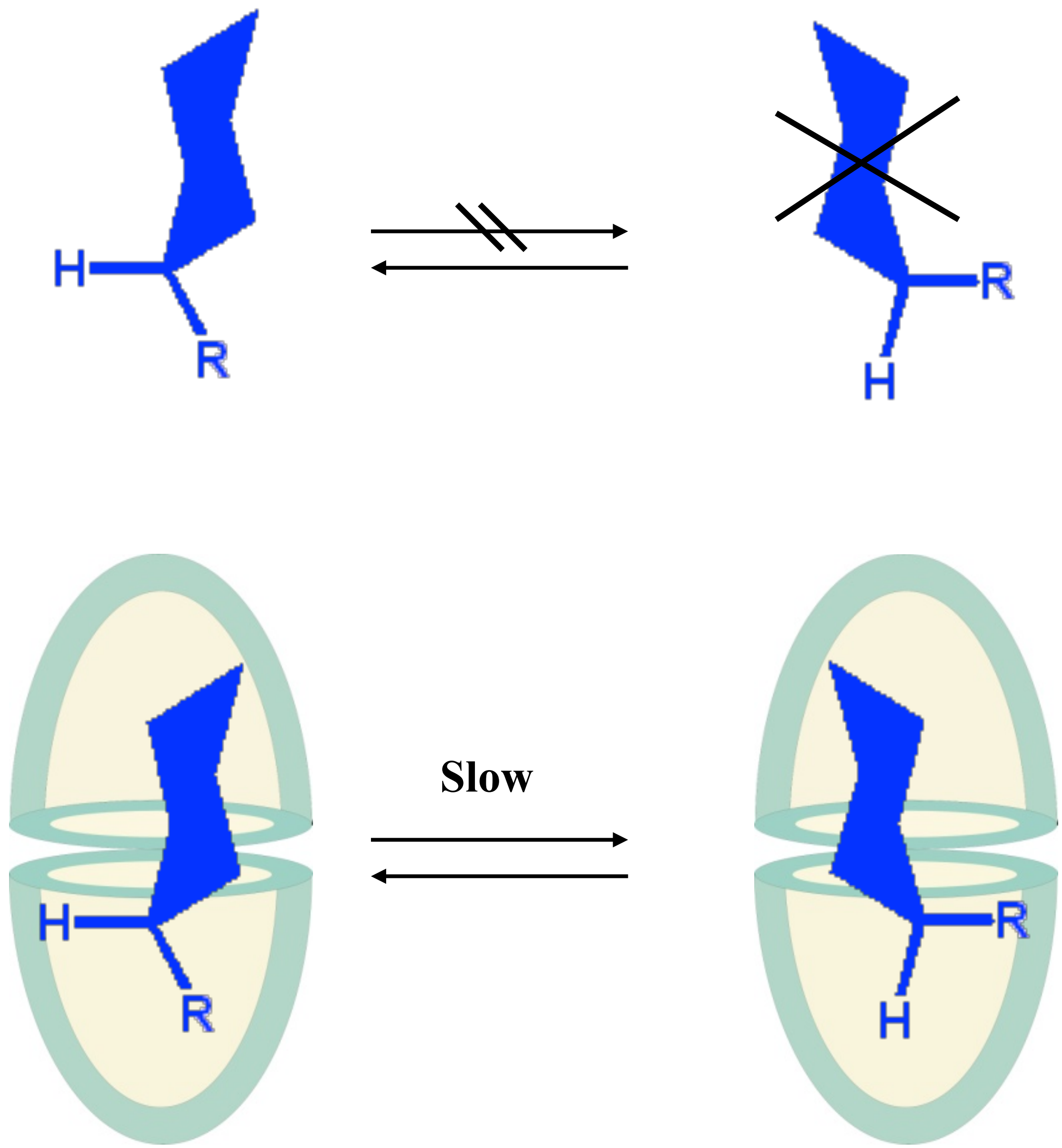

a
b
c
d
e
f
g
h
HO
OH
O


1
2
3
4
5
6
7
N
O
Ha
He
a
e


(i)
(ii)
(iii)
a
b
c
d
e
f
2a, 2e
7
8.0
7.5
7.0
6.5
6.0
ppm
1
0
−1
−2
ppm

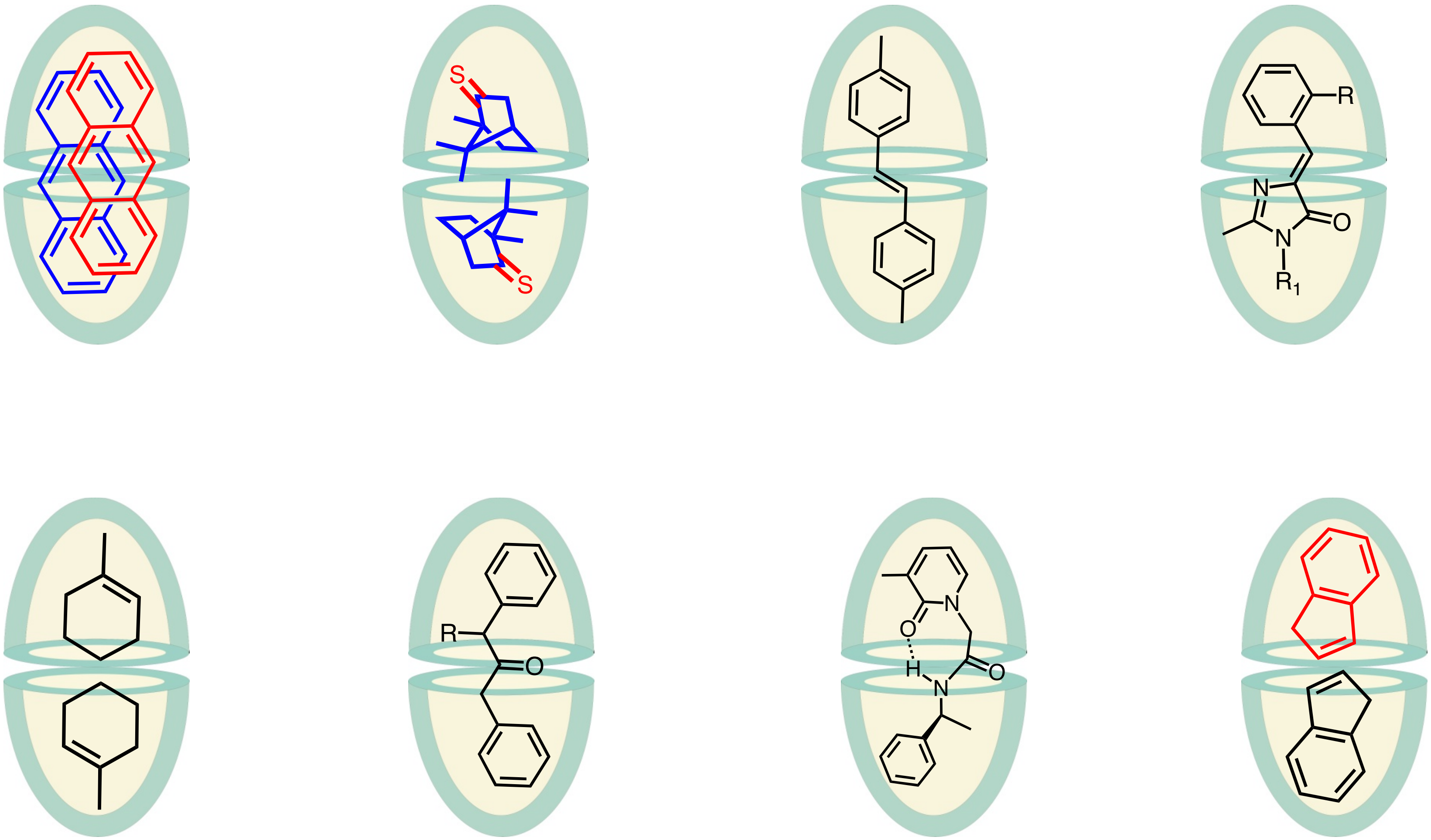


k1
k-1
3a,2'
2
2'
2
3e,3e'
1,3a'
1',5'
5
4a,4e'
7'
7
6'
6
ppm
A
7'/7
B
6'/6
C
D
2'/2
2'/2
3e'/3a
3a'/3e
1'/1
5'/5
4e'/4a
E

