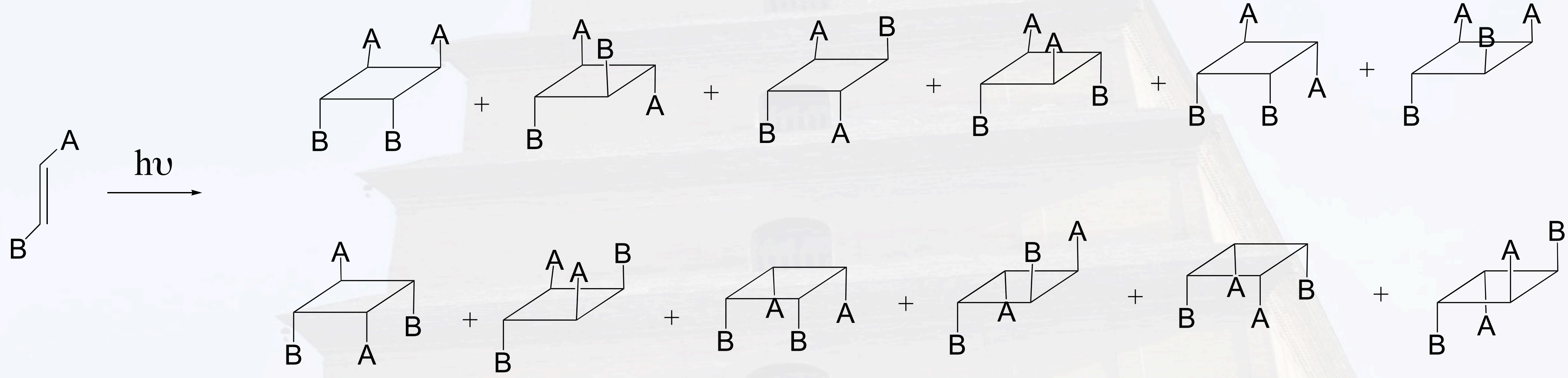
Supramolecular Photochemistry

Controlling photocycloadditions through pre-organization and templatation

Concept

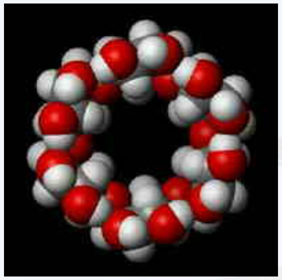
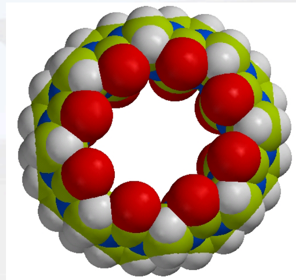
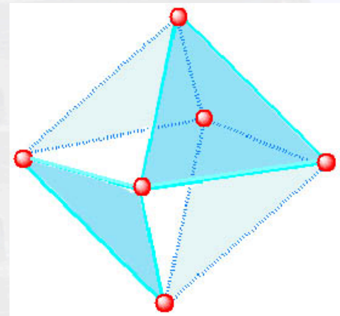
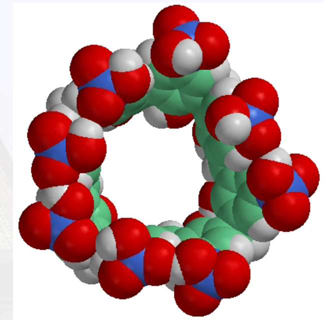
Examples

In the absence of control photoaddition leads to multiple products

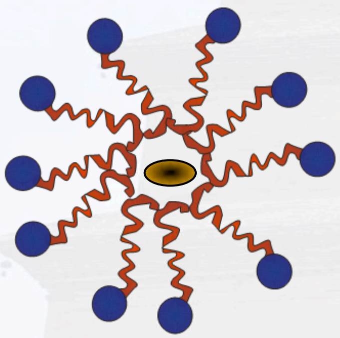
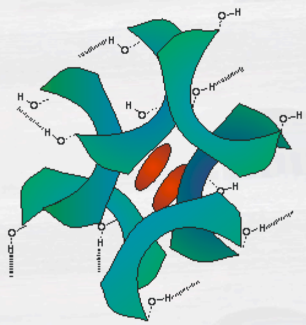
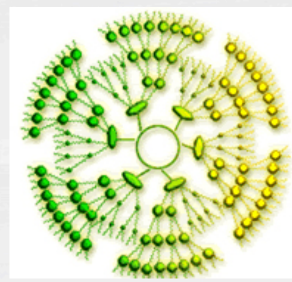
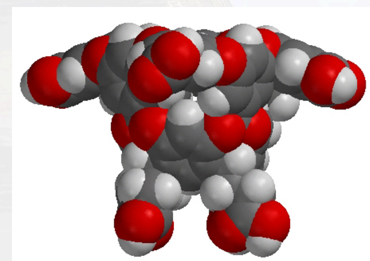


- Multiple products with different stereo and regiochemistry possible (assuming no electronic or steric preference).
- Pre-organization is essential to achieve selectivity. The cost for selectivity should be pre-paid, *i.e.*, system should be entropically prepared.

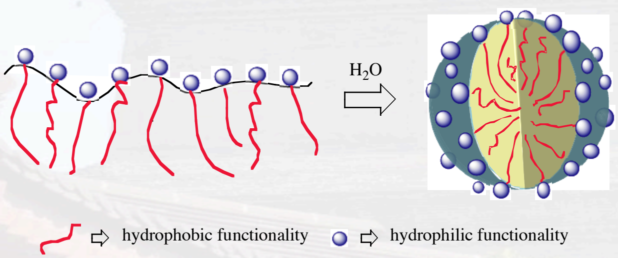
Supramolecular Containers as Reaction Vessels

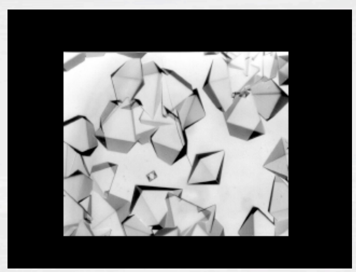
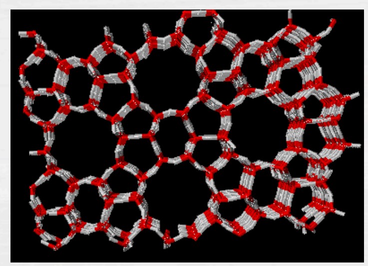
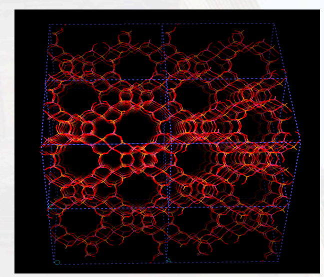





Cyclodextrins | Cucurbiturils | Pd Nano Cage | Calixarenes

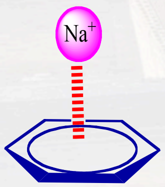
SDS / CTAC | NaCh / NaDCh | Dendrimers | Octa acid



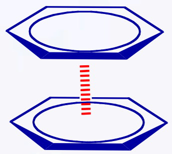




Water soluble polymer | Crystals | Zeolites

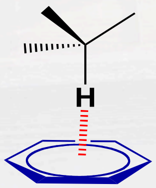
Role of Weak Interactions



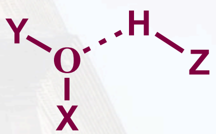
Cation---π



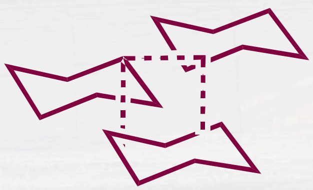
π---π



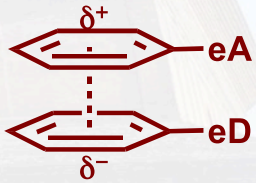
C–H---π



Hydrogen bond



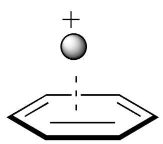
van der Waals



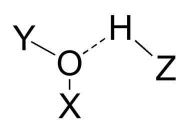
Charge transfer

Weak interactions often utilized in templation

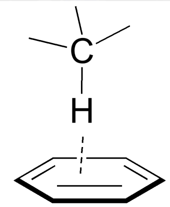
Examples of weak intermolecular bonds (typical energies vary from <1 kcal mol^{-1} to ~ 10 kcal mol^{-1}



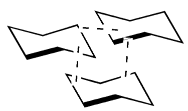
Cation---π bond



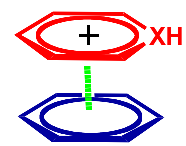
Hydrogen bond

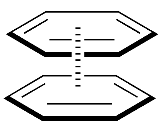


CH---π bond

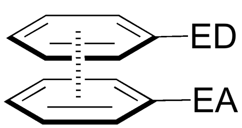


van der Waals bonds



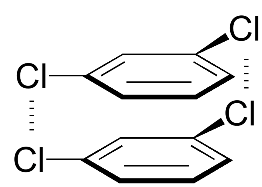


π–π bond

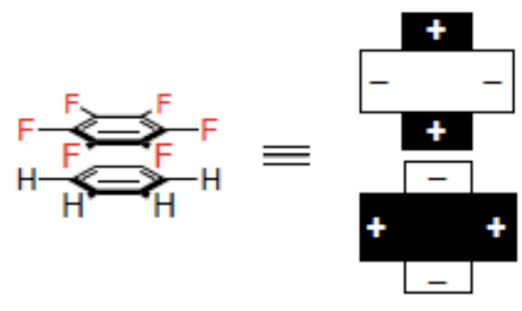


Charge transfer bond

ED = electron donor
EA = electron acceptor



Chlorine---Chlorine



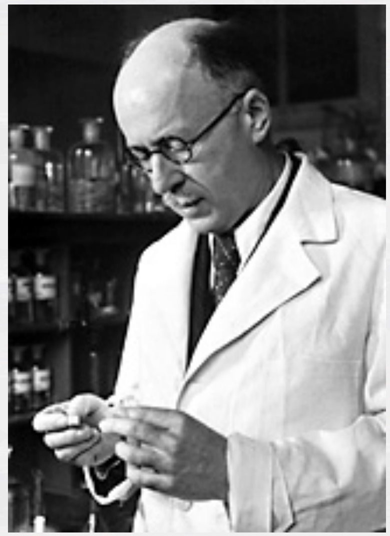
Quadrupole---Quadrupole

Photochemistry in Solid State

Kanchennjunga at sunrise (28, 169')

Photoreactions in Crystals

(Stobbe, *Ber.*, **1922**, *55*, 2225; de Jong, *Ber.*, **1922**, *55*, 463)

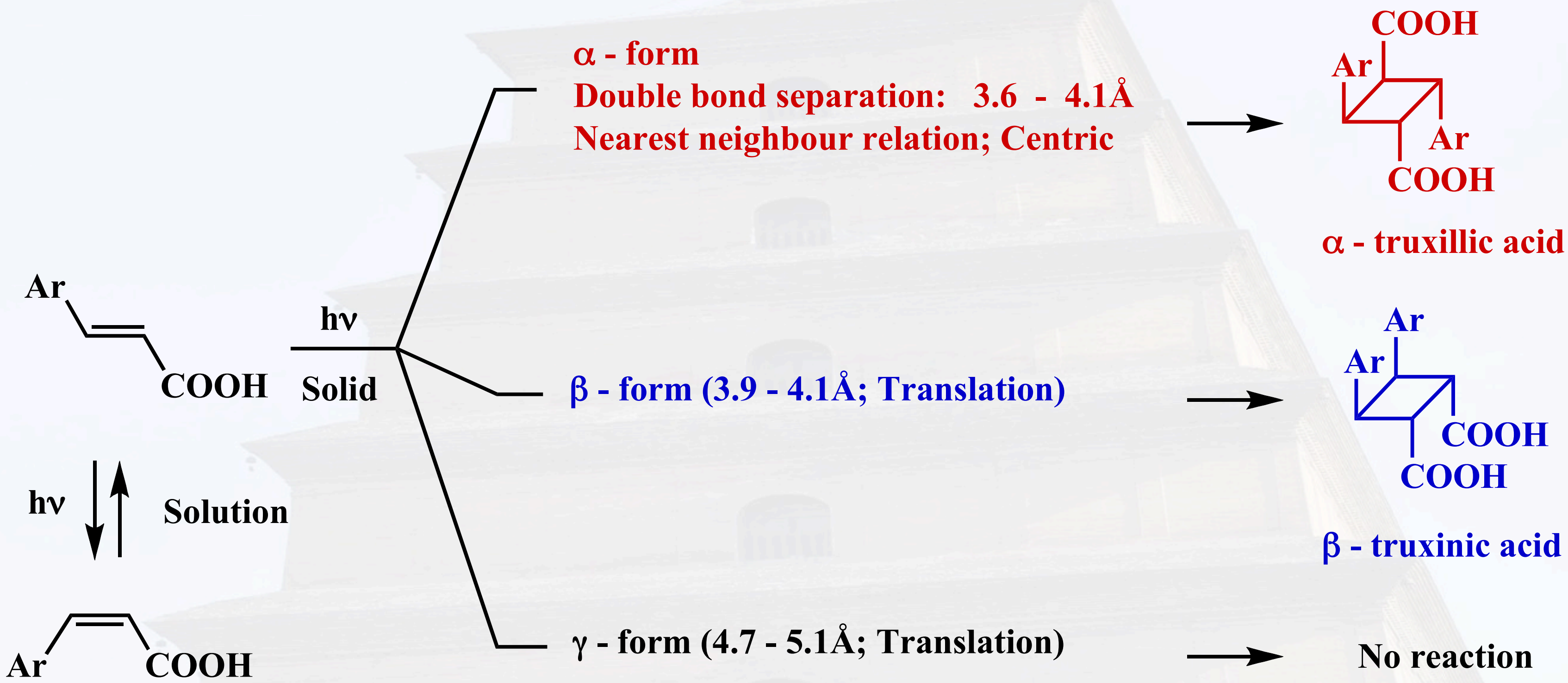


L. Ruzika

"A crystal is a chemical cemetery"

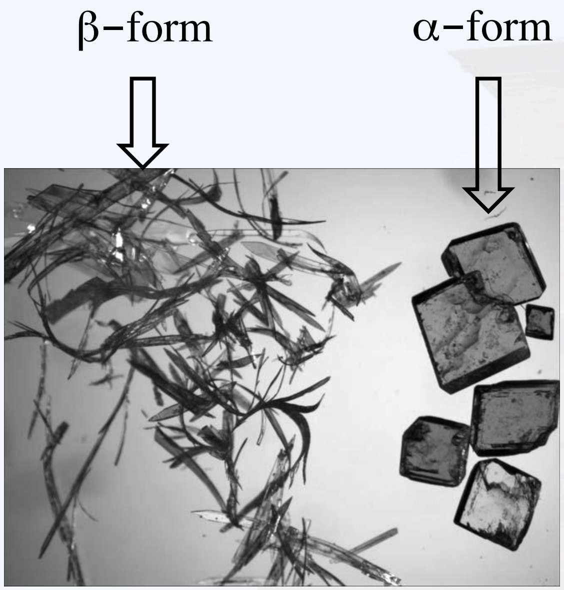
Nobel Laureate L. Ruzika (1930s)

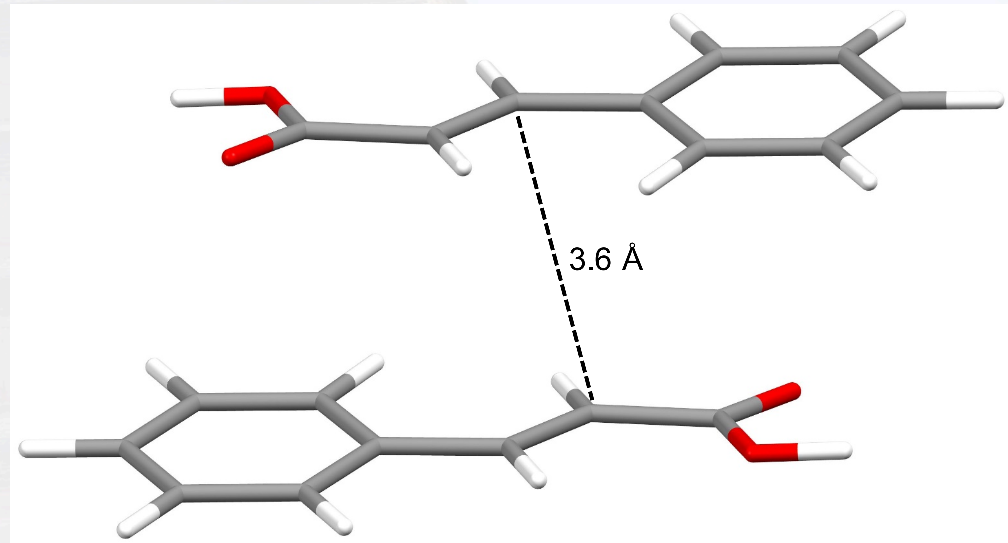
Photodimerization of *trans*-Cinnamic acids

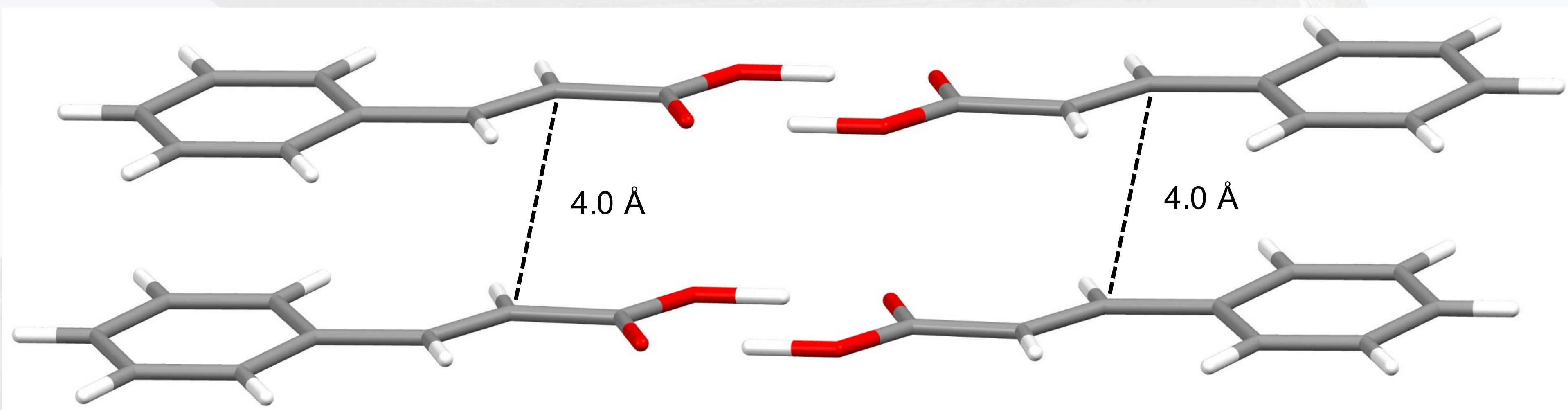


Topochemical principle: Reactions in the solid state take place with minimum atomic movements.

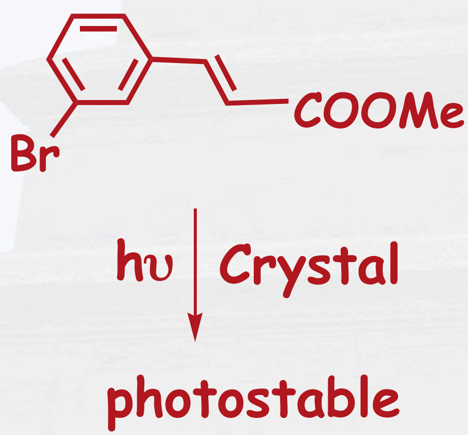
G. M. J. Schmidt et al. '*Solid State Photochemitsry, A Collection of Papers*', Verlag Chemie, 1976.

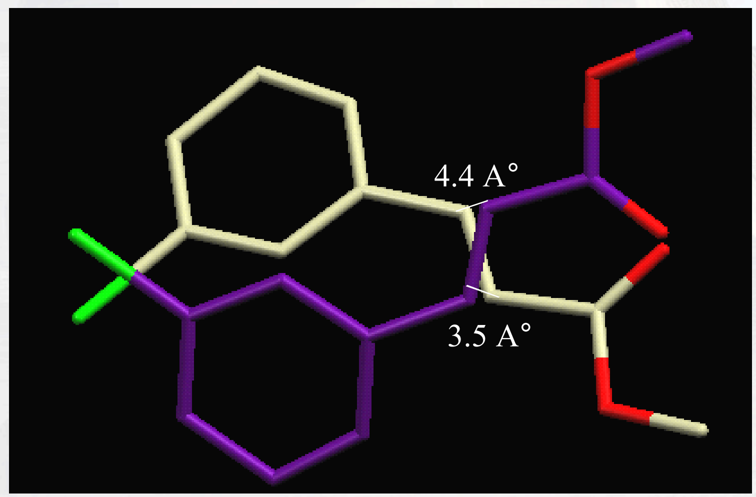

β−form
α−form


3.6 Å


4.0 Å
4.0 Å


Ph
COOH
hν / Crystals
γ-form (4.7--5.1 A°);
Translation
No Reaction


COOMe
Br
hυ
Crystal
photostable

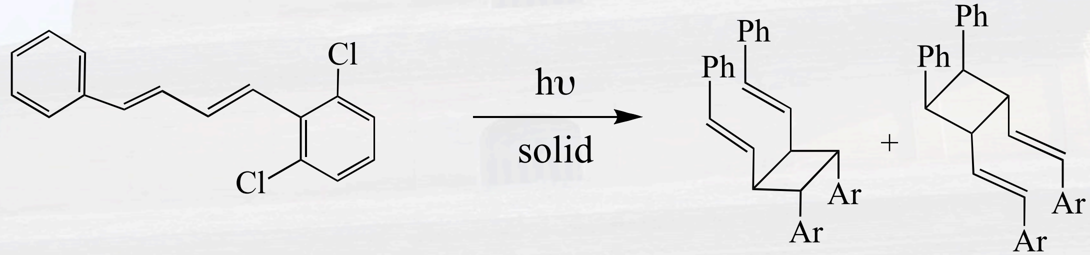

4.4 A°
3.5 A°

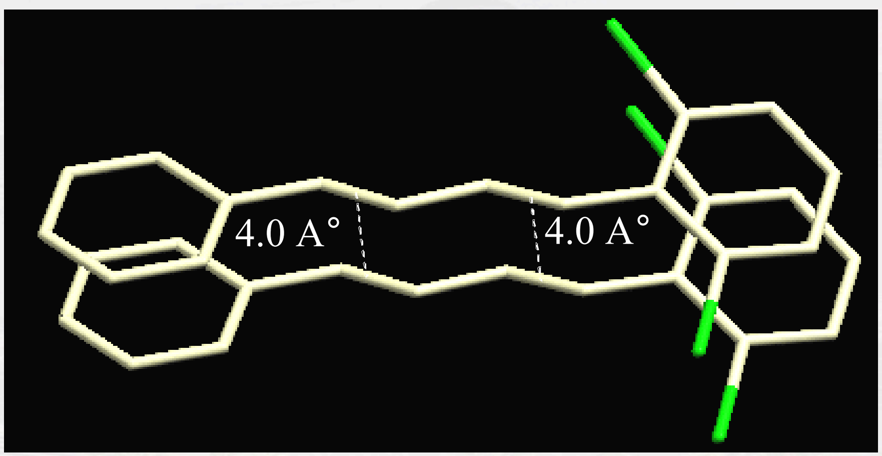
Topochemical principle: Reactions in the solid state take place with minimum atomic movements.