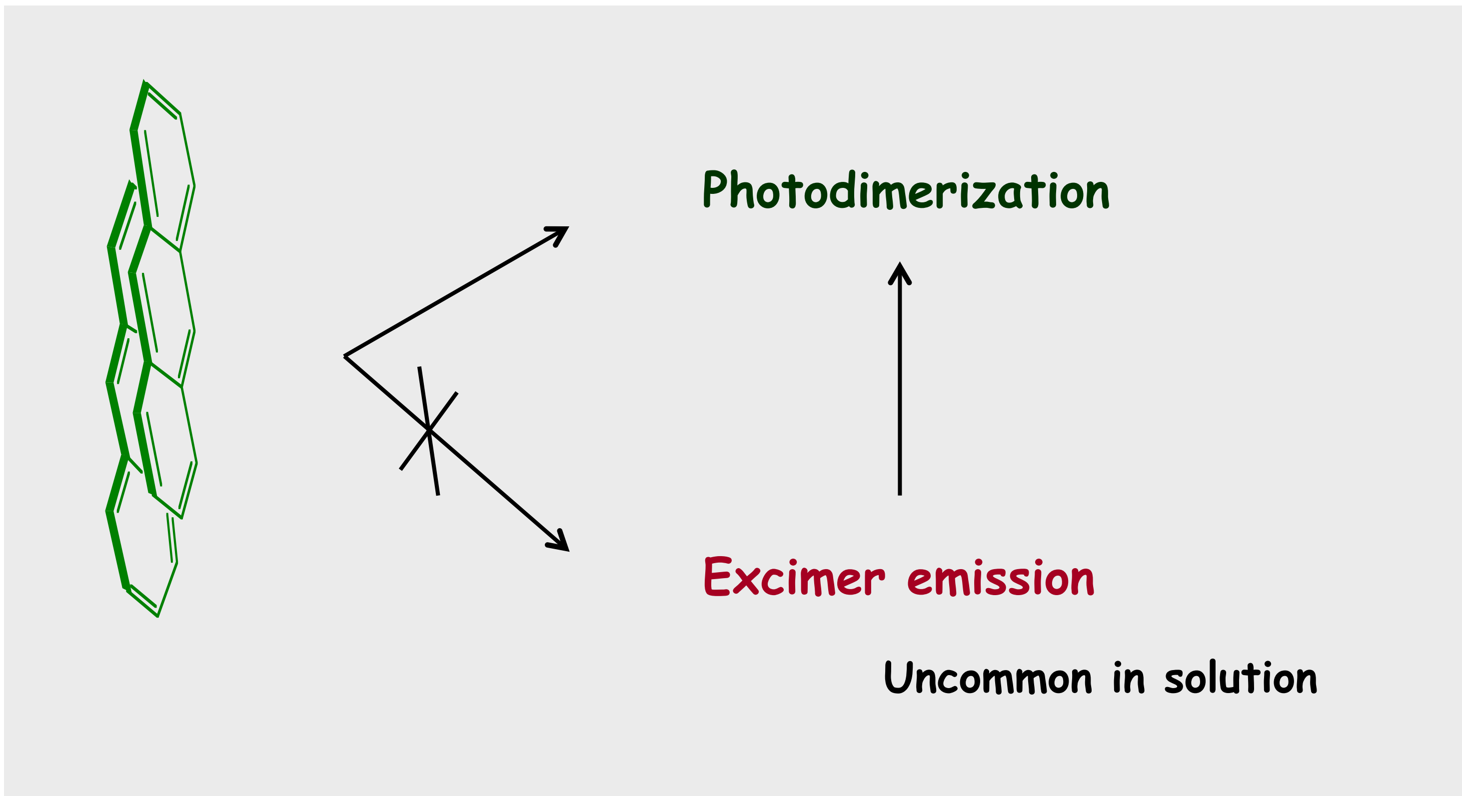


H
R
R
H
Slow
H
R
R
H

Manipulating photophysics and photochemistry through confinement

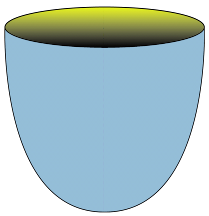


Photochemistry and Photophysics of Anthracene

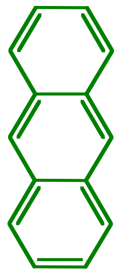


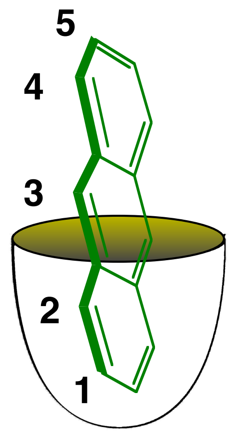
OA-anthracene complex

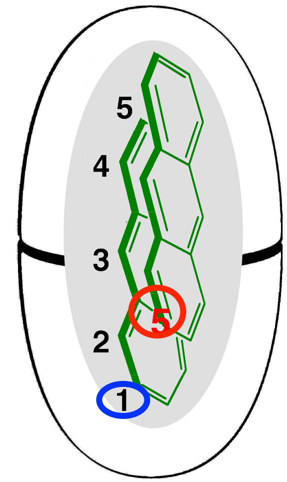
Octa Acid



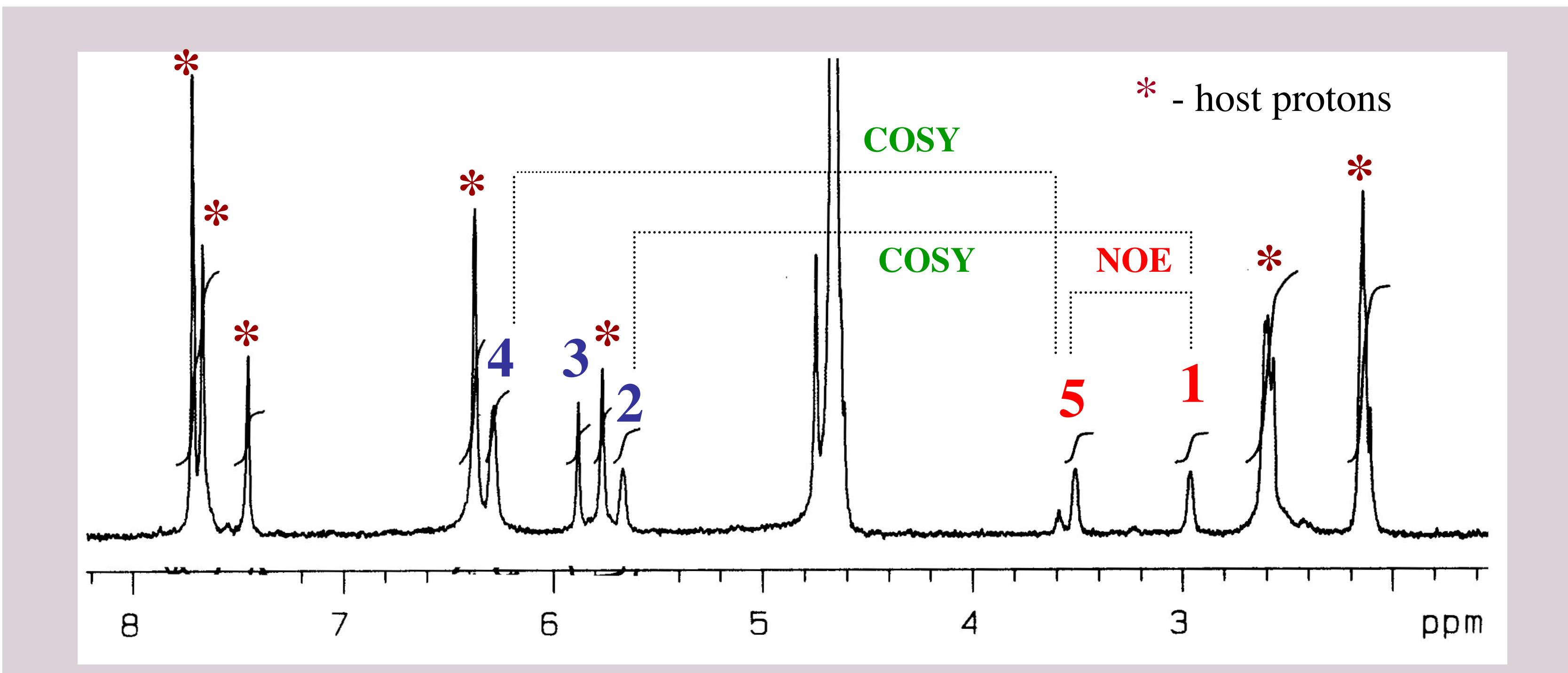
Anthracene



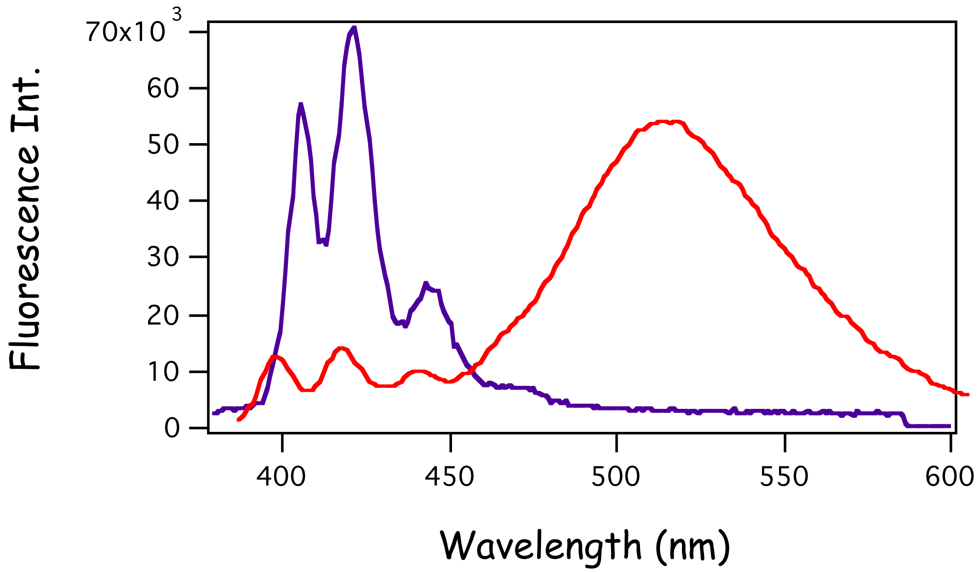




Five Signals



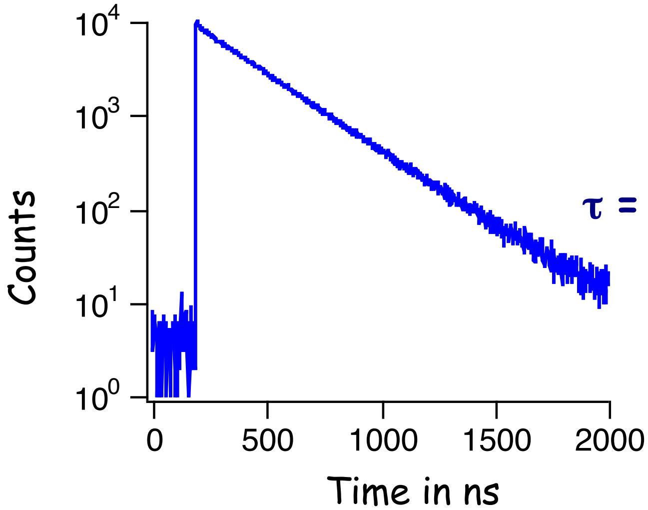
Photophysics of OA-Anthracene Complex



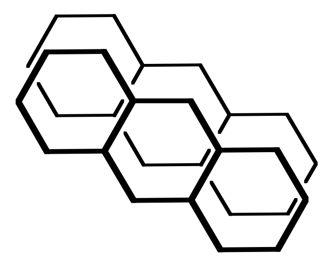
---- Anthracene in water

---- Anthracene in octa acid

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

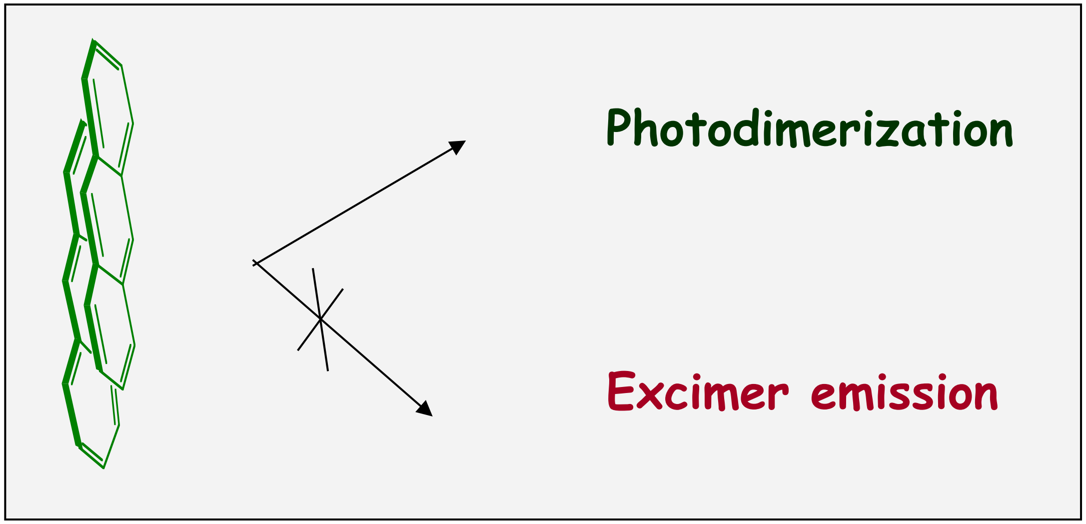


τ = 263 ns

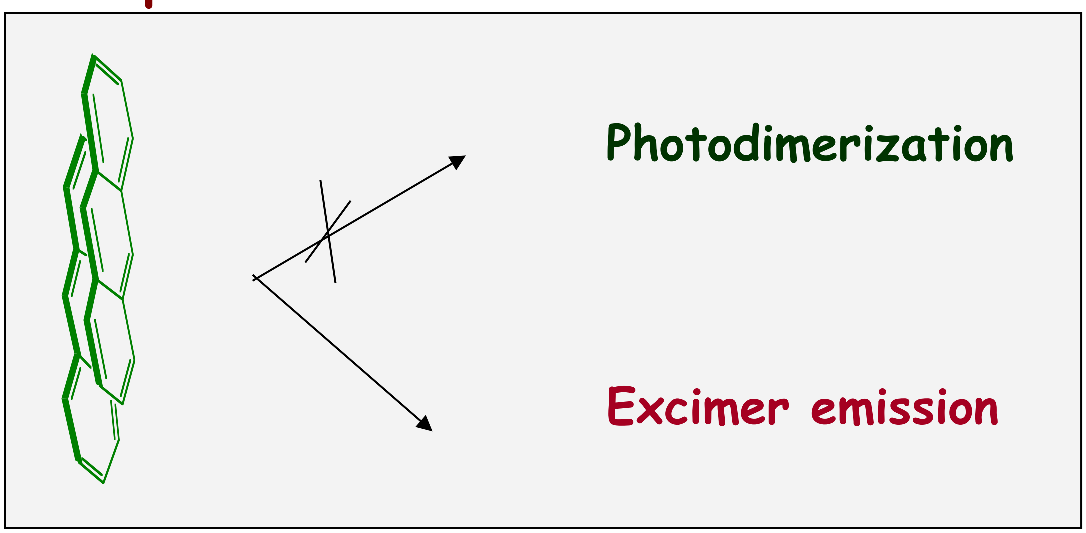


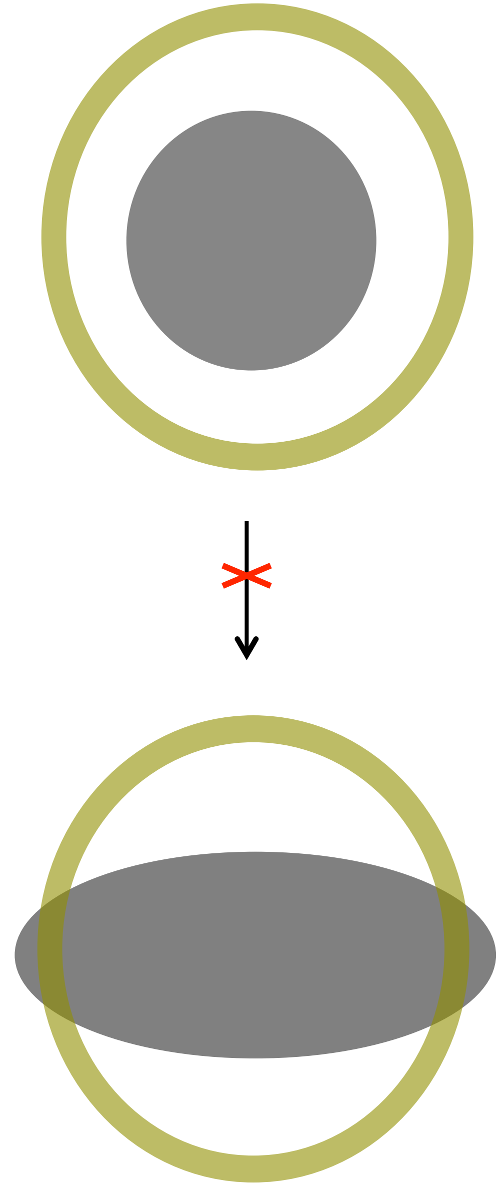
Sandwich excimer – τ 210 - 225 ns

Isotropic solution



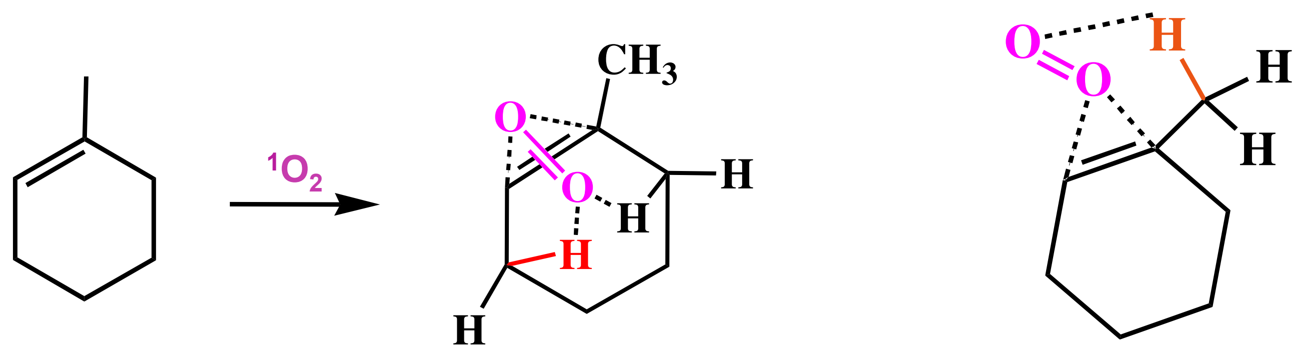
OA complex

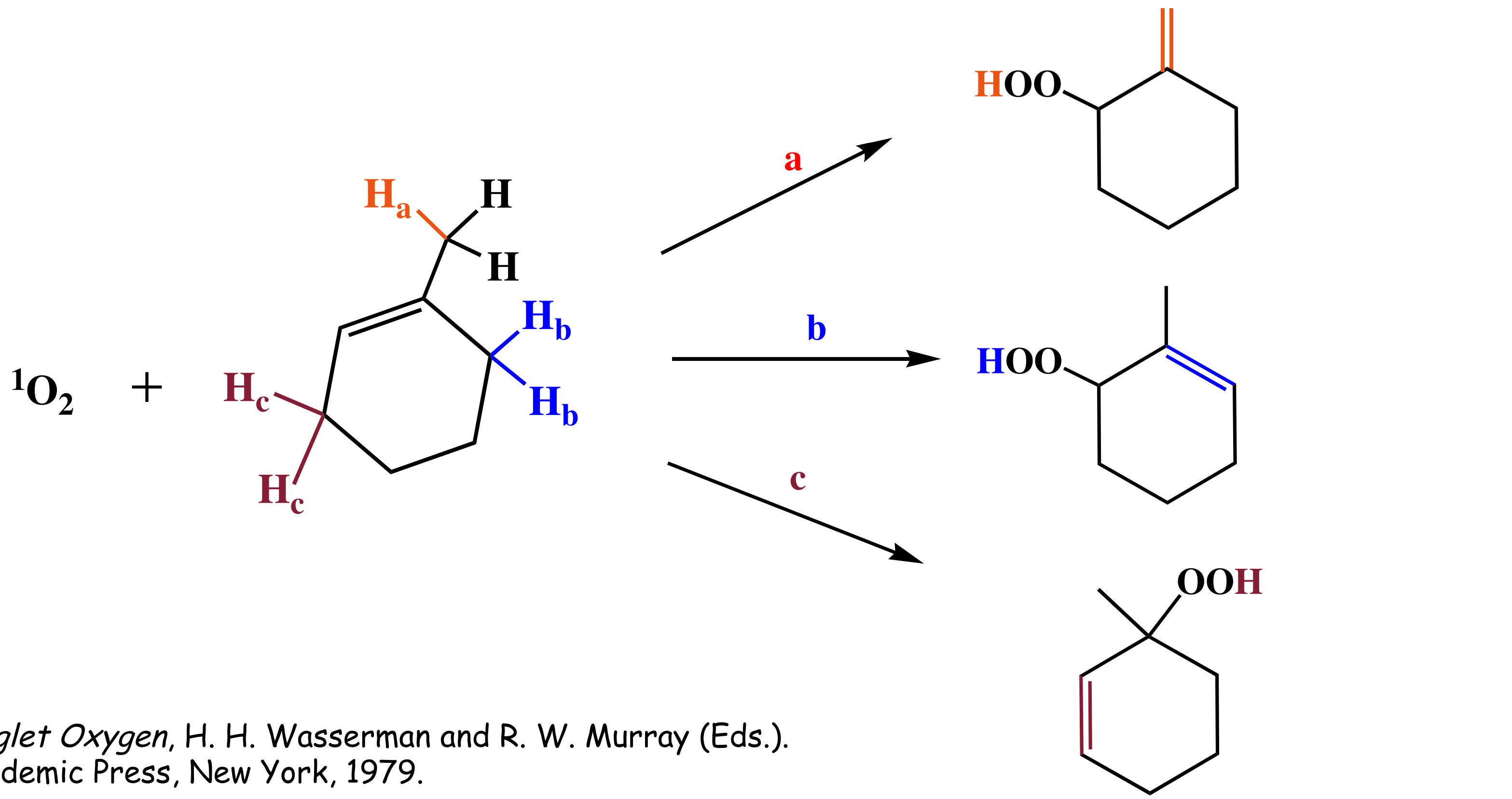




Product too large to fit in

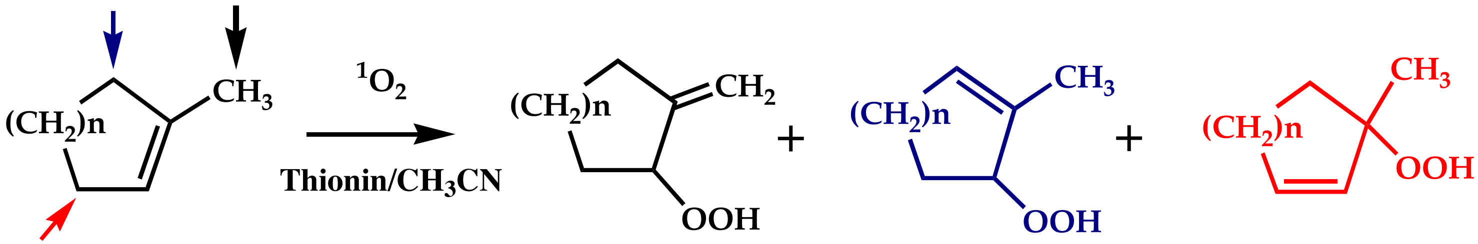
Oxidation of olefins by singlet oxygen: Ene reaction

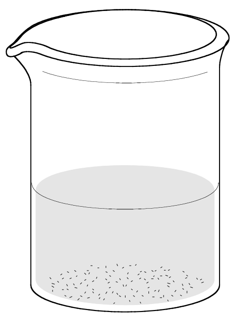


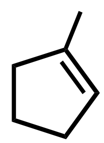
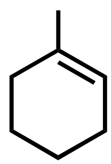
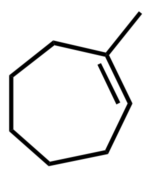
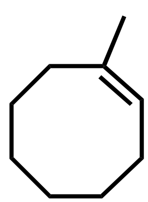


Singlet Oxygen, H. H. Wasserman and R. W. Murray (Eds.).
Academic Press, New York, 1979.

Goal: To conduct regioselective ene reaction in water

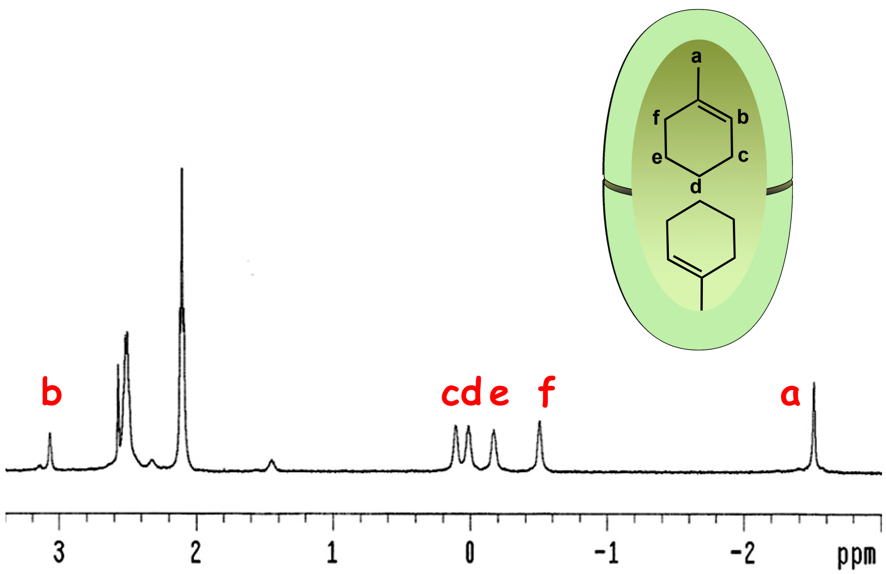


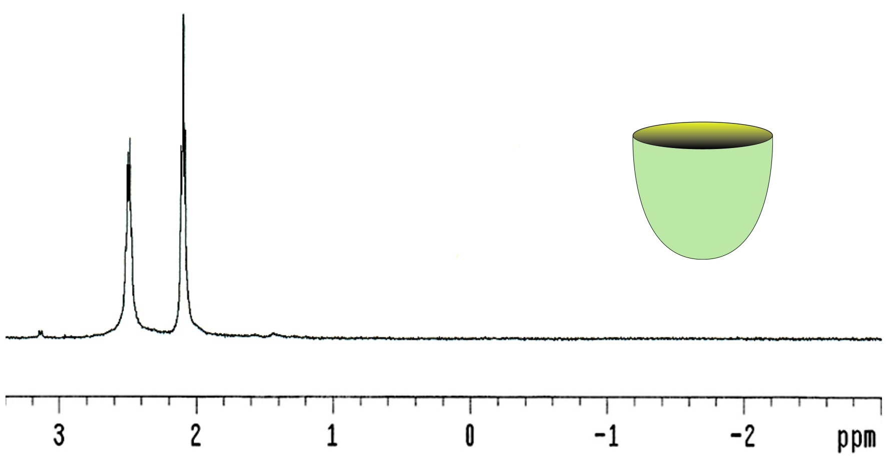


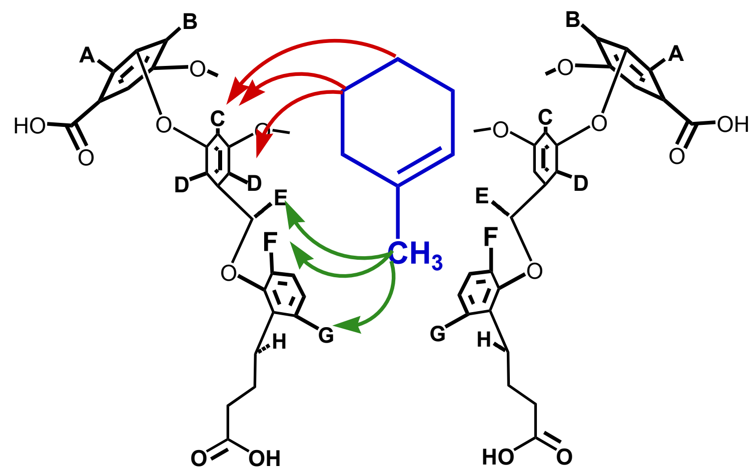
	Product Yield (%)		
	6	45	48
	40	15	45
	10	47	43
	30	49	21