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

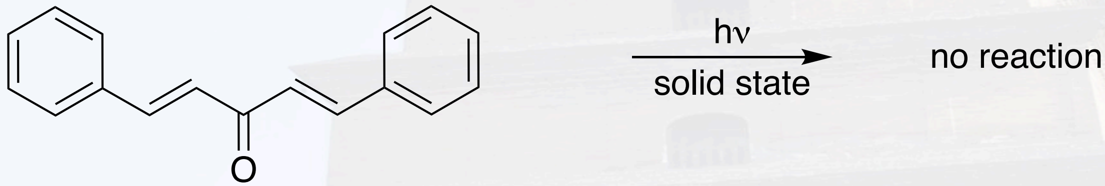
G. M. J. Schmidt

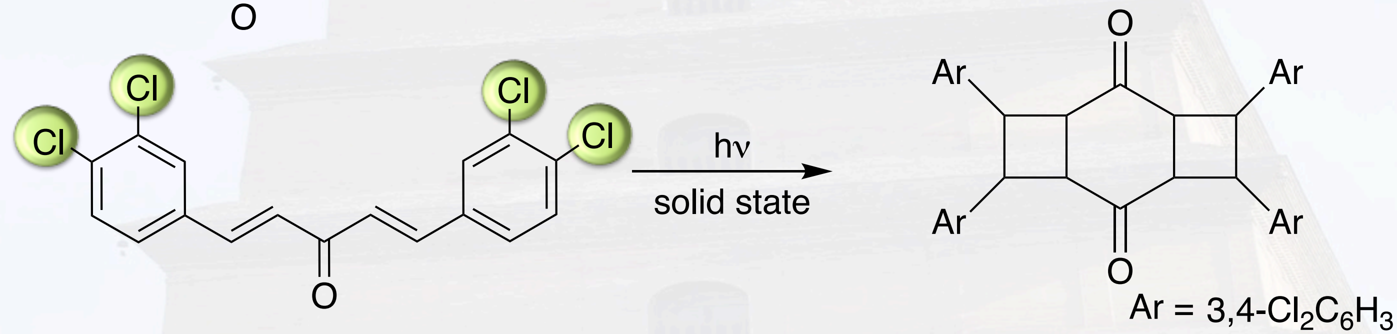
Templation through Cl---Cl interaction: Crystal engineering

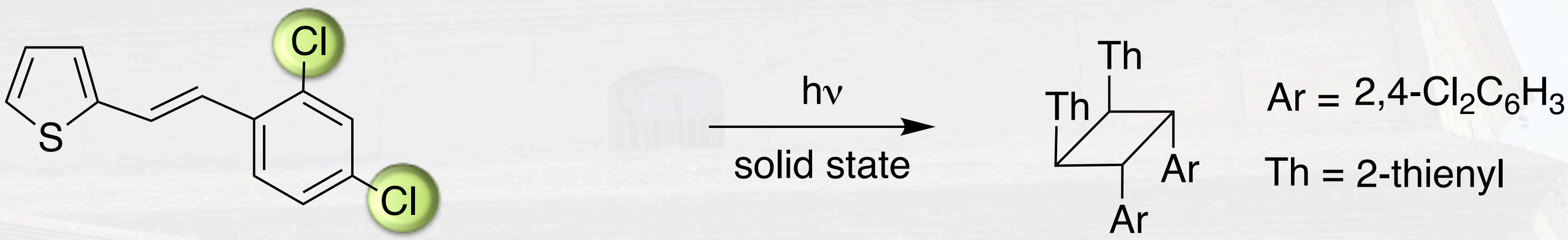




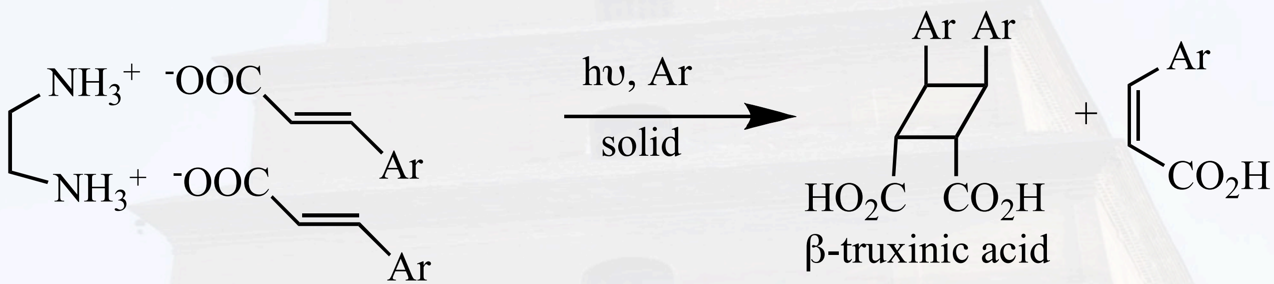
Templation through Cl---Cl interaction



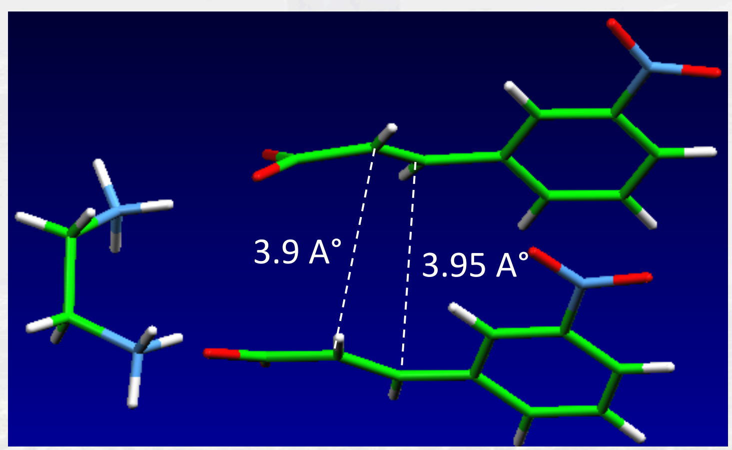




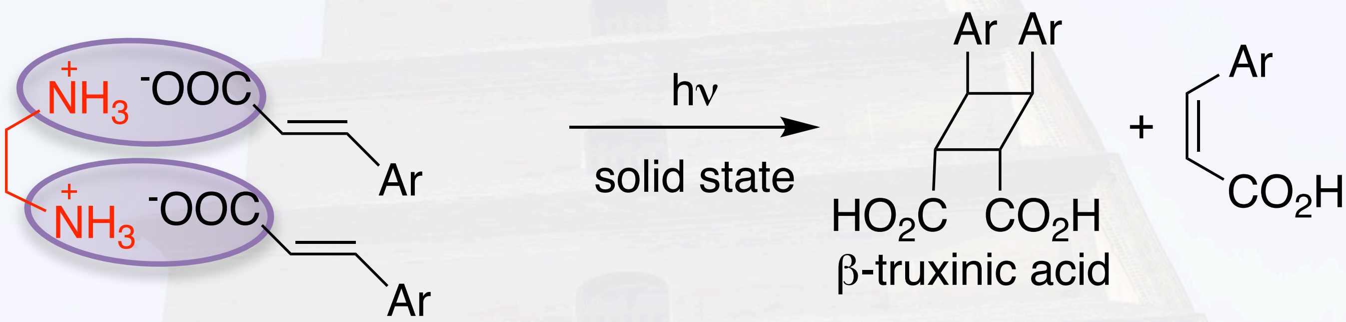
Templation through ionic interaction



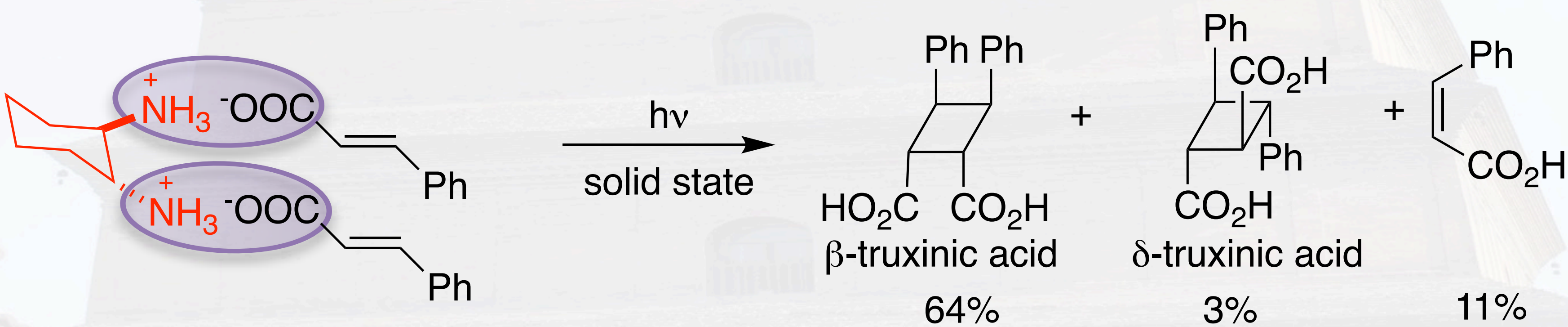
Ar = *o*-MeC_6H_4	30%	23%
Ar = *o*-ClC_6H_4	84	9
Ar = *m*-$NO_2C_6H_4$	70	4
Ar = 2-thienyl	13	0