C. S. Foote, *Pure Appl. Chem.*, 27, 635 (1971)

Characterization of Olefin-OA Complex by ^{1}H NMR

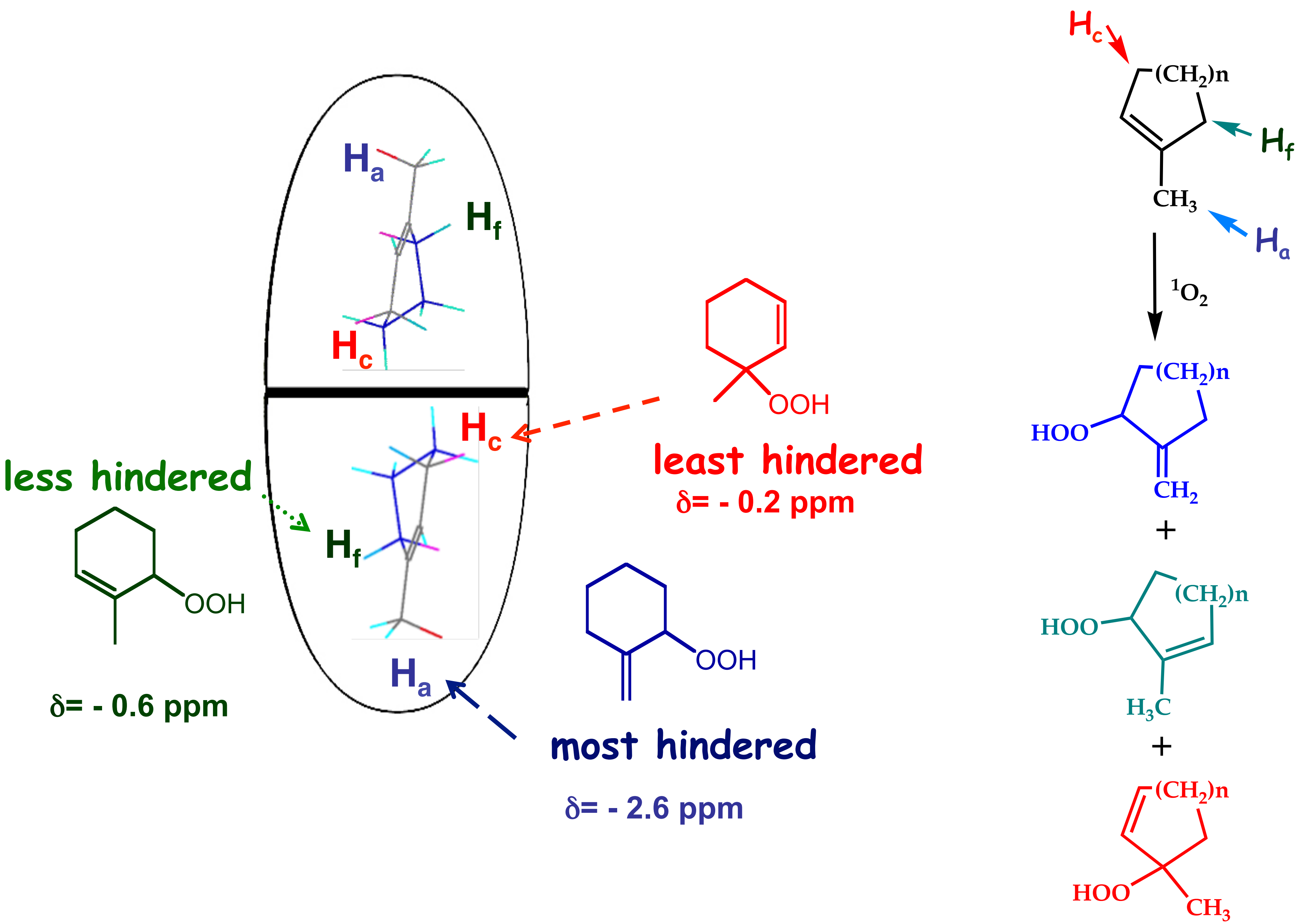




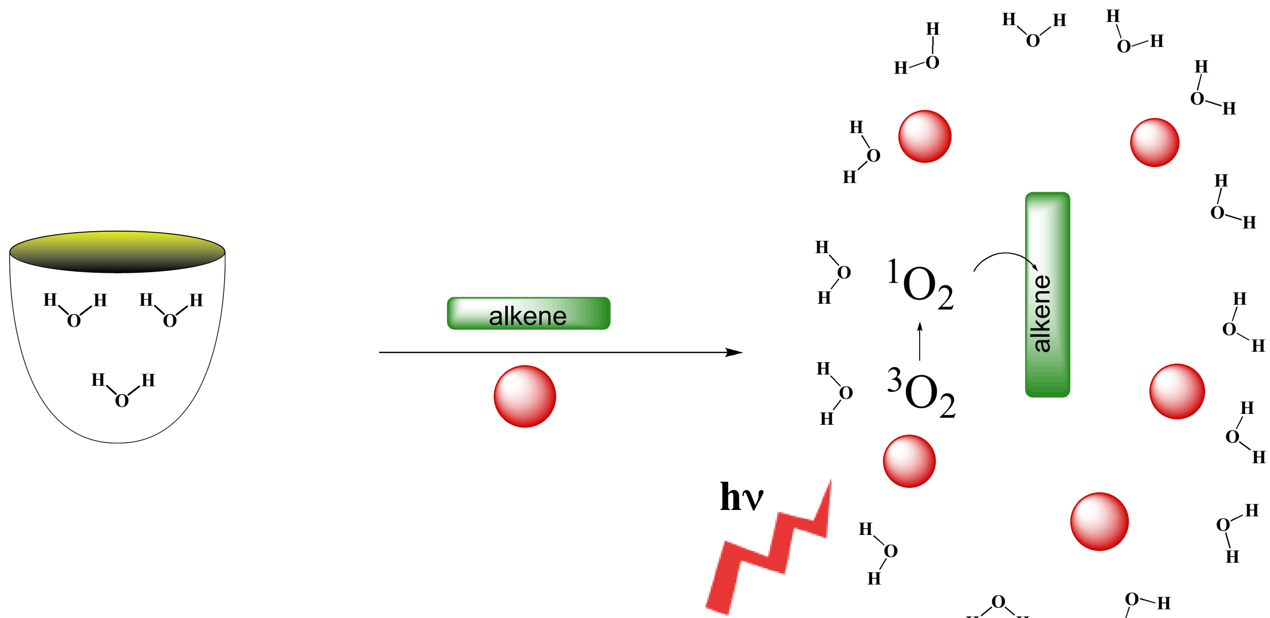


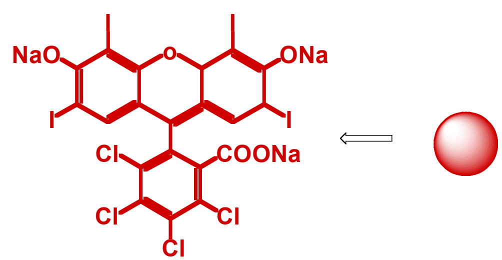
NOE interactions between the host and the guest

1-Methylcyclohexene anchored through methyl group within OA



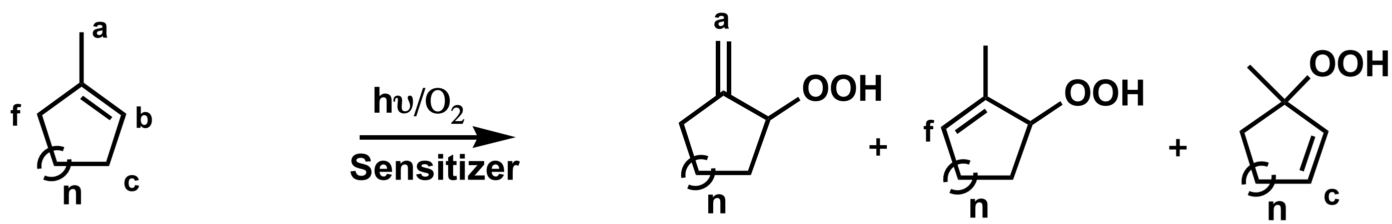
Singlet oxygen generation for oxidation of encapsulated olefins





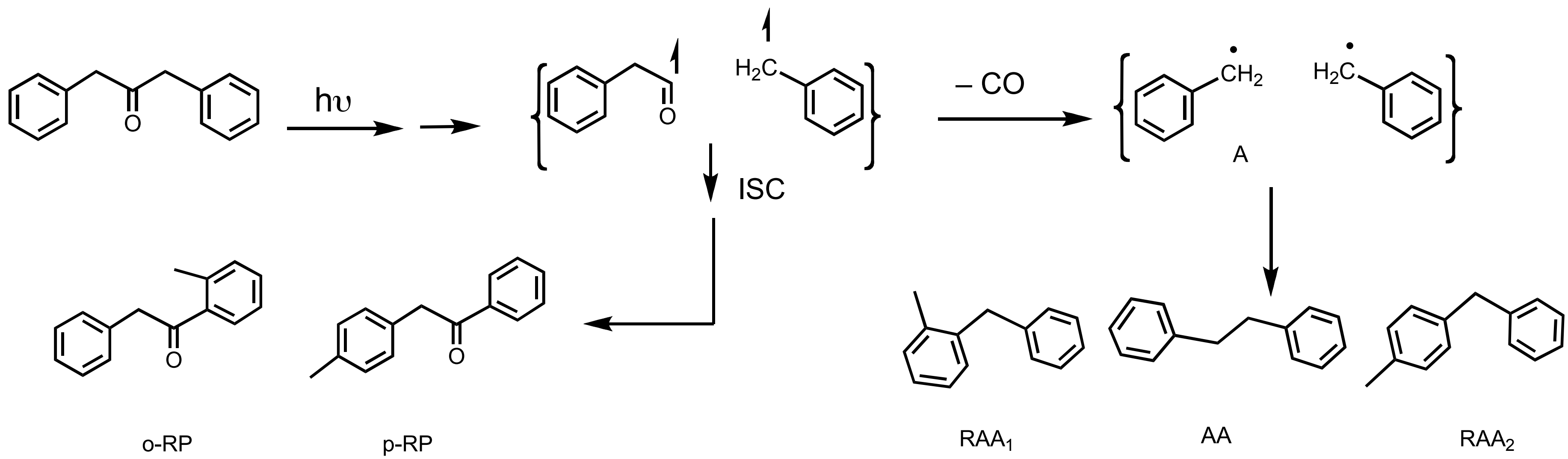
Rose Bengal
Hydrophilic Sensitizer

Selective oxidation of 1-methyl cycloalkenes-OA complex



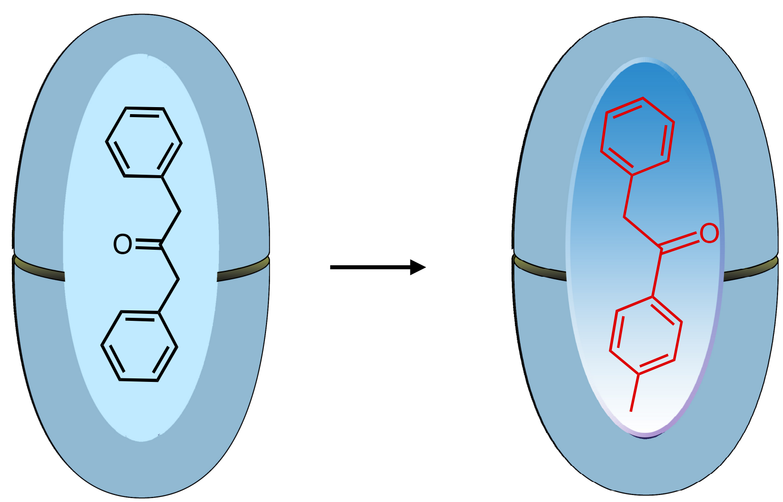
n=1	CH_3CN / Rose bengal	4%	43%	53%
	Octa acid / Rose bengal	-	5%	95%
n=2	CH_3CN / Rose bengal	44%	20%	36%
	Octa acid / Rose bengal	10%	-	90%
n=3	CH_3CN / Rose bengal	4%	48%	48%
	Octa acid / Rose bengal	4%	6%	90%

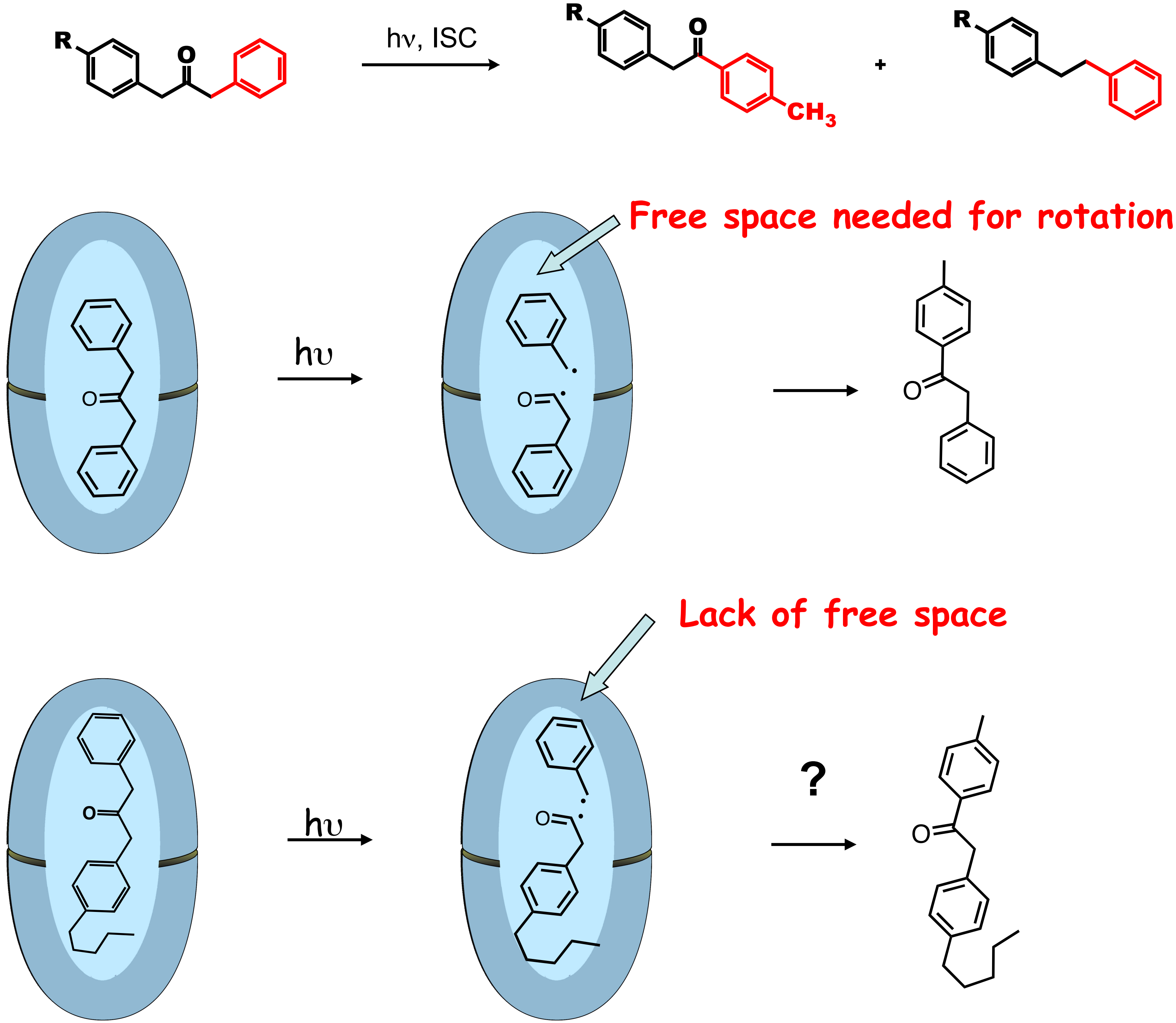
The primary radical pair prefers to rotate than decarbonylate

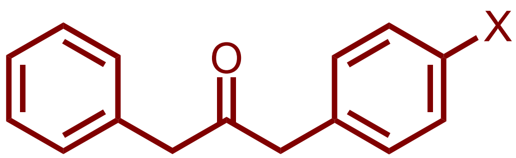


Relative product distribution (%)

Medium	RAA$_1$+RAA$_2$	AA	*p*-RP
Hexane	--	>99	--
Octa acid	10	34	56




R
O
hν, ISC
R
O
CH3
+
R
Free space needed for rotation
O
hυ
O
O
Lack of free space
O
hυ
O
?
O