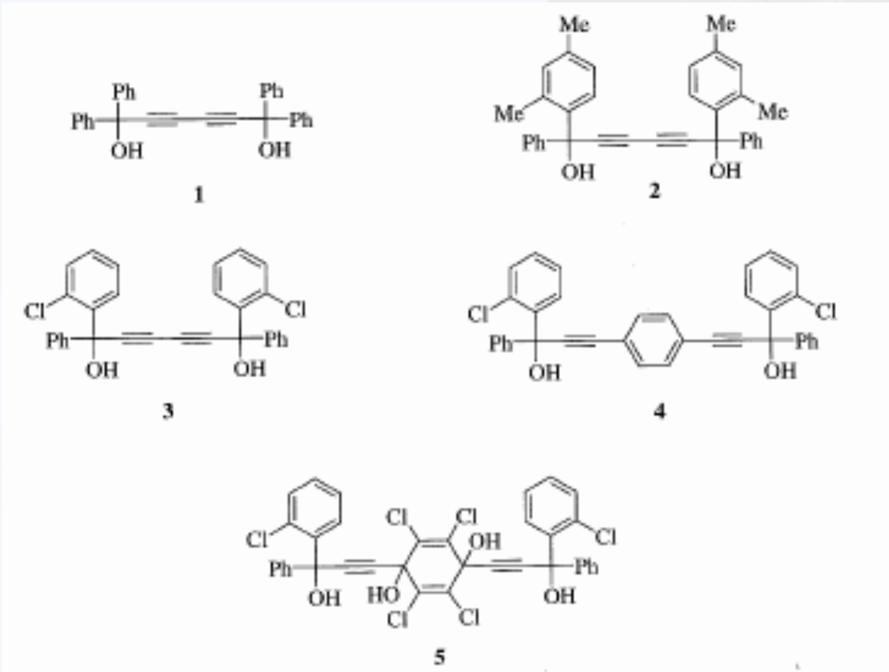
Templation through ionic interaction

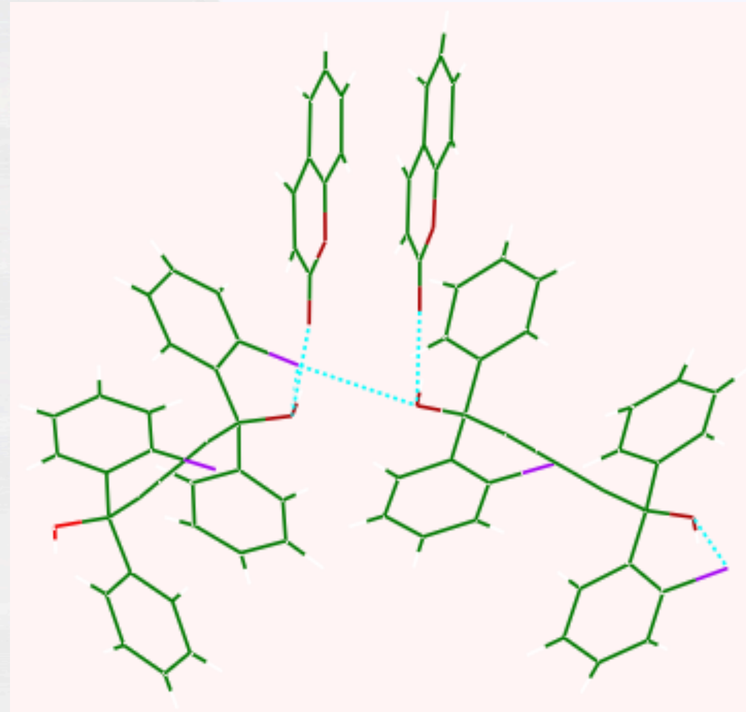


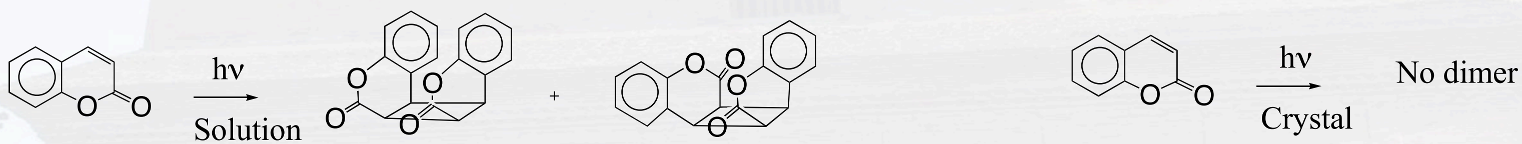
Ar = *o*-MeC_6H_4	30%	23%
Ar = *o*-ClC_6H_4	84%	9%

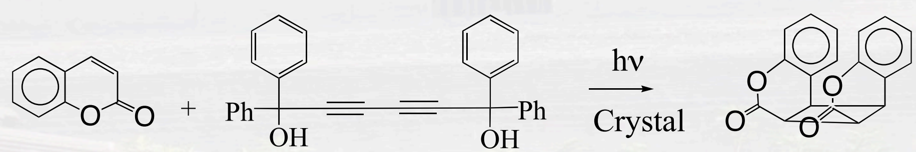


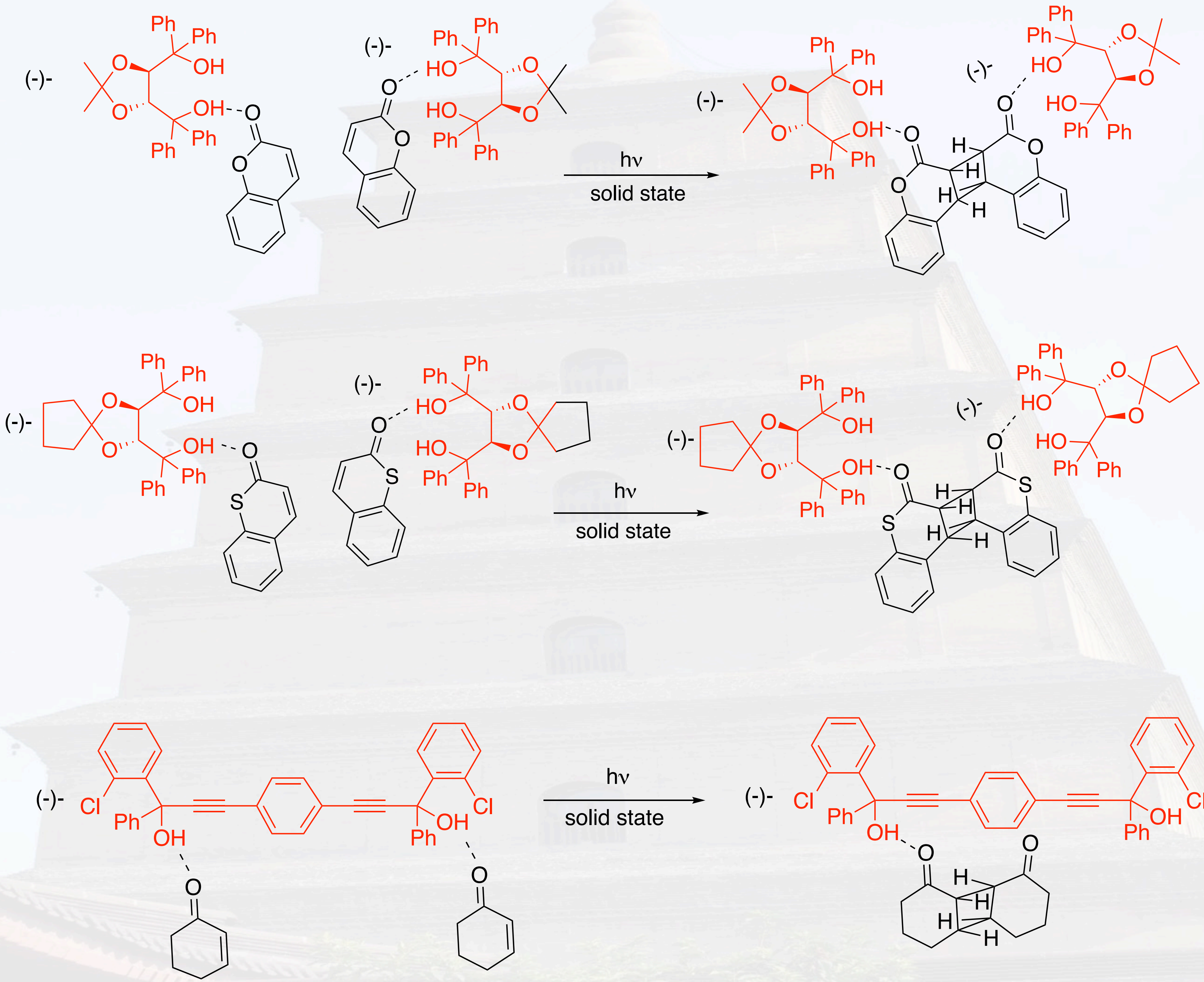
Templation through hydrogen bonding



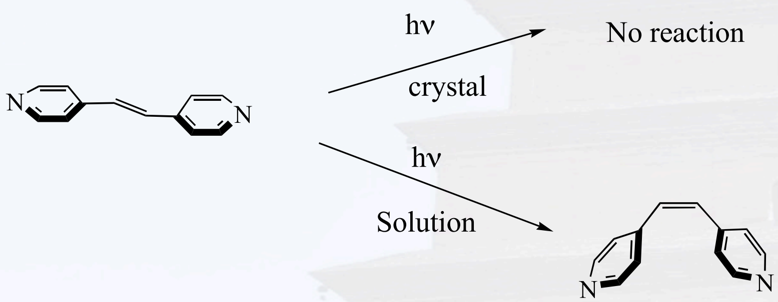


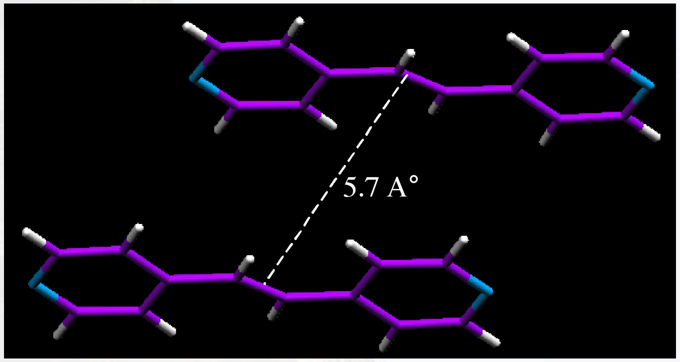


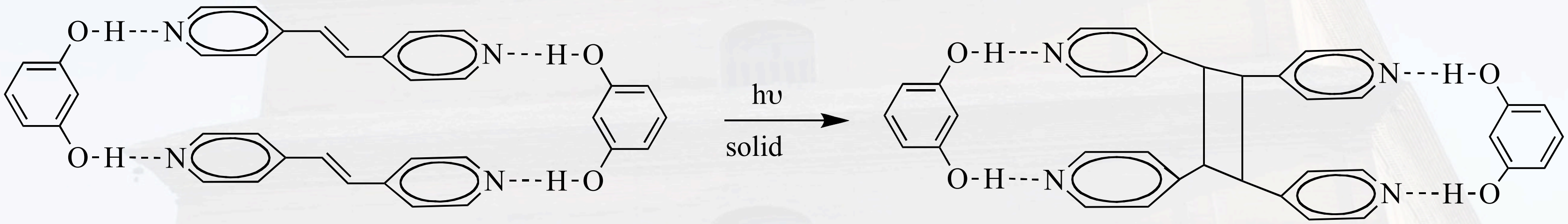


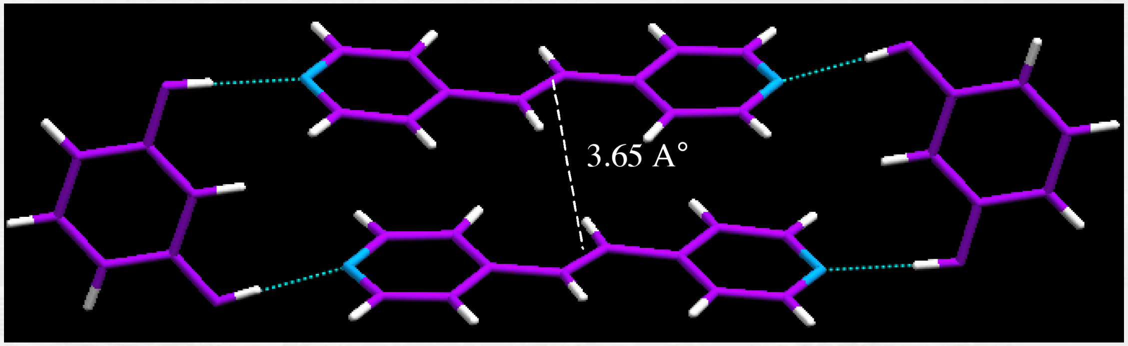

(-)-
(-)-
hν
solid state
(-)-
(-)-
(-)-
(-)-
hν
solid state
(-)-
(-)-
(-)-
hν
solid state
(-)-

Templation through hydrogen bonding

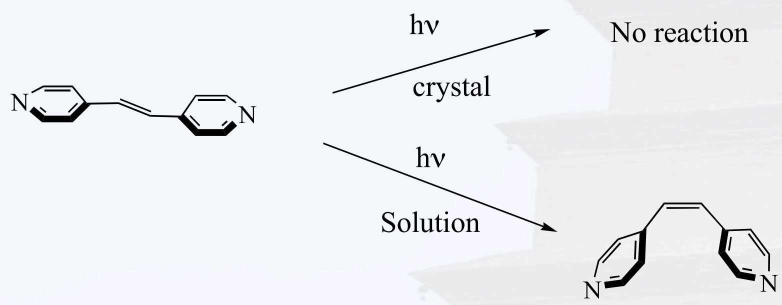


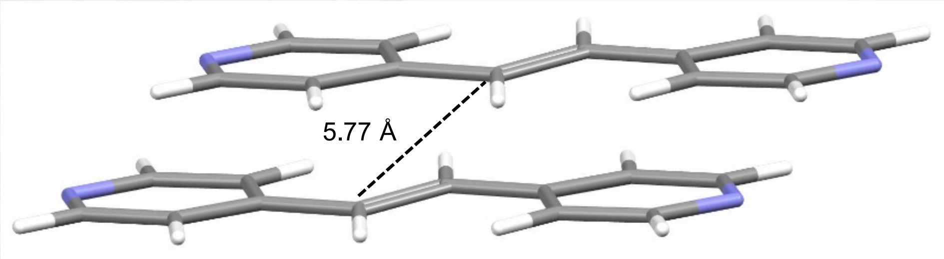


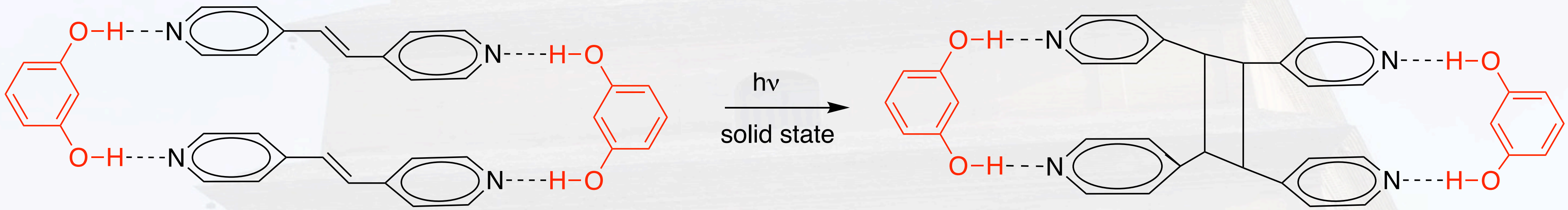


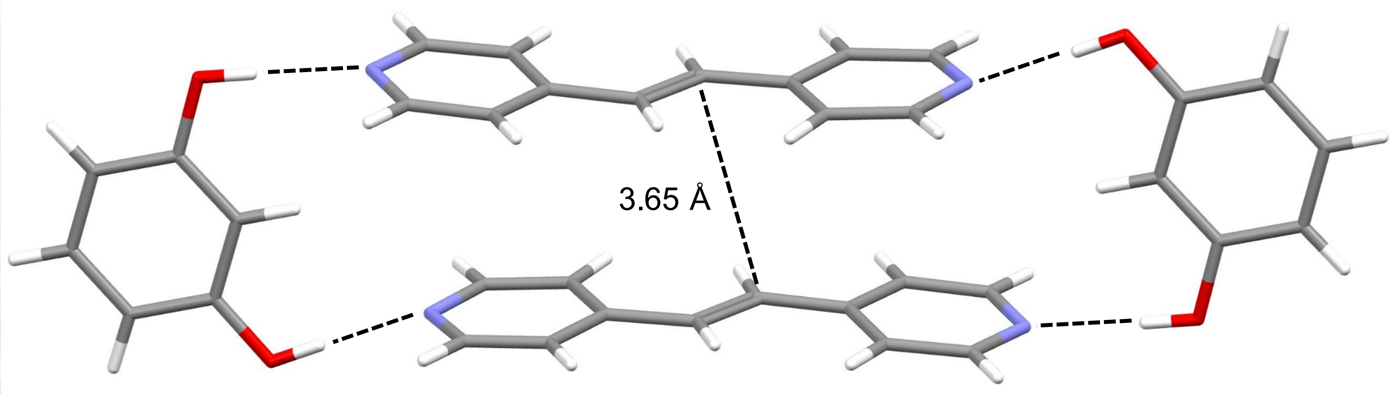


Templation through hydrogen bonding

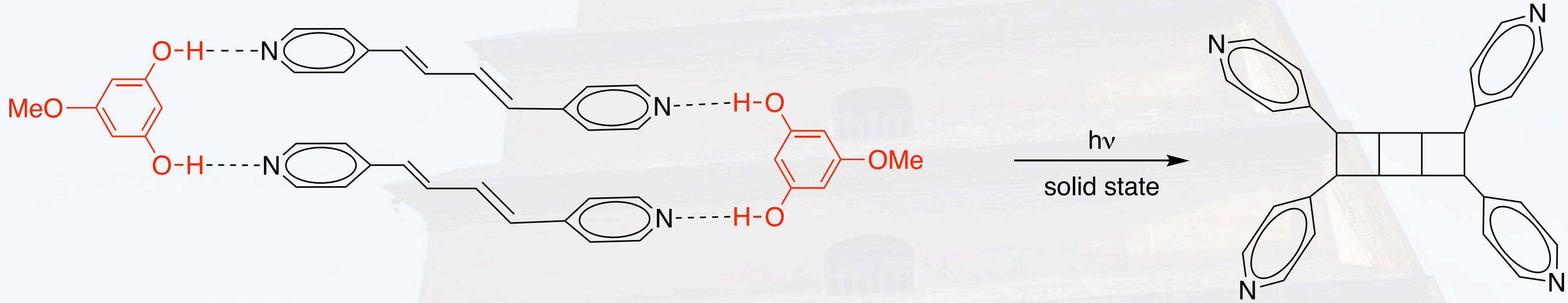


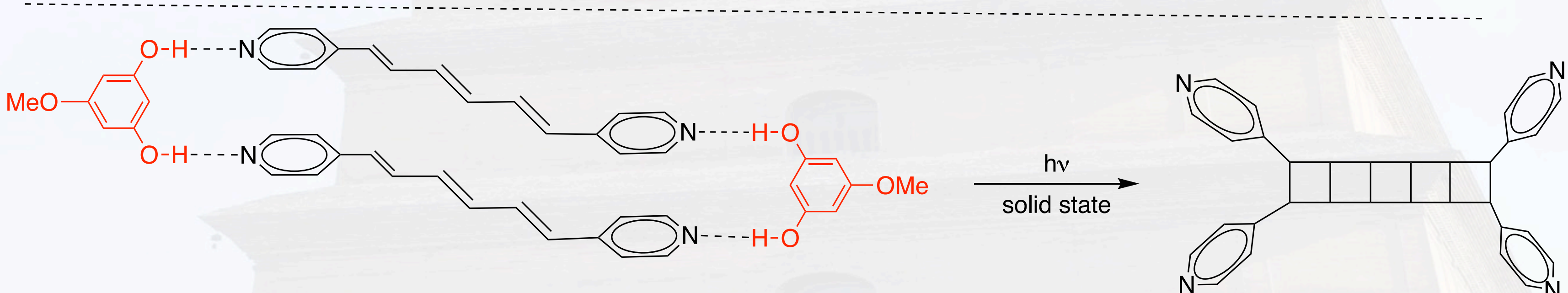


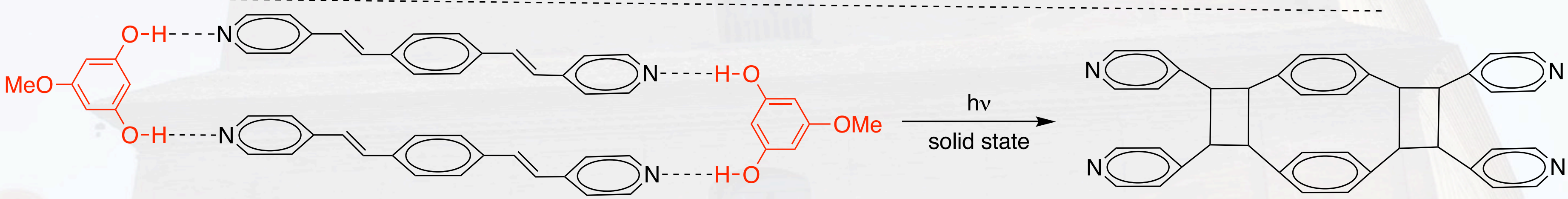




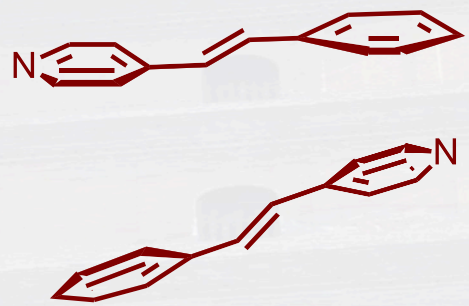
Templation through hydrogen bonding

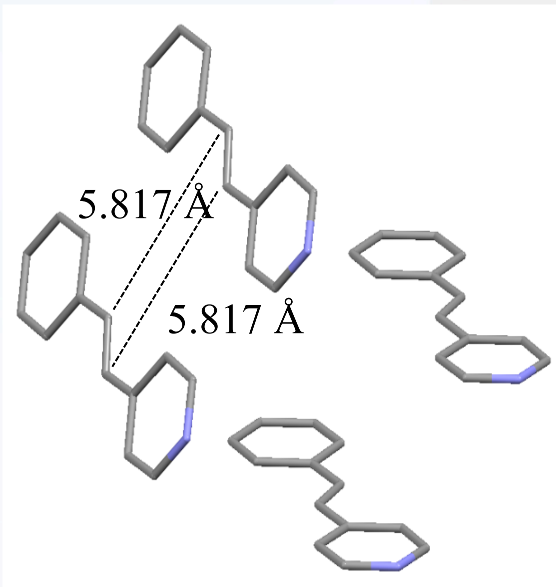


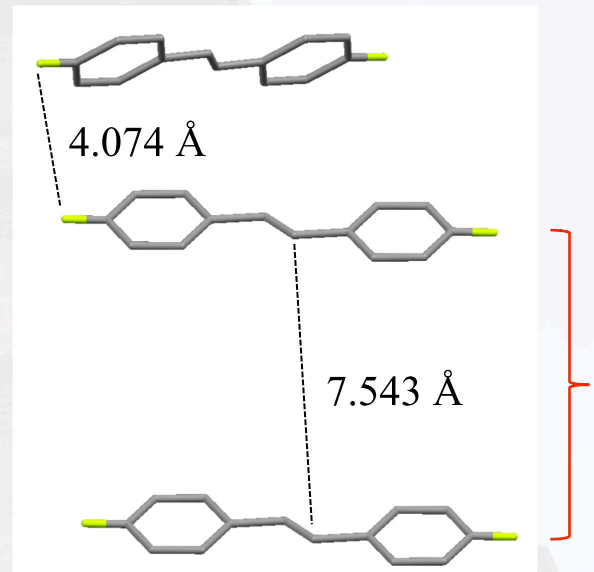




Stilbazoles not oriented suitably for photodimerization