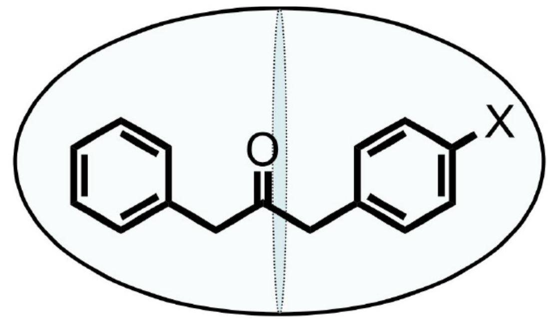


$X = CH_2CH_3$

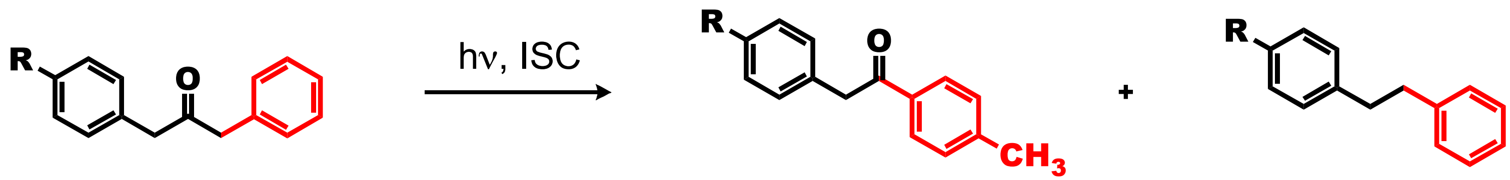
$X = (CH_2)_2CH_3$

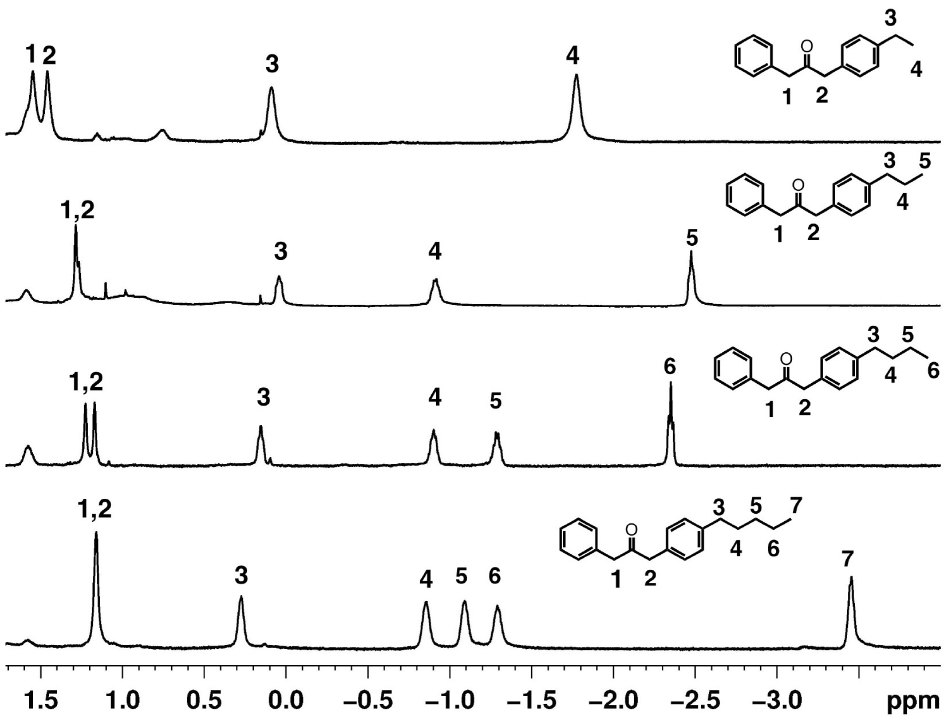
$X = (CH_2)_3CH_3$

$X = (CH_2)_4CH_3$

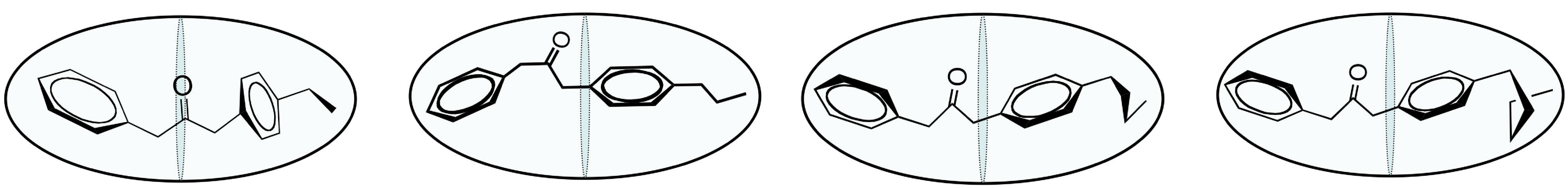


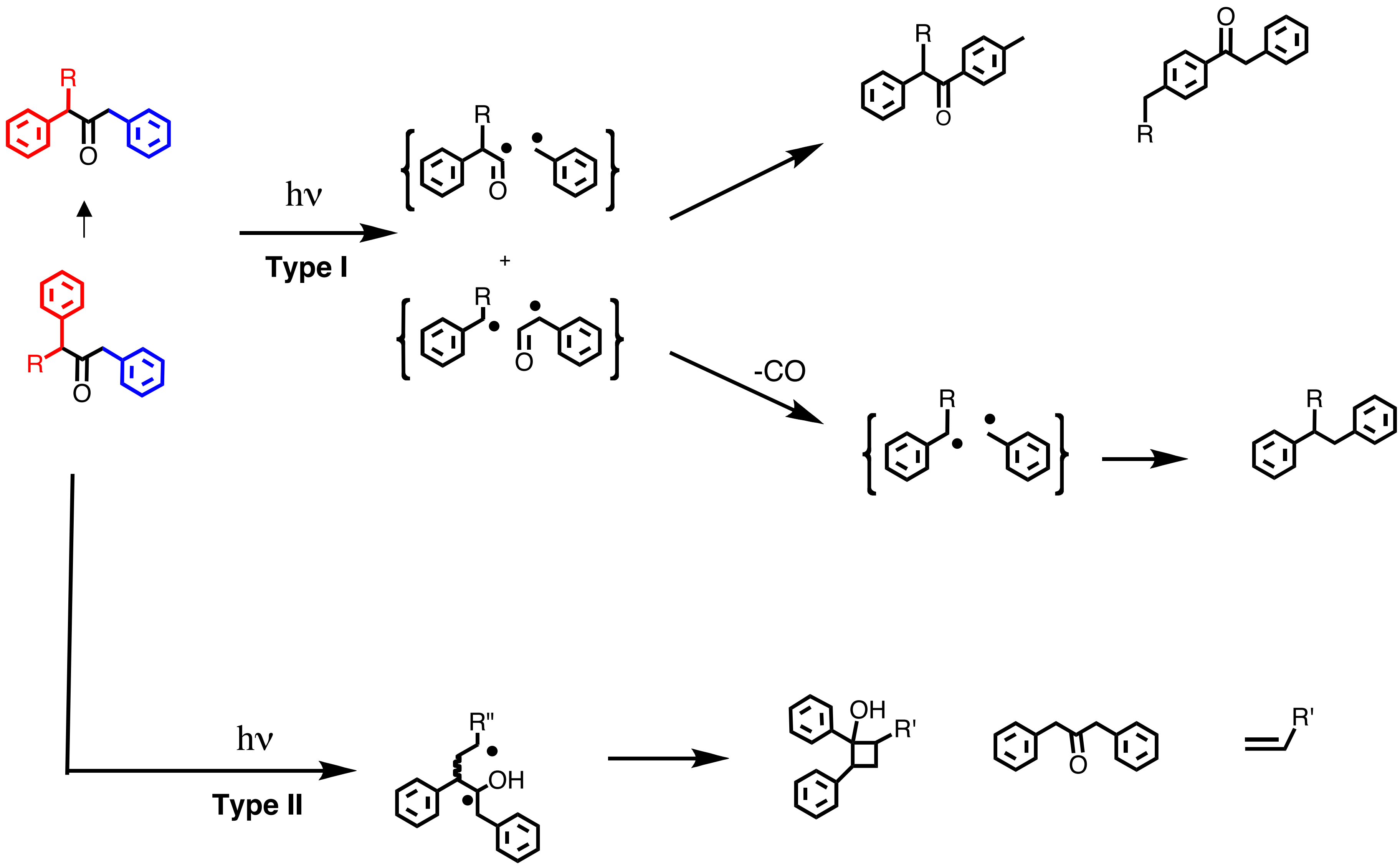
Controlling free space through an alkyl tail