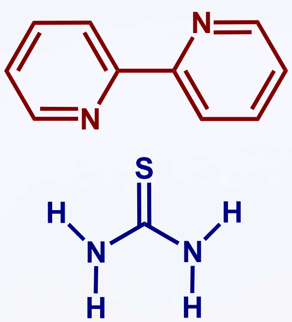


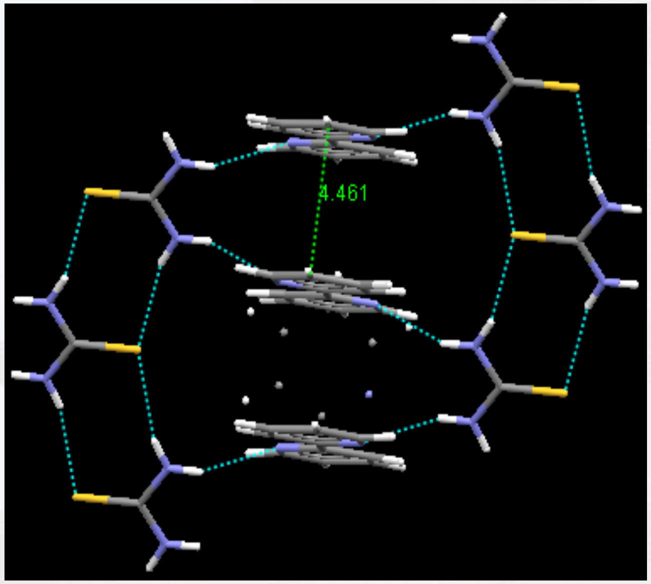


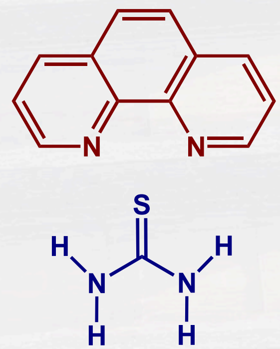
Stilbazole

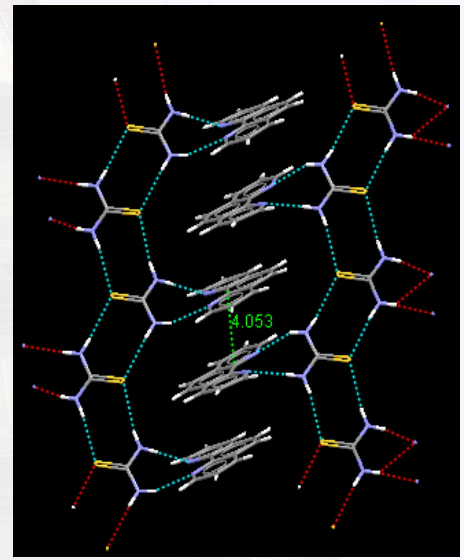
4-Fluorostilbazole

Thiourea as a Template: Importance of hydrogen bonding



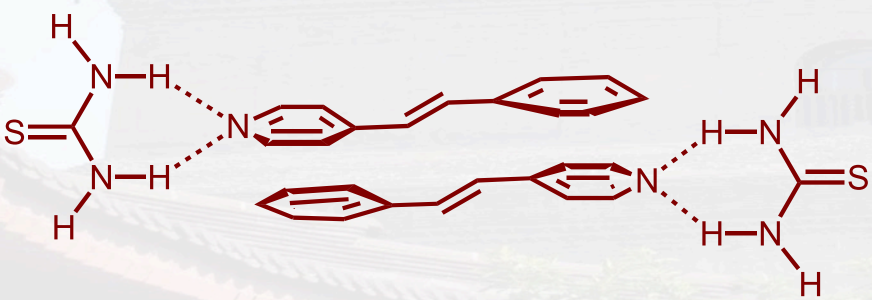


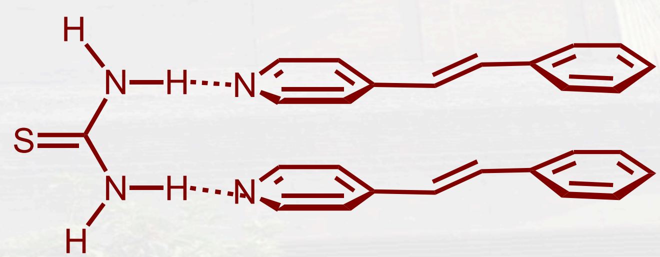


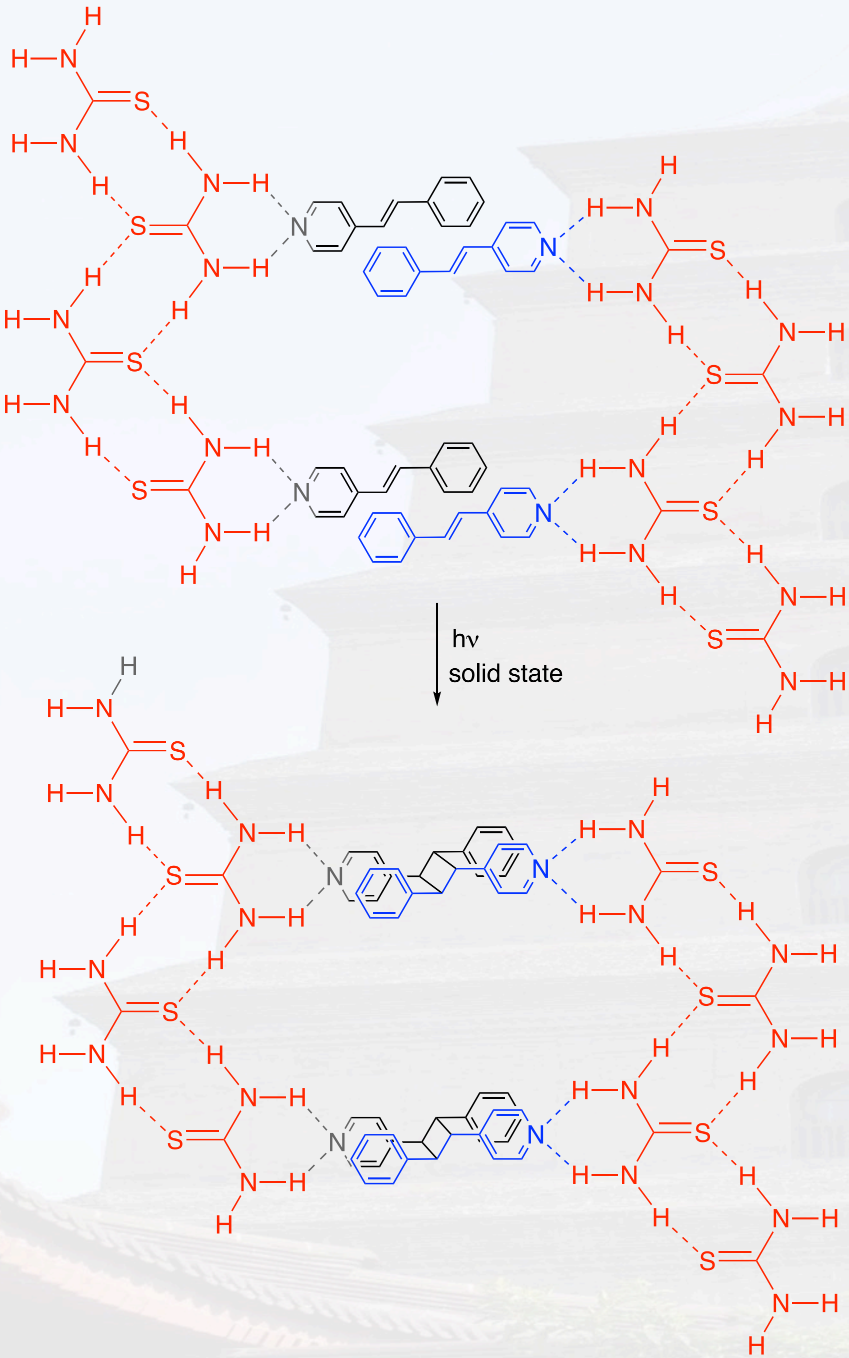


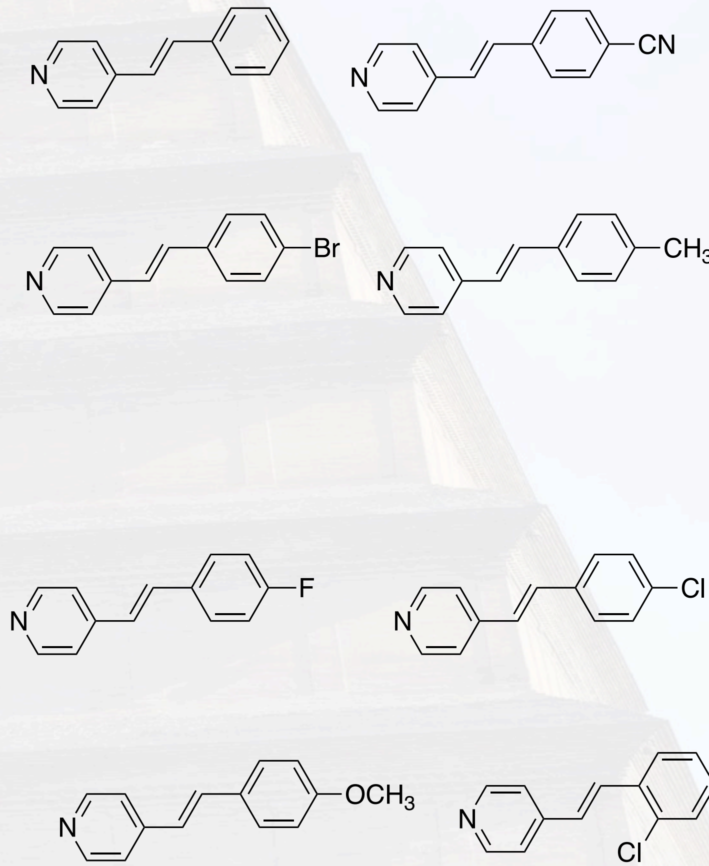
CSD entry: AMILIR

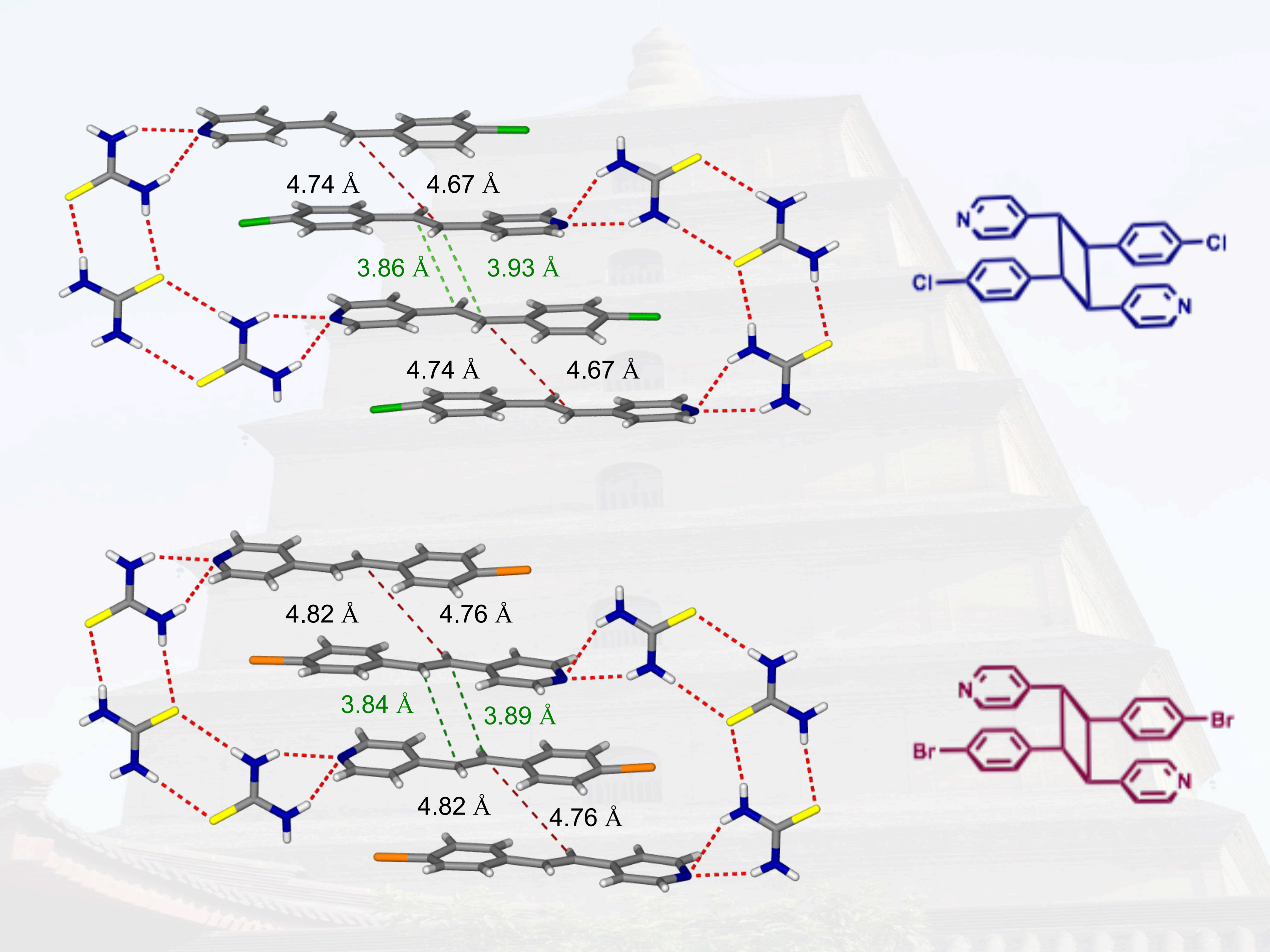
CSD entry: AMILOX





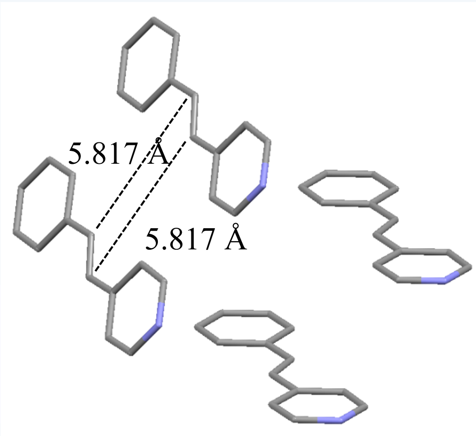

hν
solid state

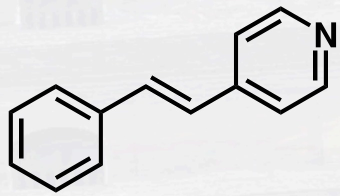