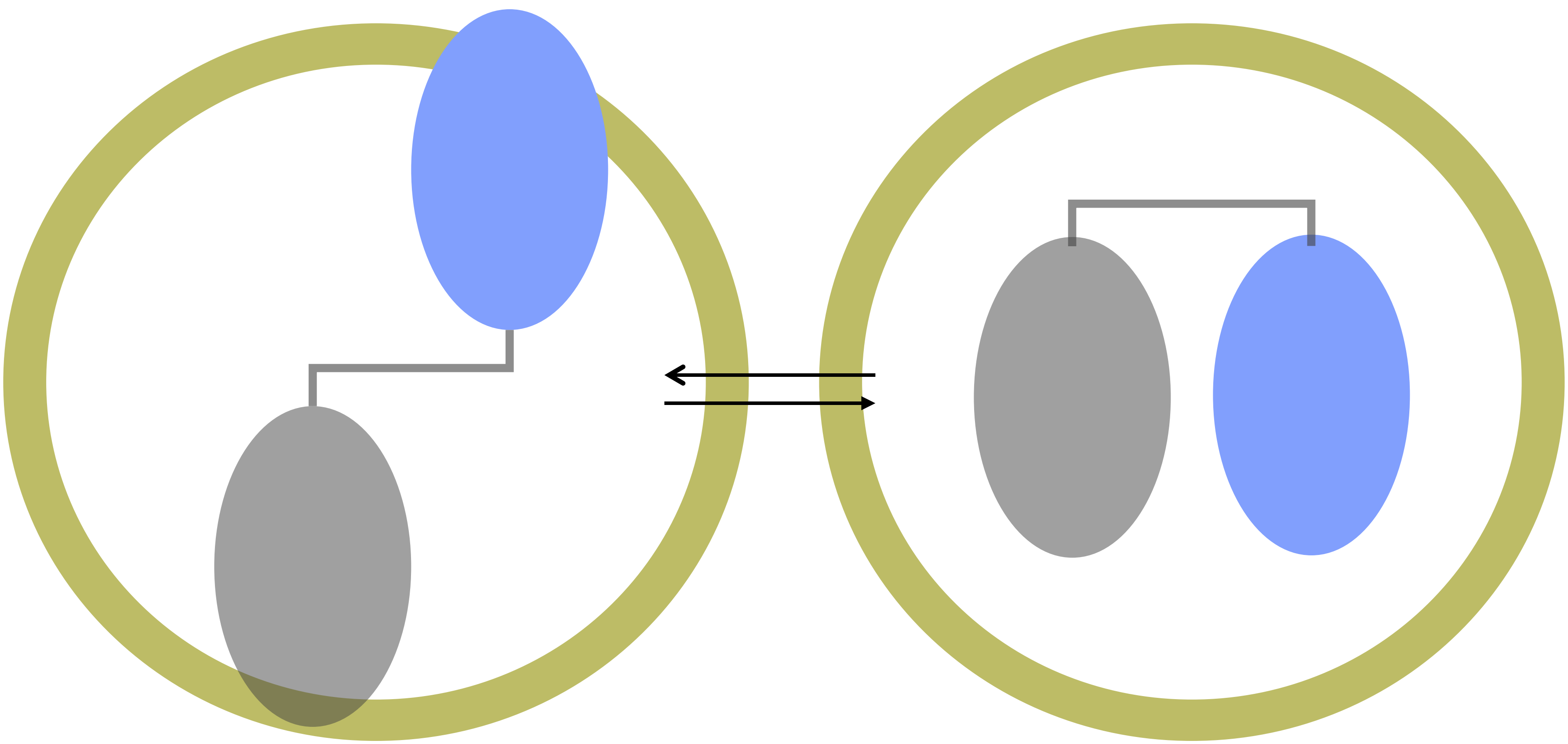
49%	51%
41	59
15	85
0	100

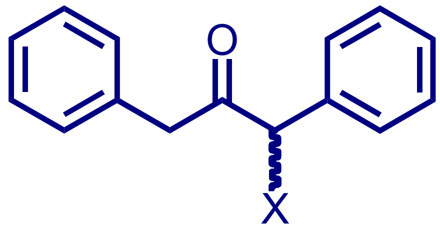




hν
Type I
-CO
hν
Type II

Conformational Control and Rotational Restriction





$X = CH_3$

$X = CH_2CH_3$

$X = (CH_2)_2CH_3$

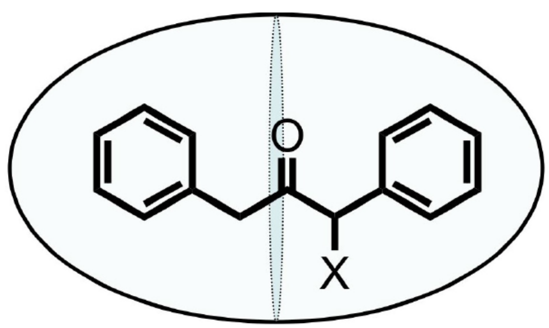
$X = (CH_2)_3CH_3$

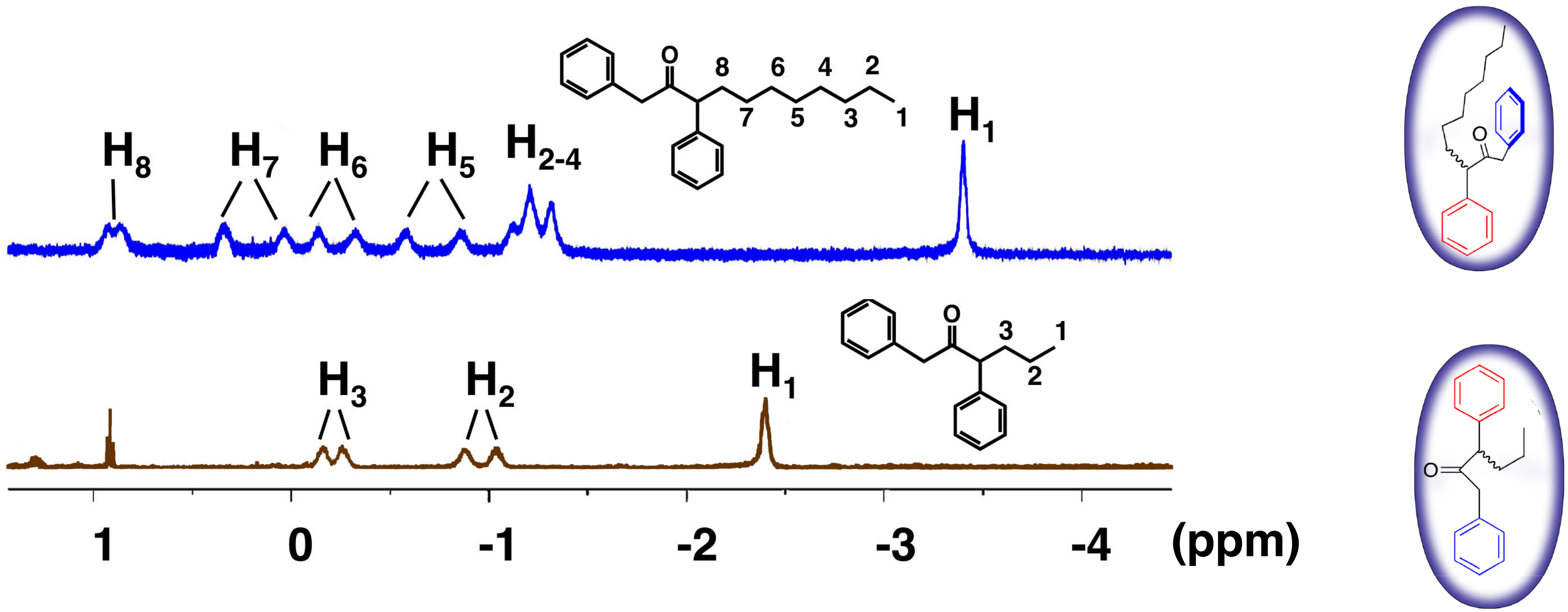
$X = (CH_2)_4CH_3$

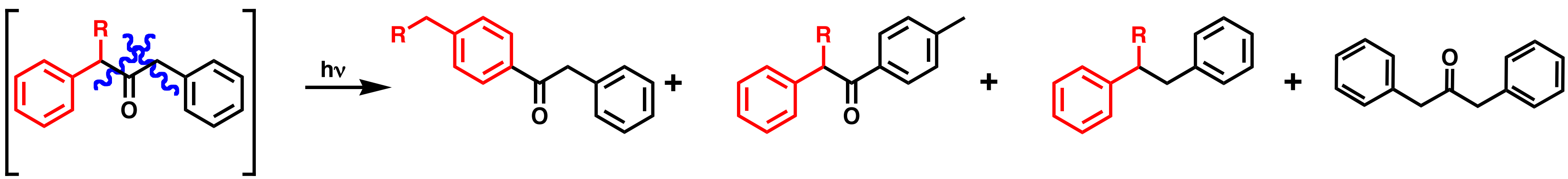
$X = (CH_2)_5CH_3$

$X = (CH_2)_6CH_3$

$X = (CH_2)_7CH_3$



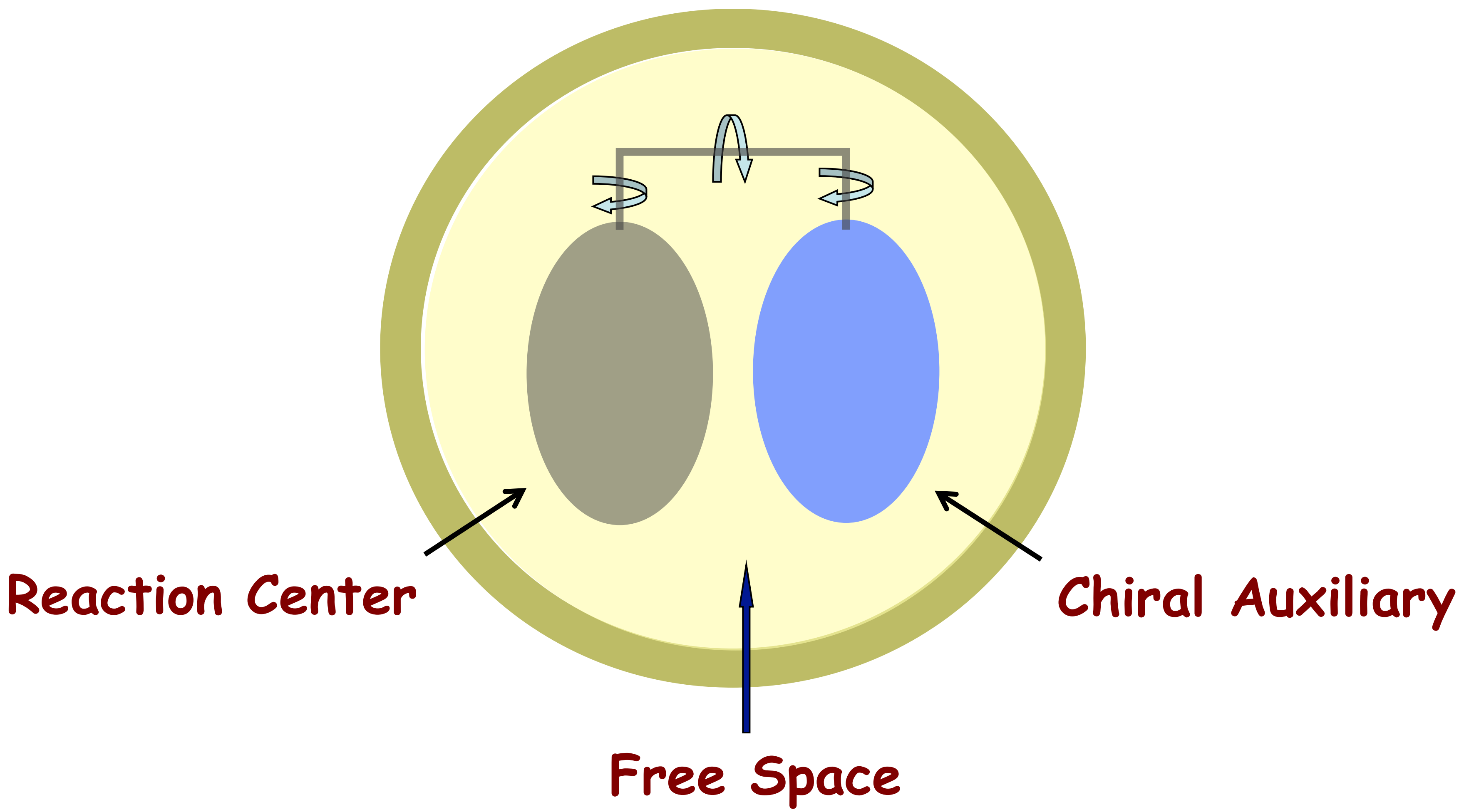




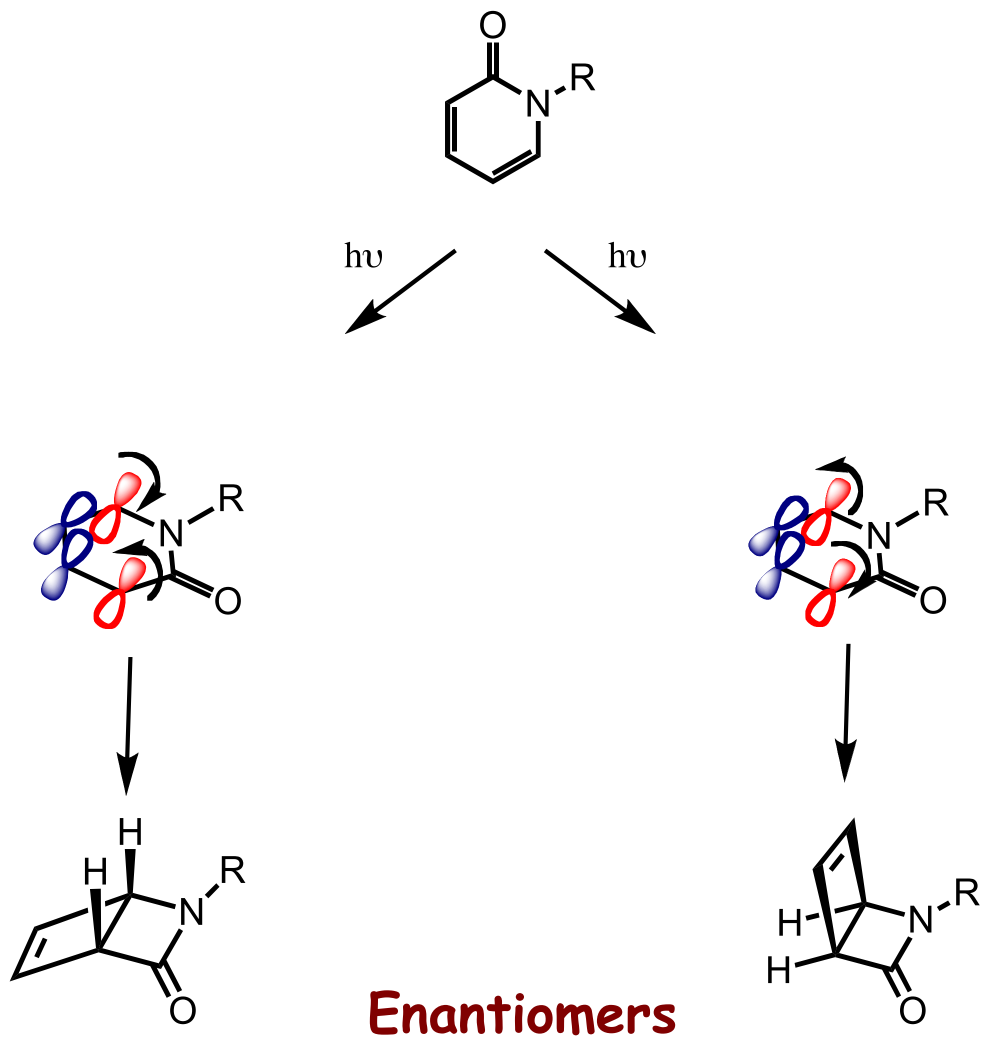
$-C_3H_7$	35	4	50	11
$-C_8H_{17}$	-	-	10	90

Role of Free Space

Conformational Control and Rotational Restriction

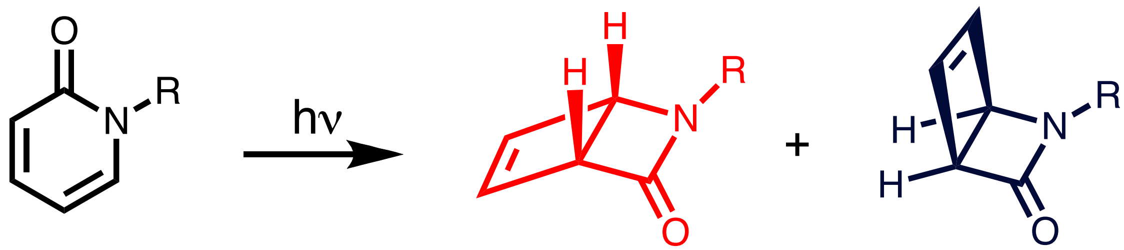


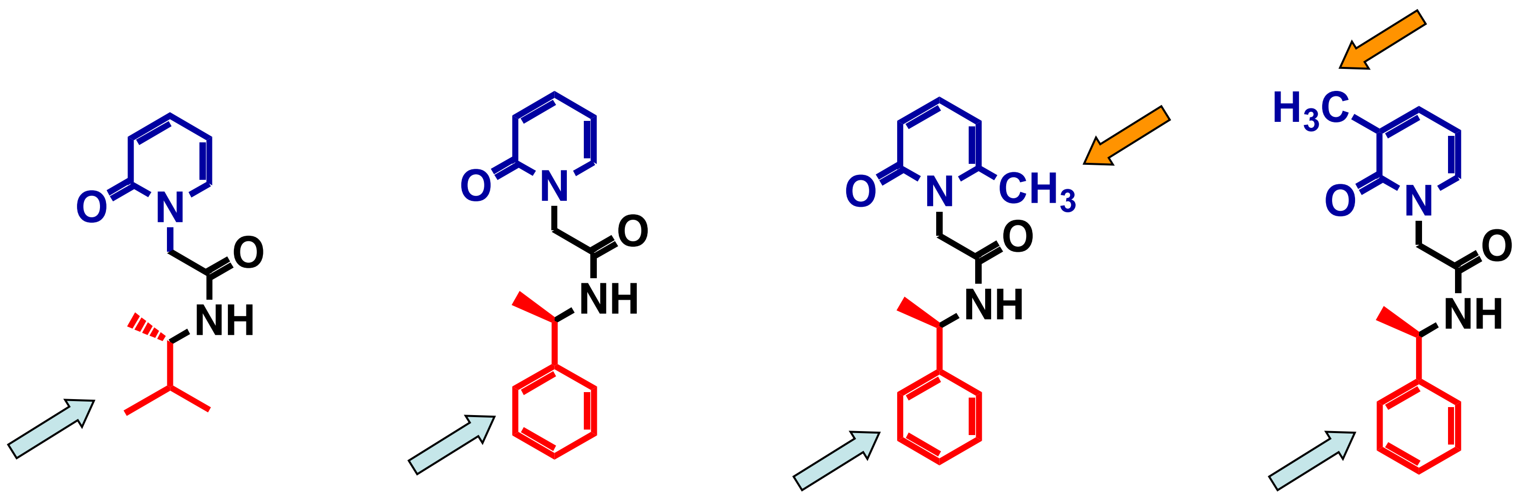
Amplified Chiral Induction in a Supramoecular Assembly



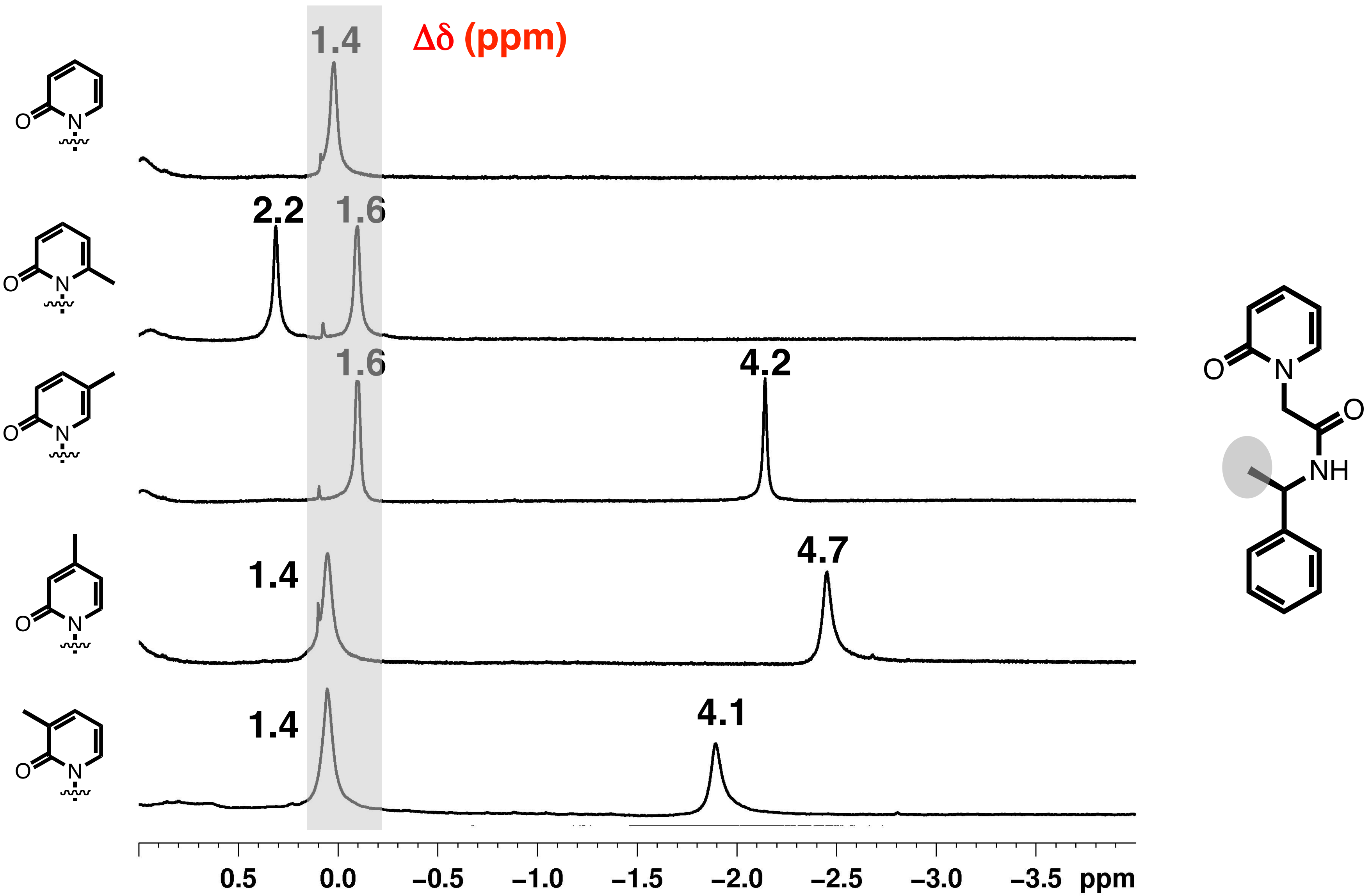
Enantiomers
Diastereomers

Importance of phenyl group and methyl substitution

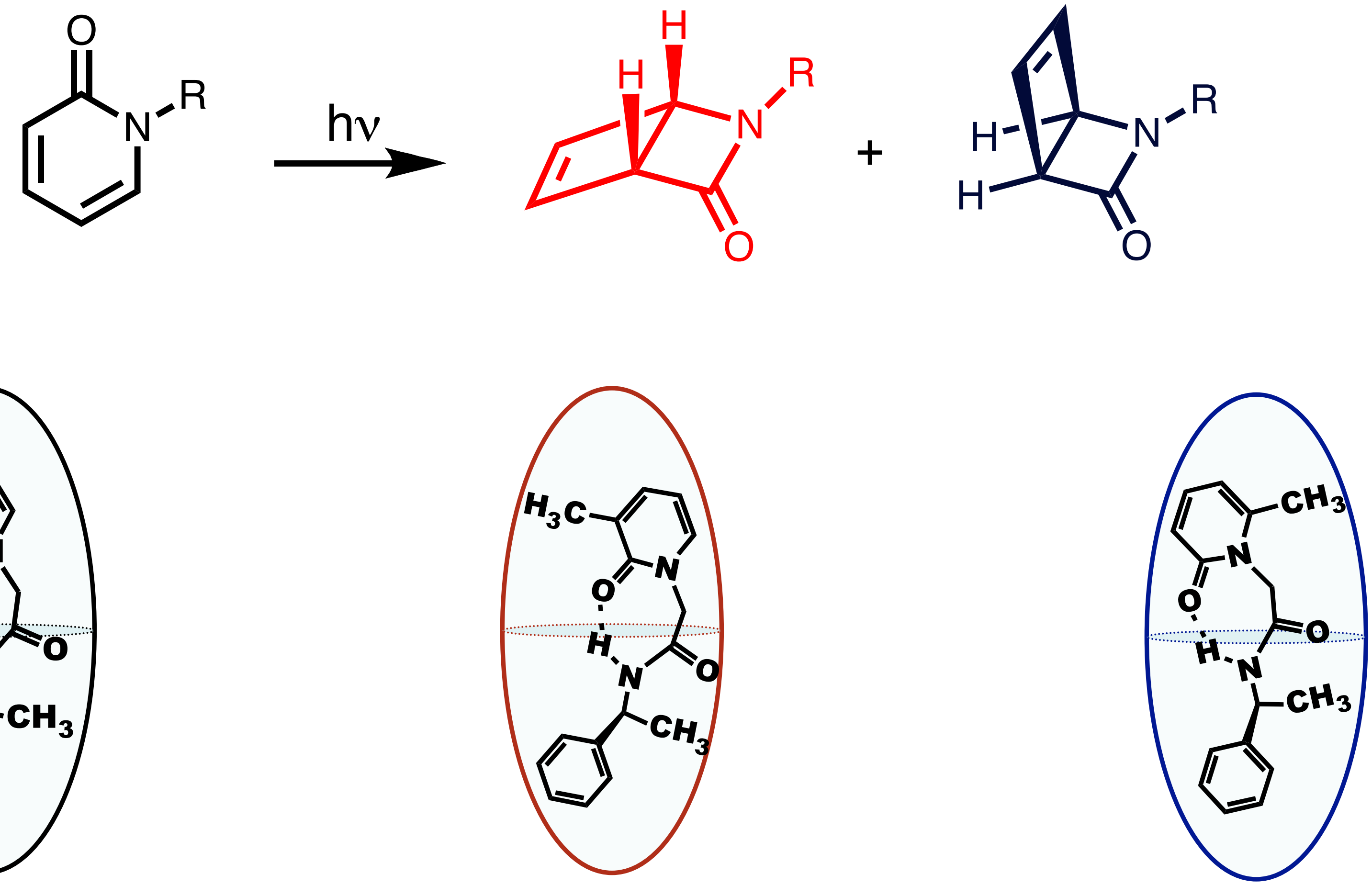




0 % 21% 56% 92%

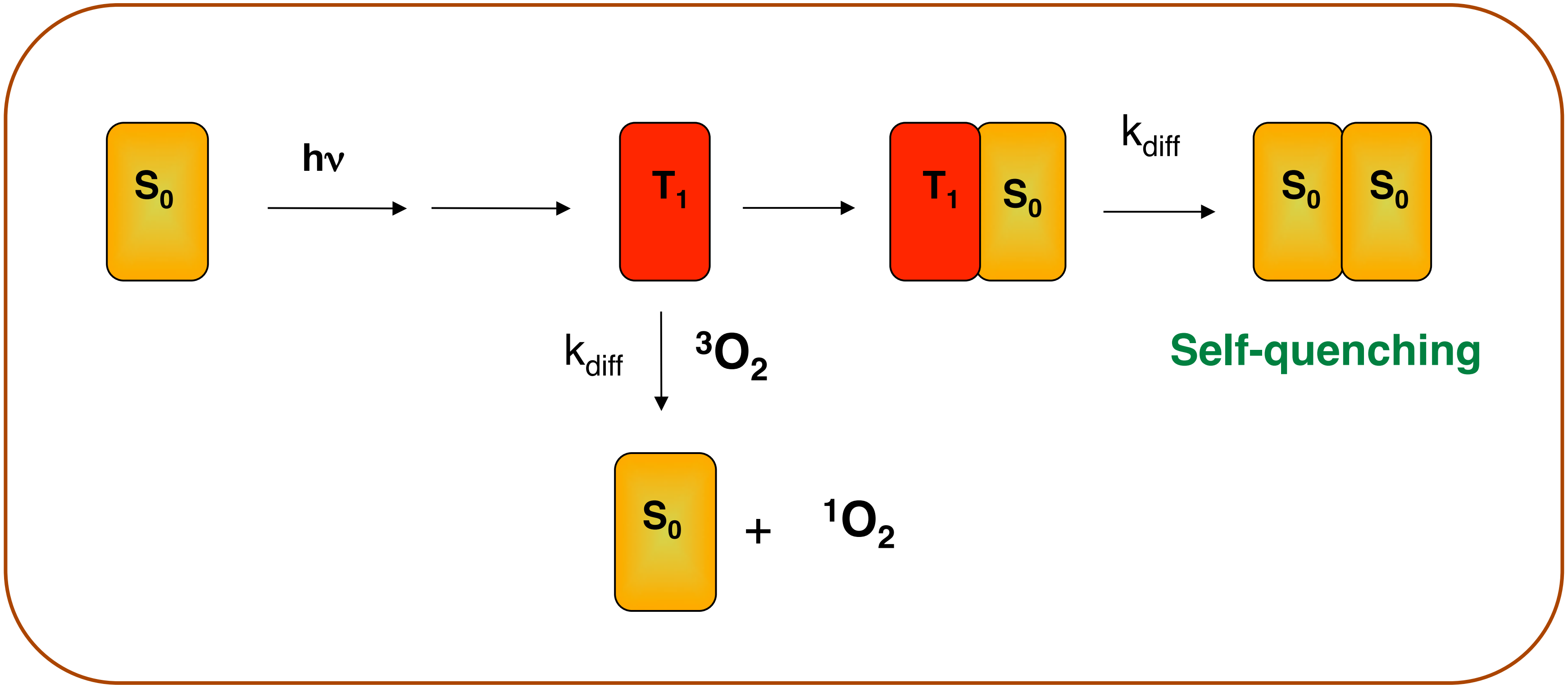


Δδ (ppm)
1.4
2.2
1.6
1.6
4.2
1.4
4.7
1.4
4.1
O
N
NH
0.5
0.0
−0.5
−1.0
−1.5
−2.0
−2.5
−3.0
−3.5
ppm



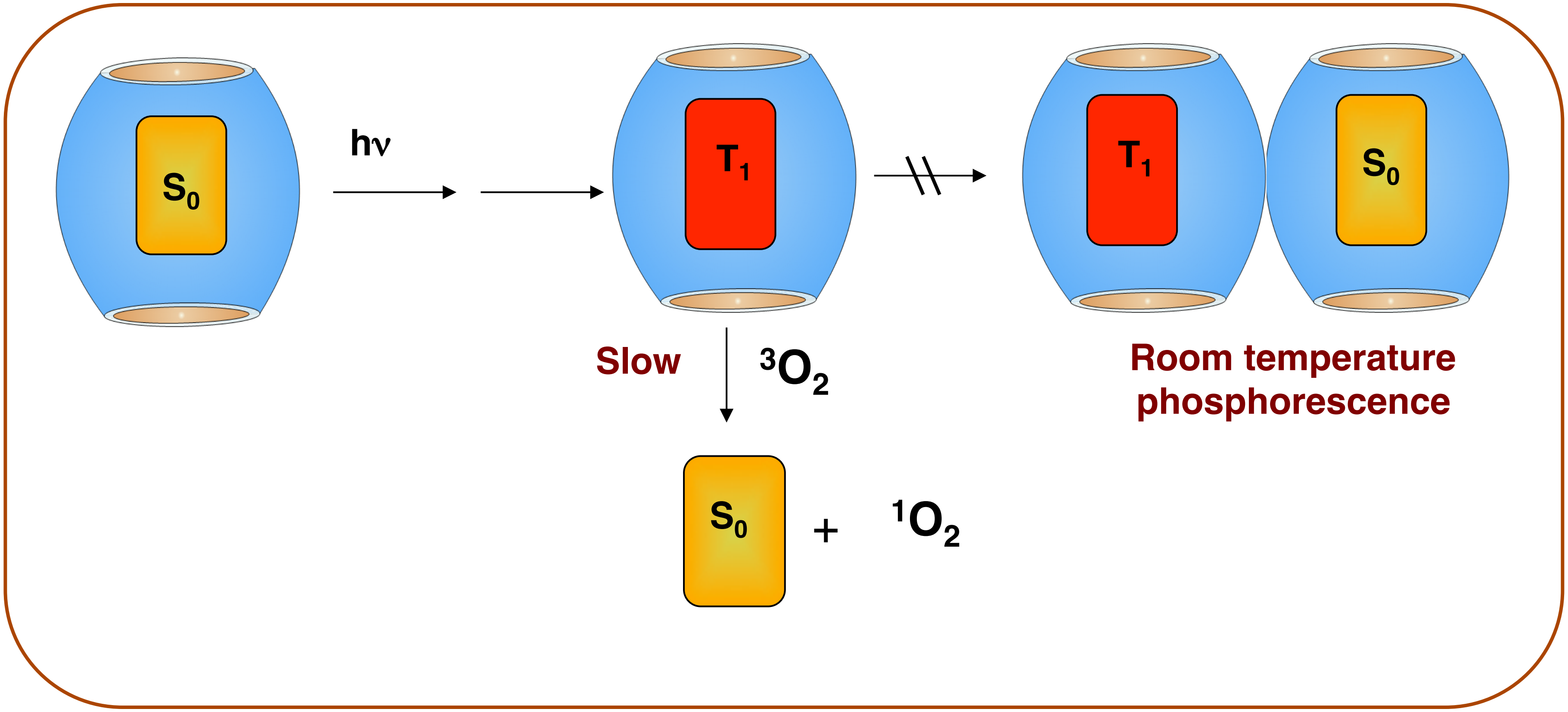
21% 92% 56%

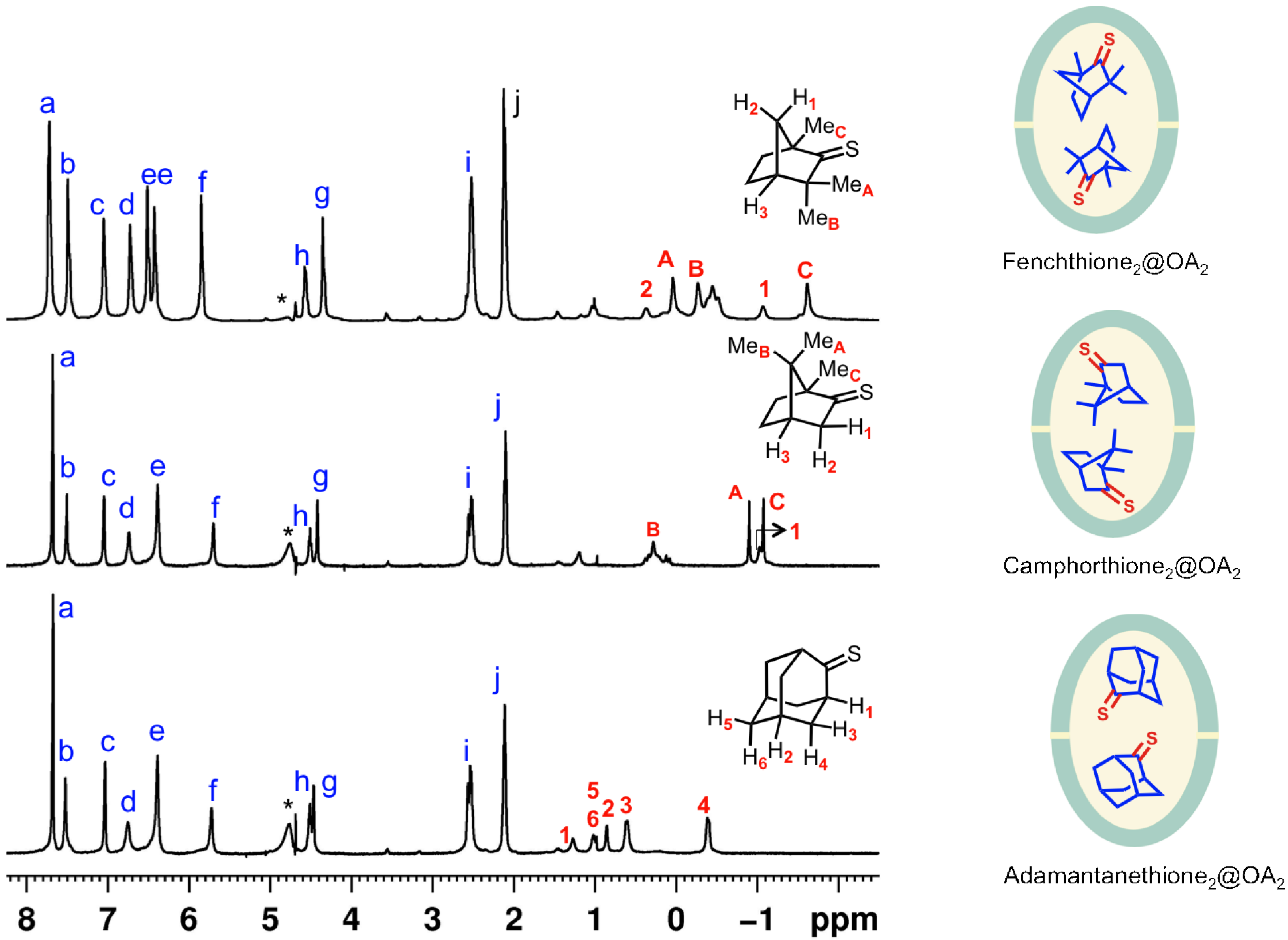
Room Temperature Phosphorescence



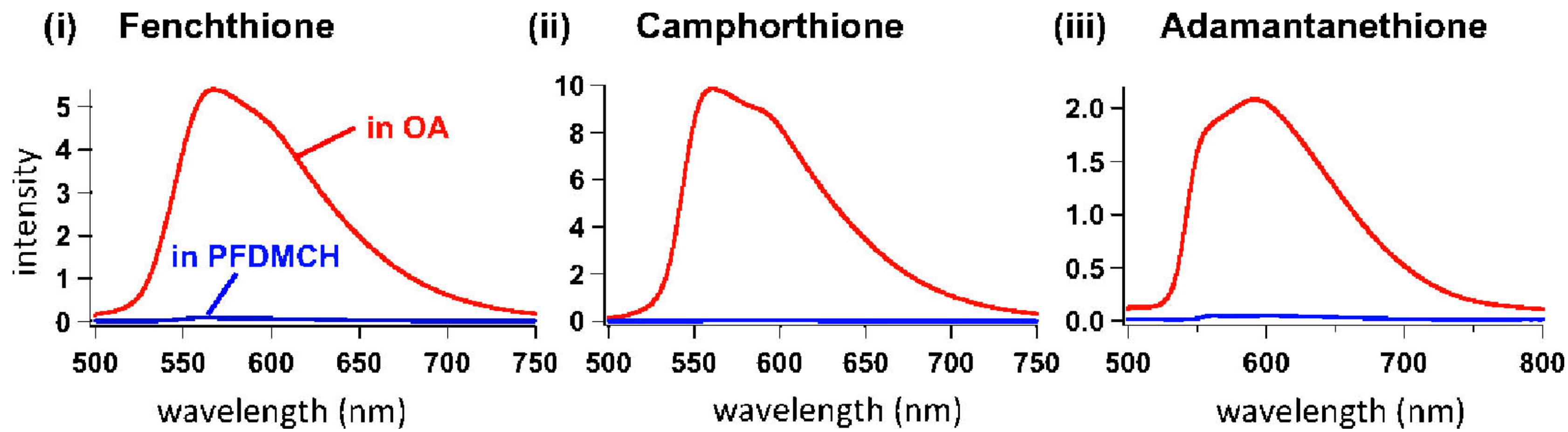
Diffusion controlled self-quenching and oxygen-quenching in solution

Prevention of self quenching with the help of containers





Fenchthione$_2$@OA$_2$
Camphorthione$_2$@OA$_2$
Adamantanethione$_2$@OA$_2$
8 7 6 5 4 3 2 1 0 −1 ppm

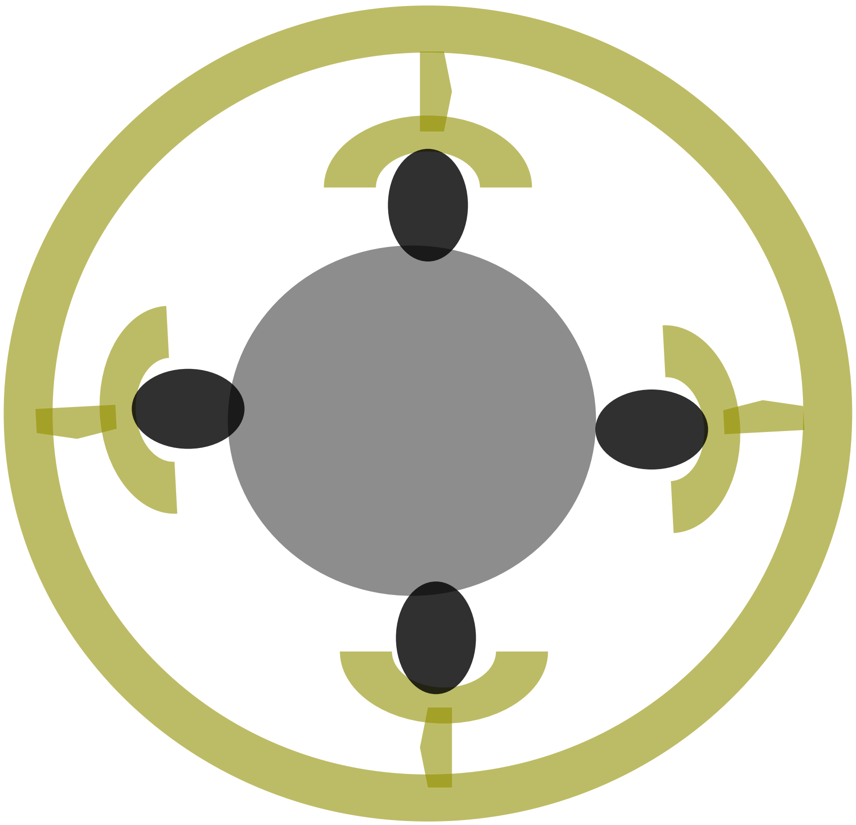


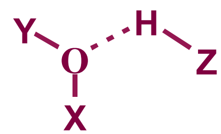
Guests	τ^{o}_{T} (μs)[a]	OA		
		H:G[c]	τ_T (μs)[b]	k_{q,O_2} ($M^{-1}s^{-1}$)
Fenchthione	154	2:2	187	$(1.6\pm0.4)\times10^{6}$
Camphorthione	46.3	2 : 2	6 5	$(2.4\pm0.1)\times10^{7}$
Adamantanethione	43.3	2 : 2	17.2	$(2.8\pm0.1)\times10^{7}$

a: exptraolated to infinite dilution in perflurodimethylcyclohexane

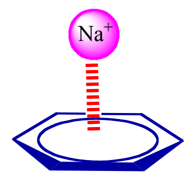
b: at 10^{-5} M of thione and 10^{-5} M of OA