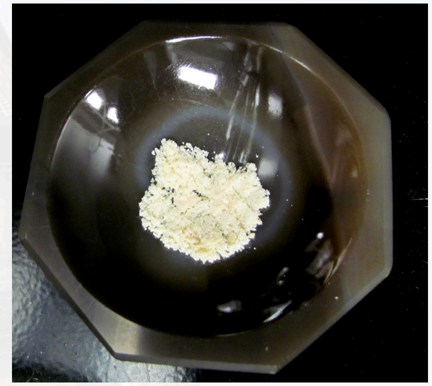
4.74 Å
4.67 Å
3.86 Å
3.93 Å
4.74 Å
4.67 Å
N
Cl
Cl
N
4.82 Å
4.76 Å
3.84 Å
3.89 Å
4.82 Å
4.76 Å
N
Br
Br
N

Stilbazole not oriented suitably for photodimerization

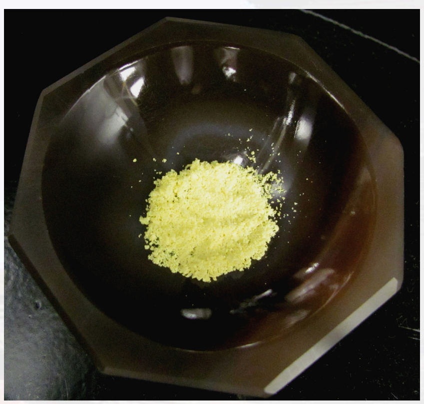


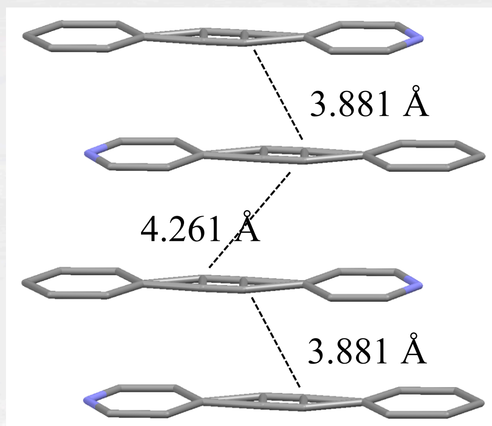


Stilbazole



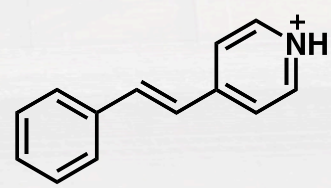
Stilbazole + HCl

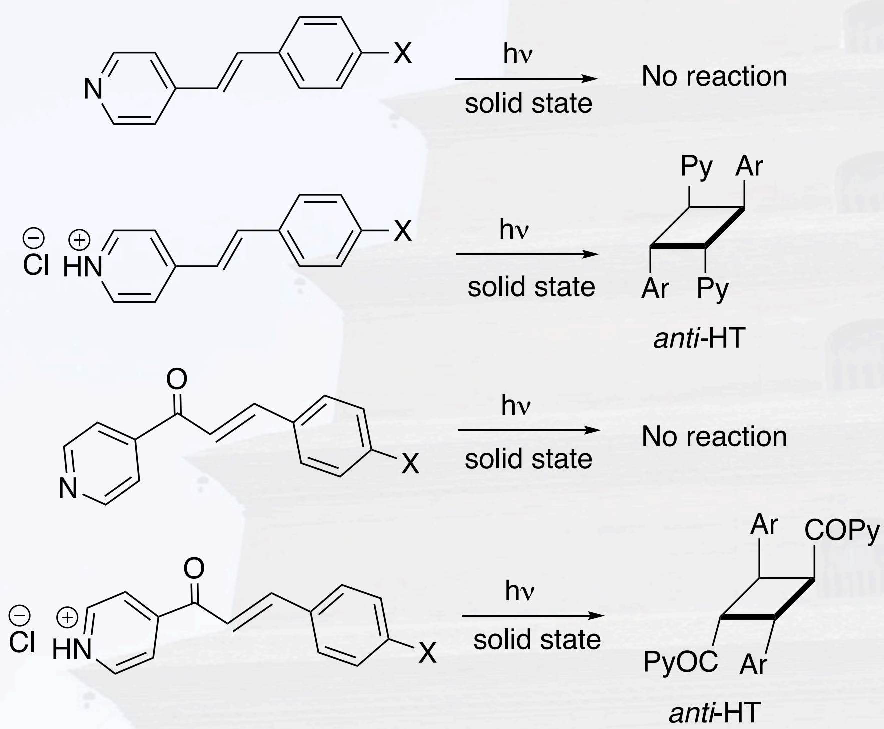




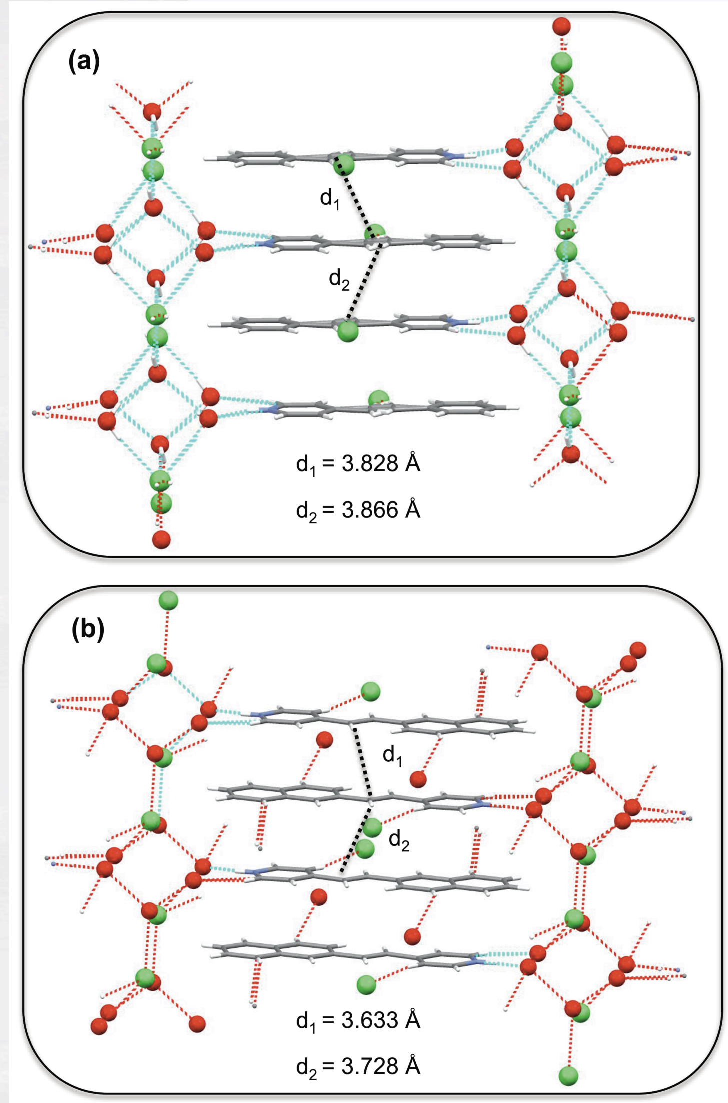
Inter-planar distance = 3.446 Å

Inter-planar distance = 3.581Å





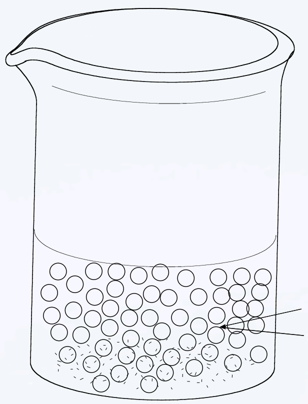
X
hν
solid state
No reaction
Cl HN
Py Ar
Ar Py
anti-HT
O
PyOC
COPy