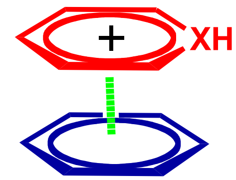
Role of Weak Interactions



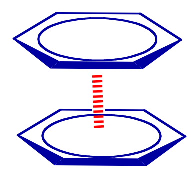


Hydrogen bond

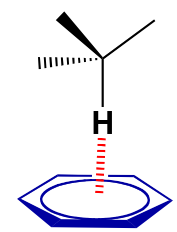




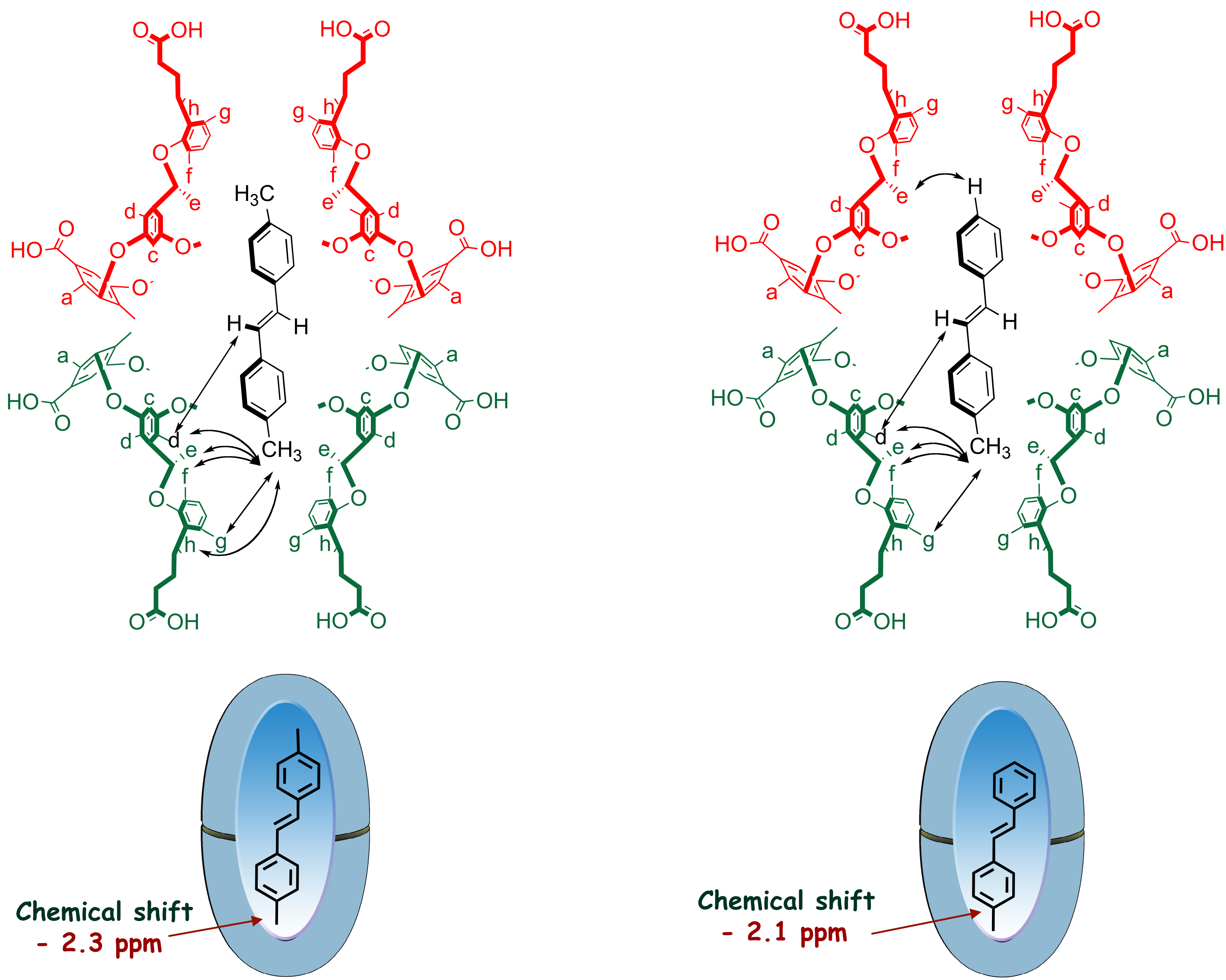
Cation---π



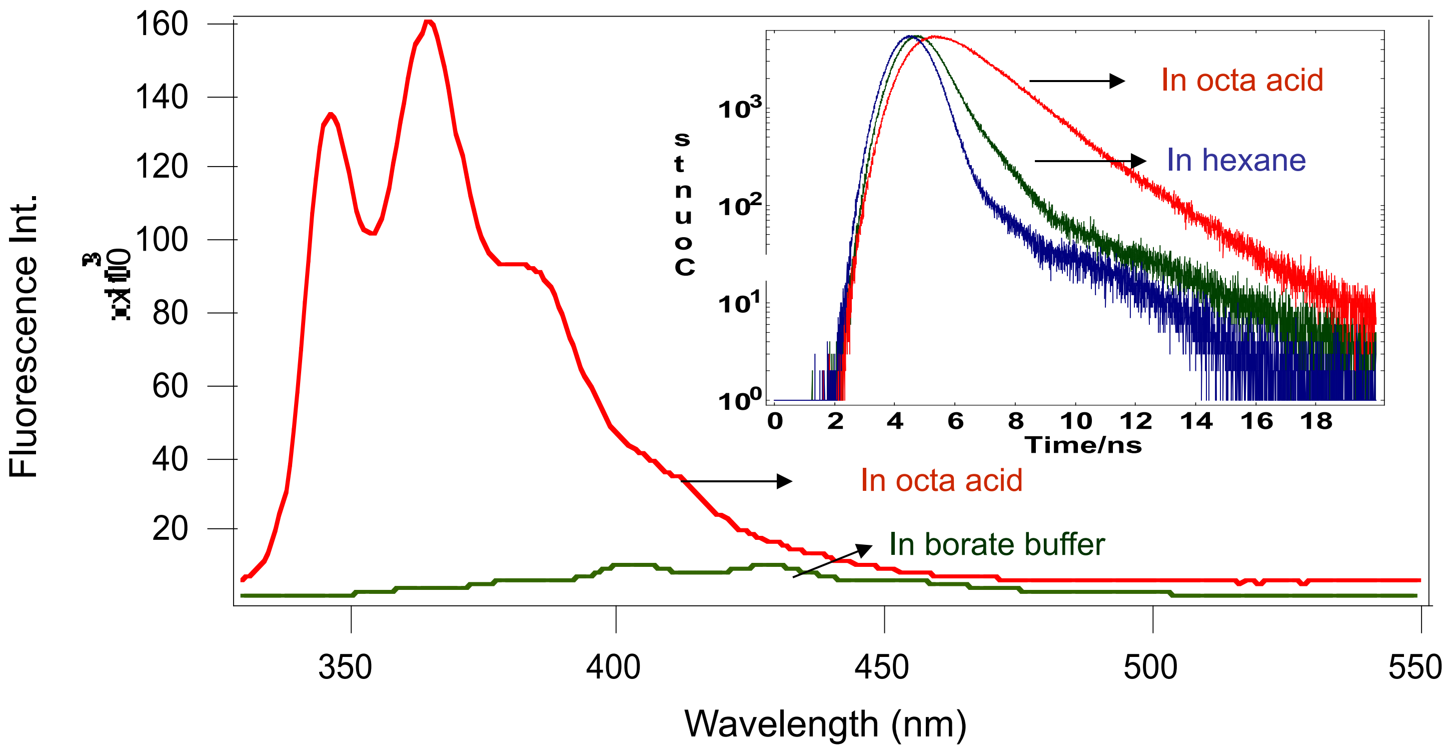
π---π

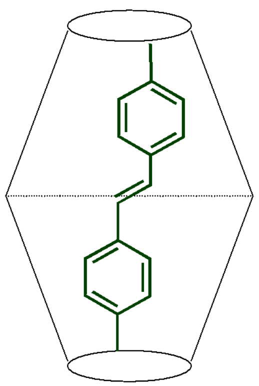


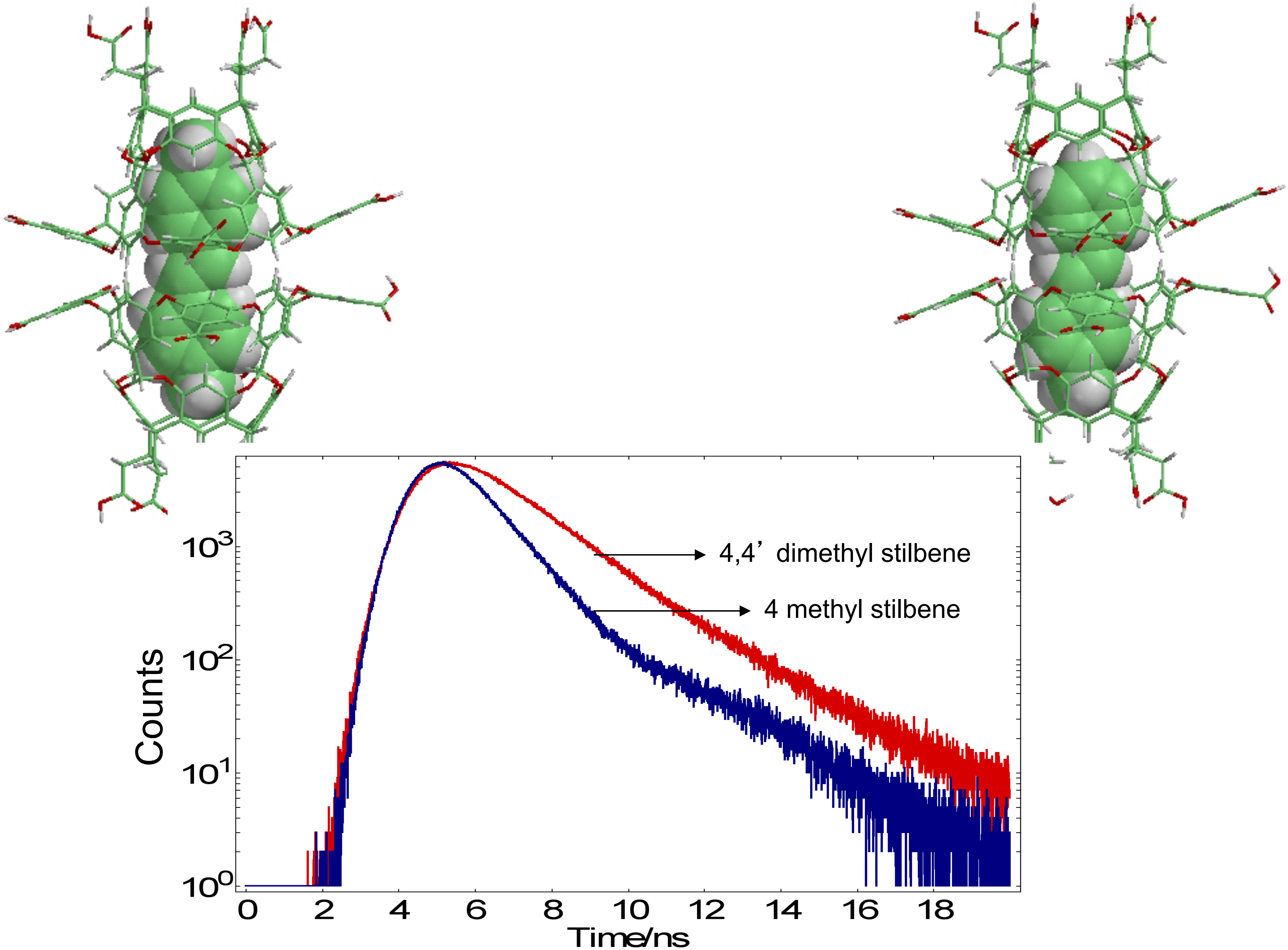
C-H---π


Chemical shift
- 2.3 ppm
Chemical shift
- 2.1 ppm

Fluorescence enhanced and lifetime lengthened within the OA capsule

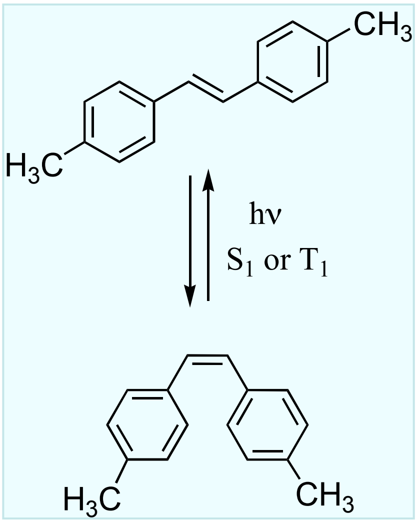


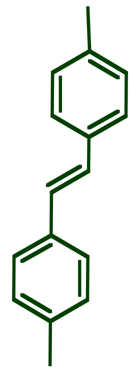




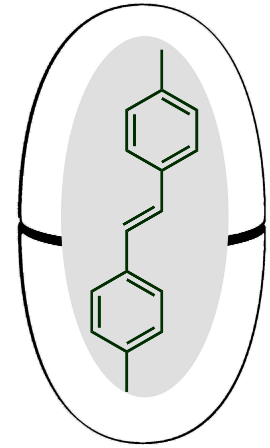
4,4' dimethyl stilbene
4 methyl stilbene
Counts
Time/ns
10^3
10^2
10^1
10^0
0
2
4
6
8
10
12
14
16
18

C–H---π Interaction Controls the Rotation





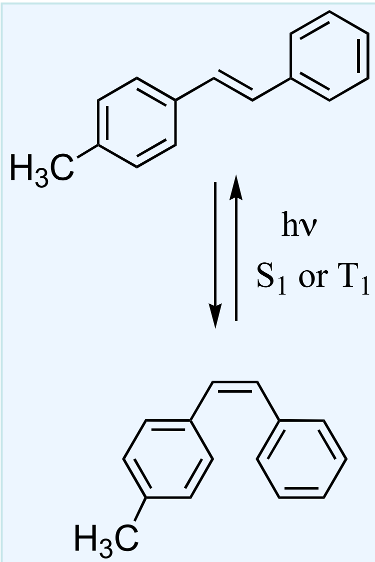
Solution
$CDCl_3$/ Hexane

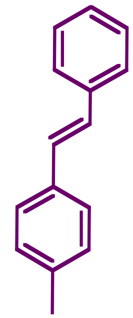


Octa acid

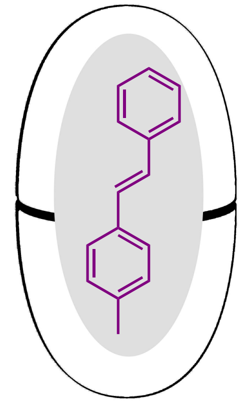
	Solution $CDCl_3$/ Hexane	Octa acid
Chemical shift δ of CH_3	2.35 ppm	- 2.3 ppm
Pseudo-photostationary state –Singlet (Cis:Trans)	76:18	20:80
Photostationary state – Fluorenone Triplet (Cis:Trans)	80:20	0:100
Lifetime (ns)	<0.7	1.74

Possible Selective Rotation of the Phenyl group



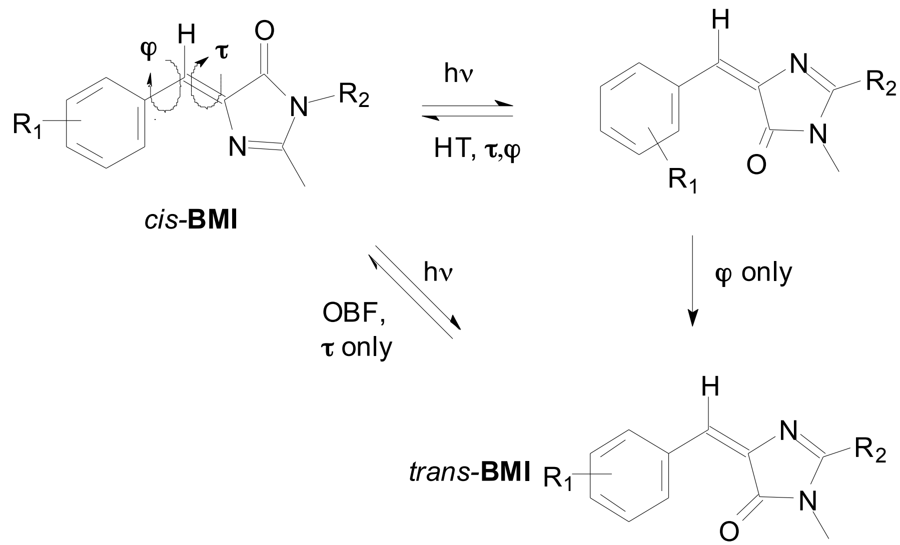


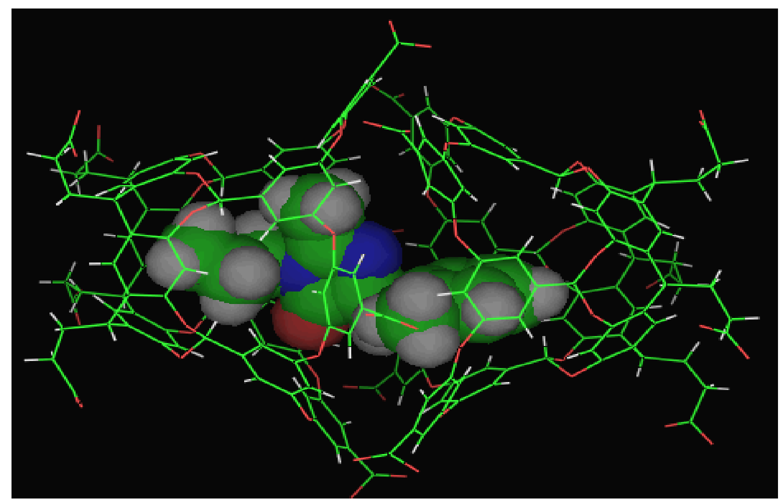
Solution
$CDCl_3$/ Hexane



Octa acid

	Solution	Octa acid
Chemical shift δ of CH_3	2.35 ppm	- 2.1 ppm
Pseudo-photostationary state –Singlet (Cis:Trans)	85:15	85:15
Photostationary state – Triplet (Cis:Trans)	82:18	86:14
Lifetime (ns)	<0.7	0.94





GFP, Roger Tsien

Summary

- Depending on the guest, the OA forms 1:1, 2:1 or 2:2 complexes.

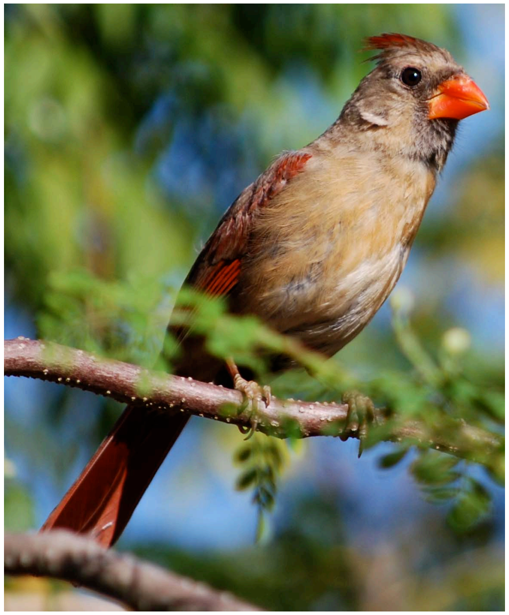
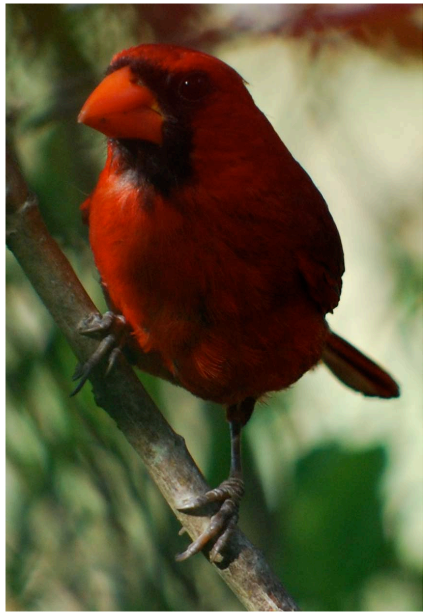
- Weak interactions and confinement could be used to control ground state and excited state properties of molecules.

- In host-guest complexes, guest and host molecules are not stationary. They undergo several different types of motions.

- Communication between molecules across molecular walls is possible.


Thank you

Container Chemistry at Backyard


Sireesha

Arun

Arun

Anand

National Science Foundation

WHERE DISCOVERIES BEGIN


Indian Palate

G. H. Hardy
1877-1947

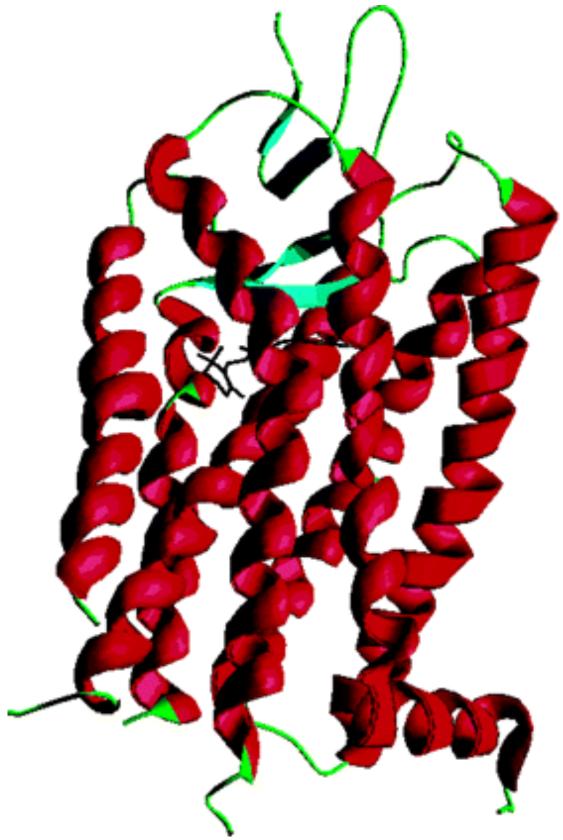
S. Ramanujan
1887-1920

Disclaimer

Invisible Value of Basic Science

No discovery of mine is likely to make-- the least difference to the amenity of the world. I have helped to train other mathematicians of the same kind---their work has been as useless as my own.---- Anyhow I have added something to knowledge and helped others to add more---these have a value----.

A Mathematician's Apology, 1940



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

Container Chemistry

Controlling Chemistry With Confinement

Medium (host): Octa Acid

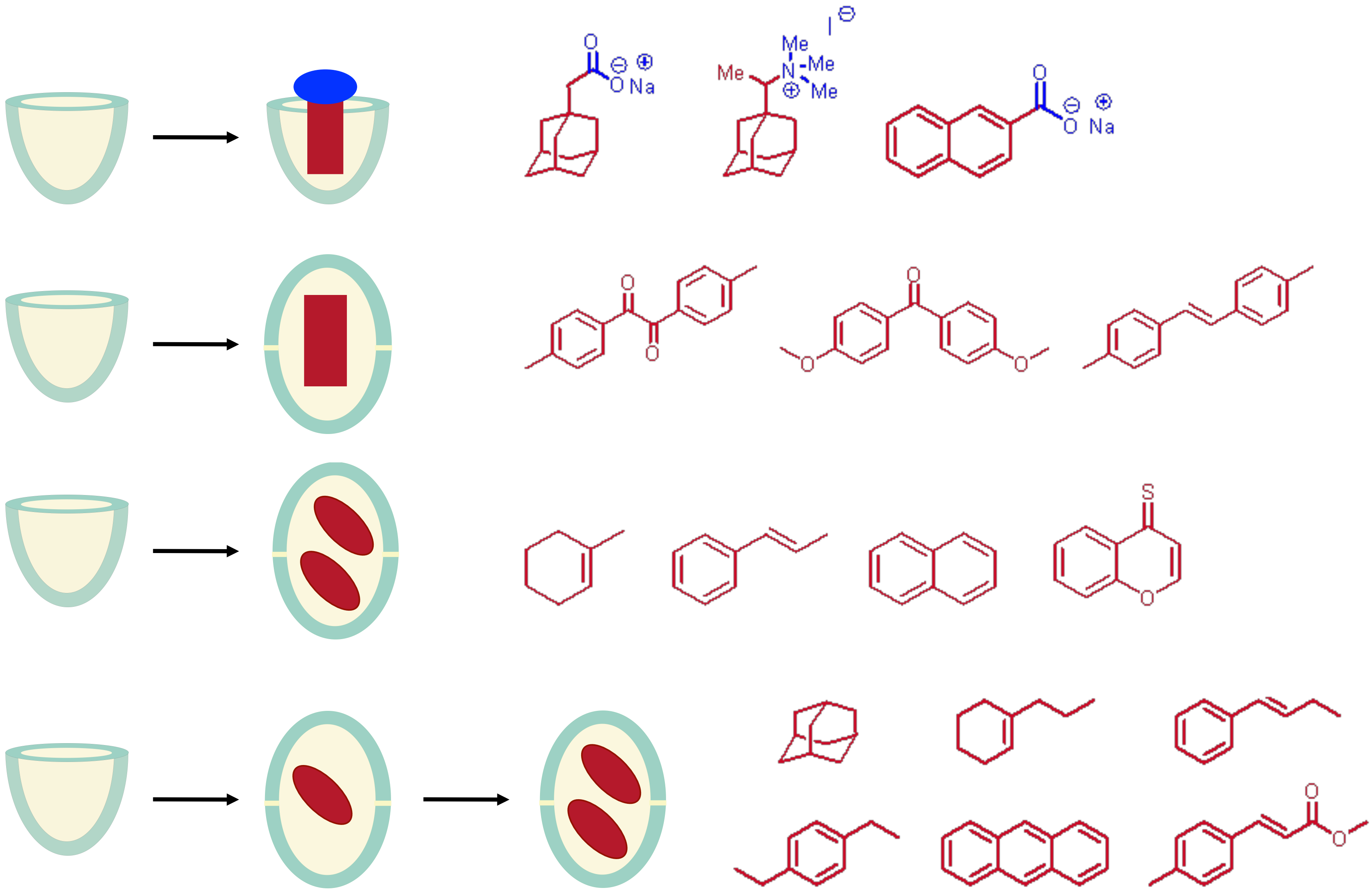
Complexation

Dynamics

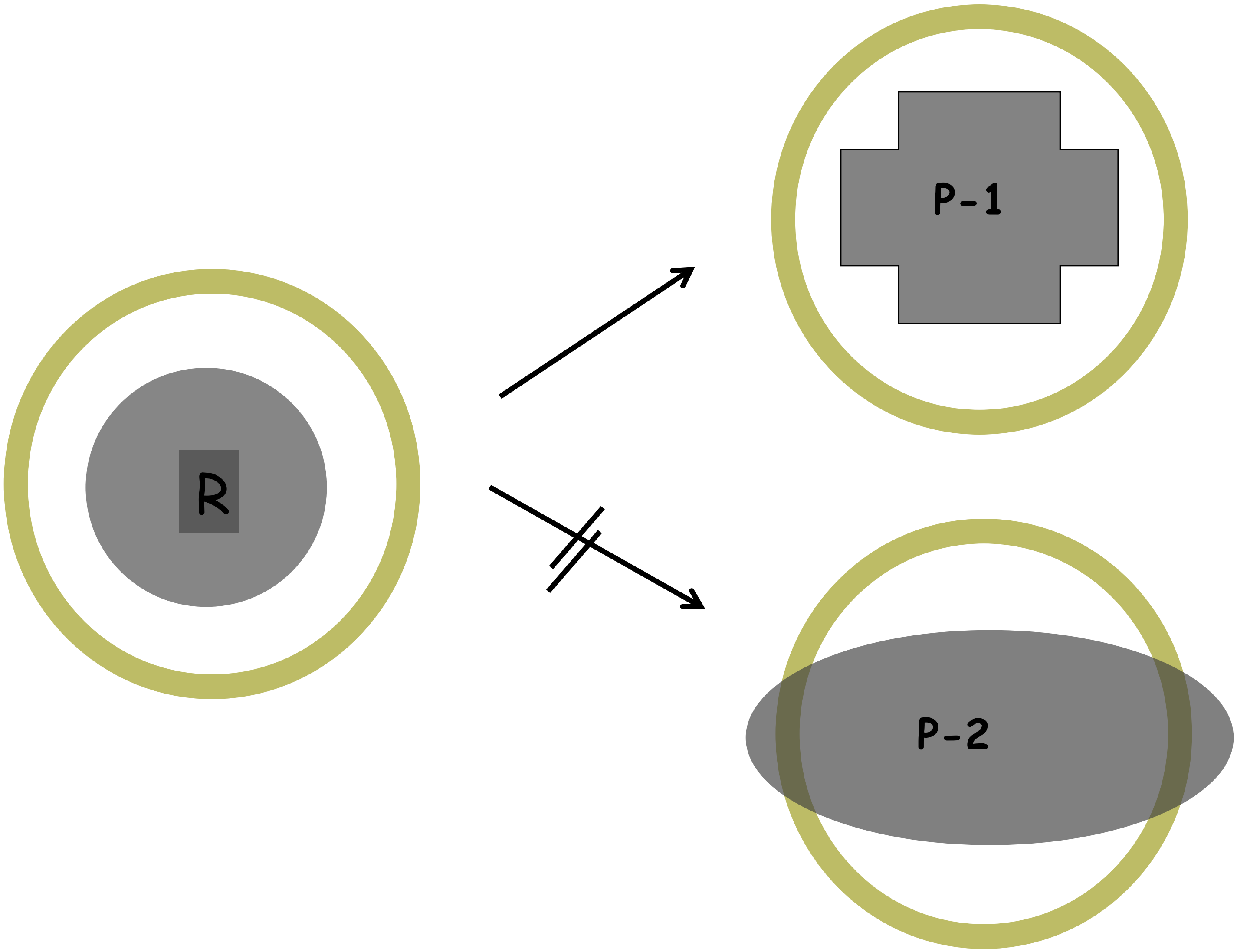
Excited state chemistry

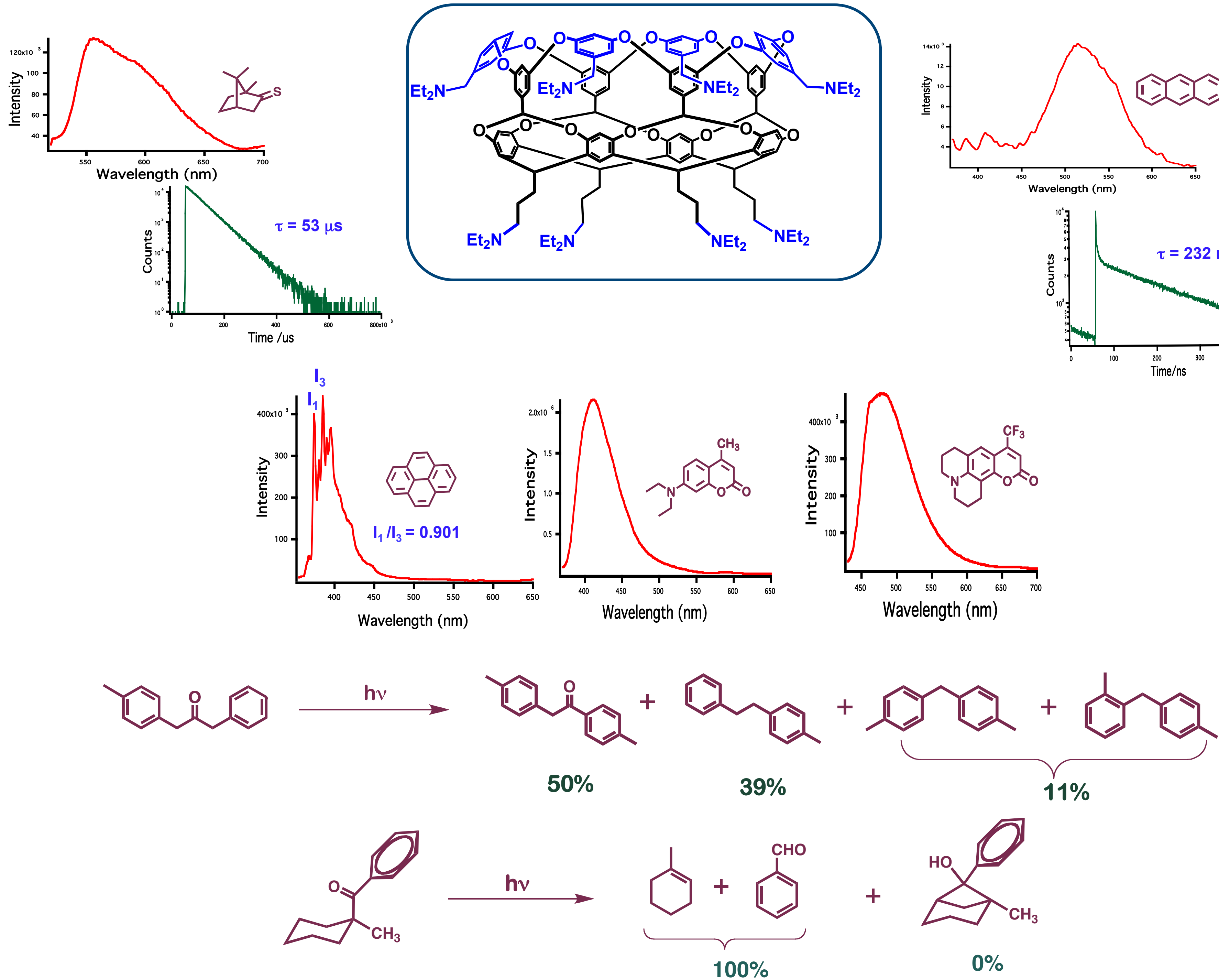
Communication

Supramolecular Host-Guest Complexes

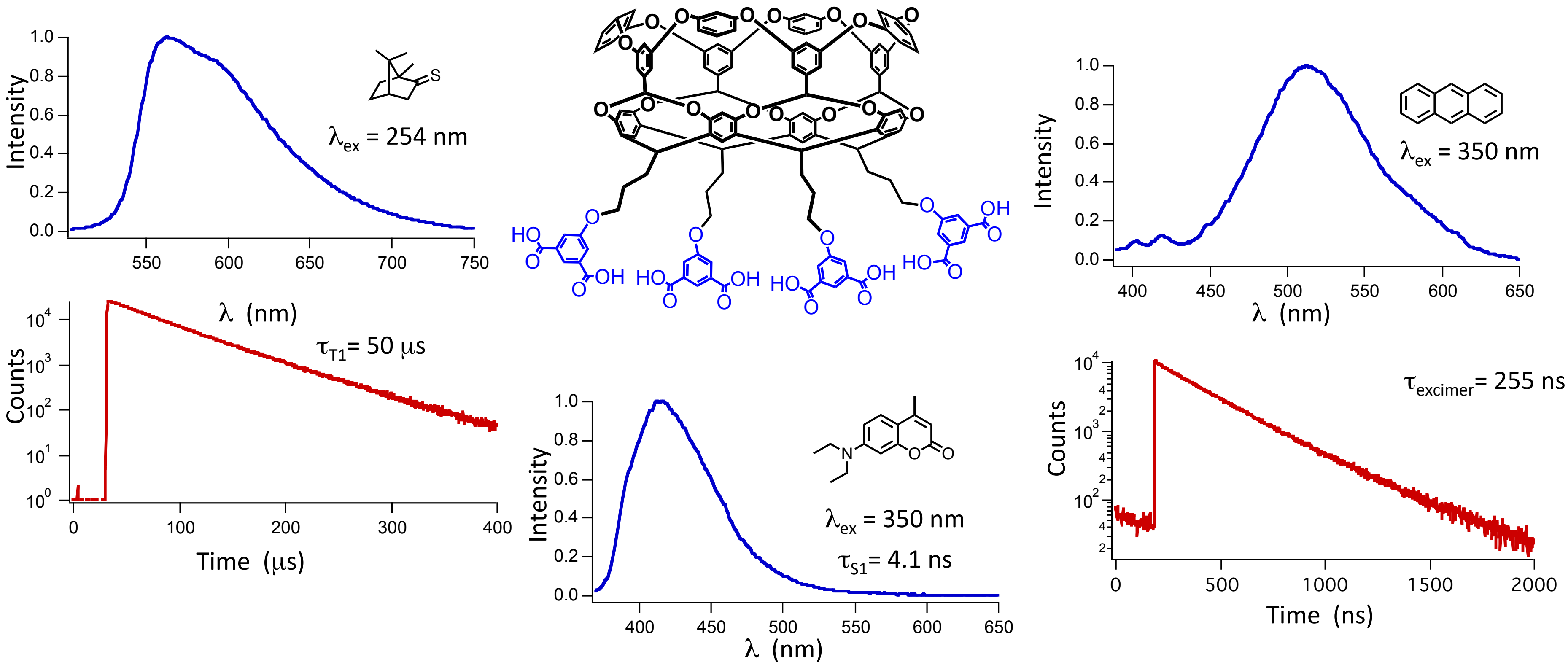


Role of Free Space: Product Must Fit the Reaction Cavity

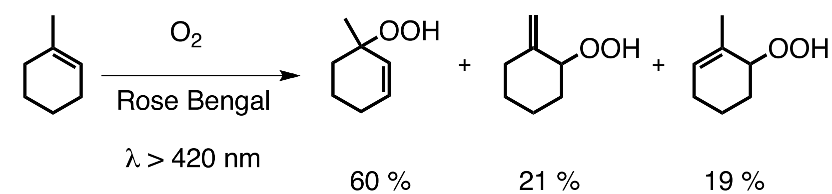




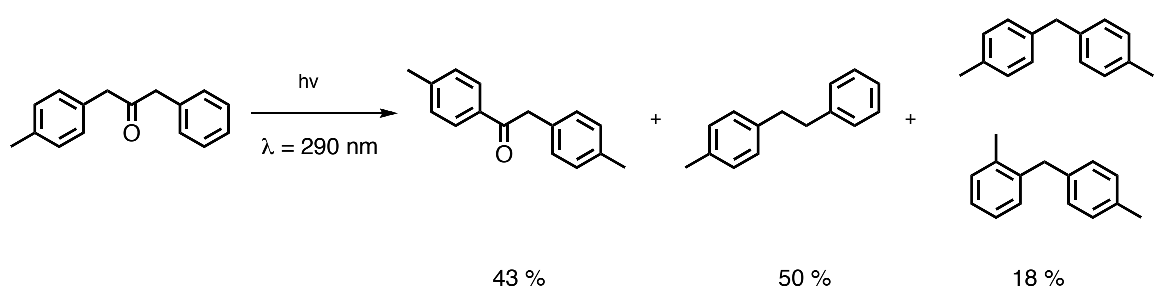
Intensity
Wavelength (nm)
Counts
Time /us
τ = 53 μs
Et2N
NEt2
Wavelength (nm)
τ = 232 ns
Time/ns
I3
I1
I1 /I3 = 0.901
CH3
CF3
hν
50%
39%
11%
CHO
HO
CH3
100%
0%



Intensity
λex = 254 nm
λ (nm)
Counts
τT1= 50 μs
Time (μs)
HO
O
OH
Intensity
λex = 350 nm
τS1= 4.1 ns
λ (nm)
Intensity
λex = 350 nm
λ (nm)
Counts
τexcimer= 255 ns
Time (ns)



O2
Rose Bengal
λ > 420 nm
OOH
OOH
OOH
60 %
21 %
19 %



hv
λ = 290 nm
43 %
50 %
18 %

Prof. Turro

Prof. Ottaviani

Dr. Jockusch

Prof. Gibbs

Exploiting C–H --- π Interaction