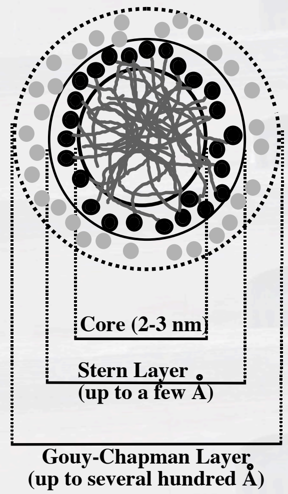
(a)
d1
d2
d1 = 3.828 Å
d2 = 3.866 Å
(b)
d1 = 3.633 Å
d2 = 3.728 Å

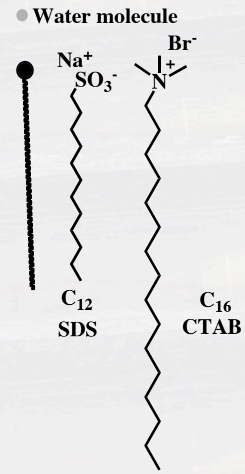
Photochemistry in Water

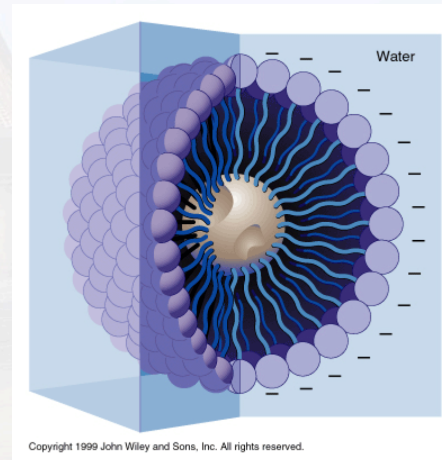
Interface helps to orient molecules

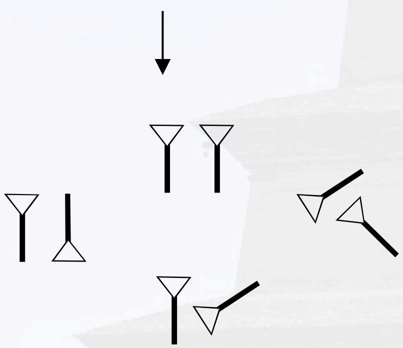


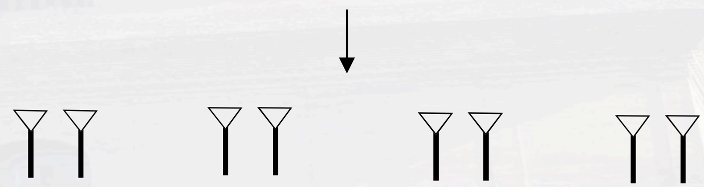
Outside
Inside
are the same











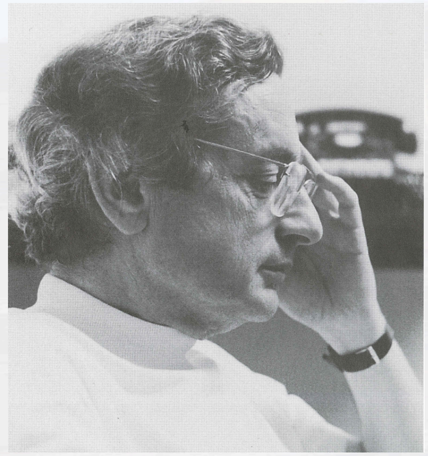
Highly aligned
Single products

Poor alignment
Multiple products

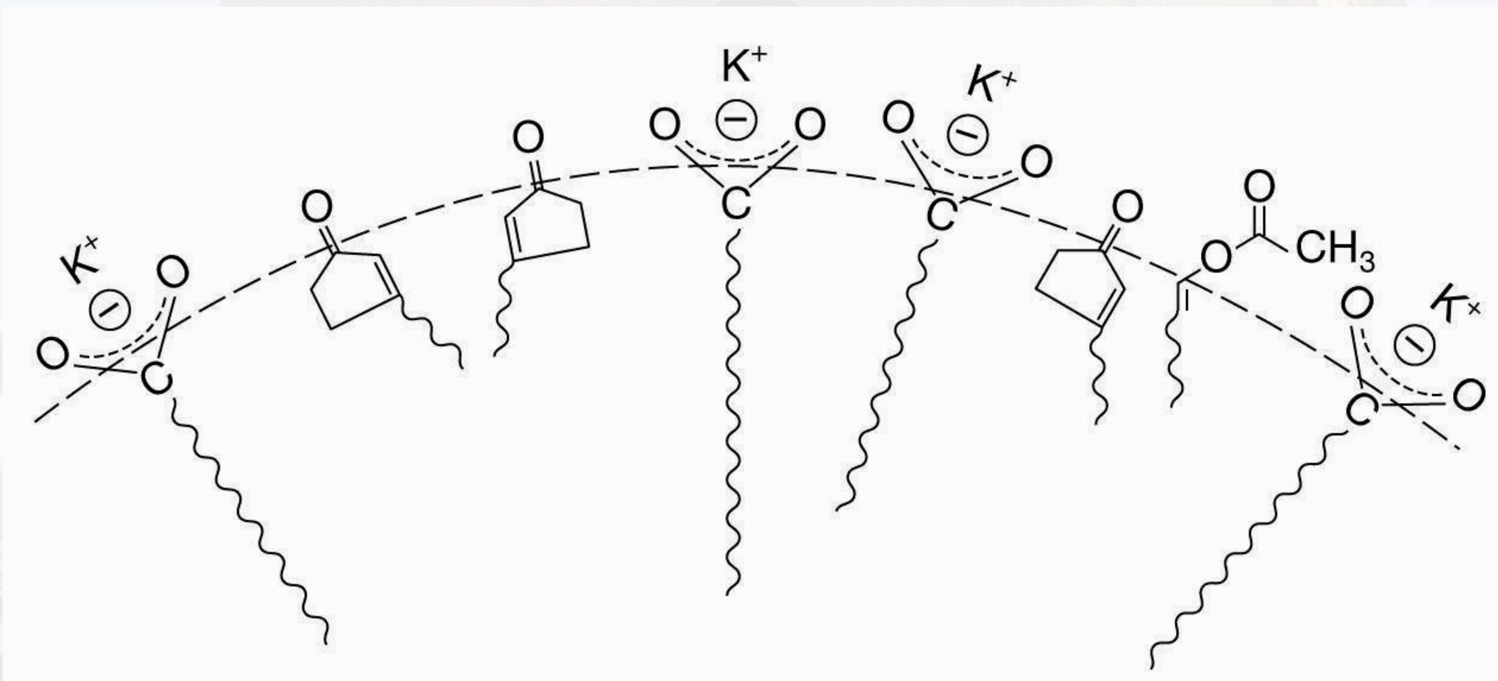
Microheterogeneous systems and some homogeneous systems : Silica, clay and zeolite surfaces, monolayers, micelles, bilayers, organic, inorganic hosts and biological systems in water.

Homogeneous Systems:
Solution, crystals

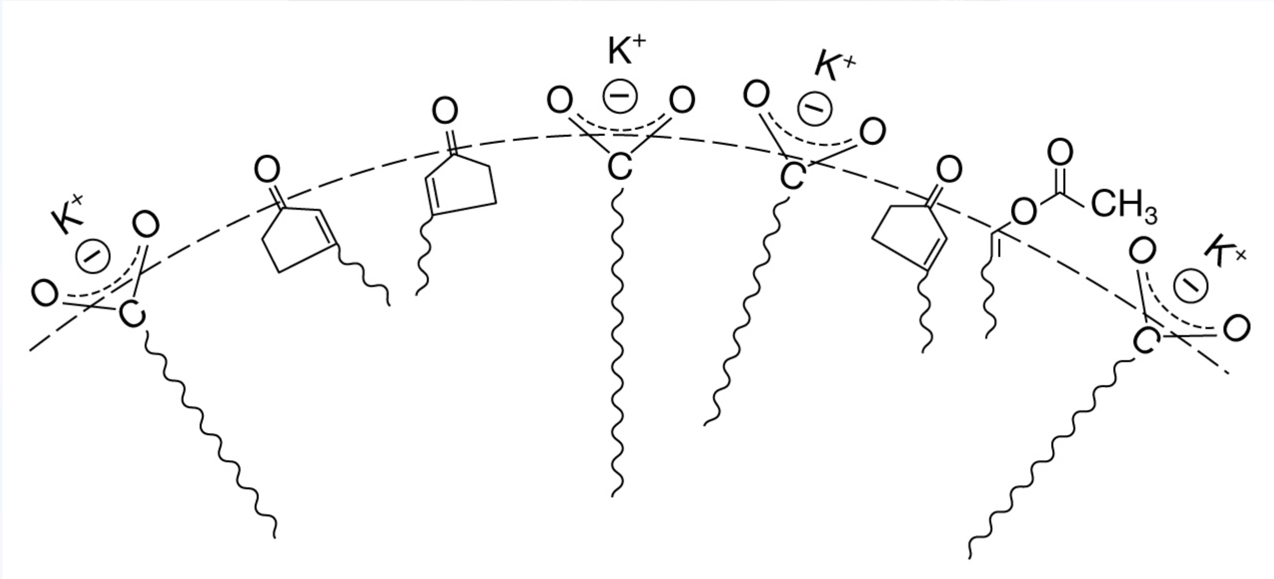
Templation in water with the help of a micelle

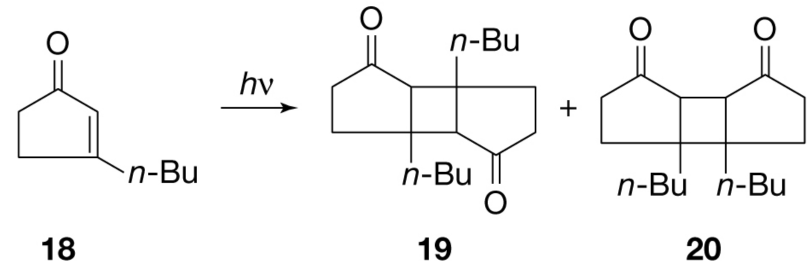


P. de Mayo



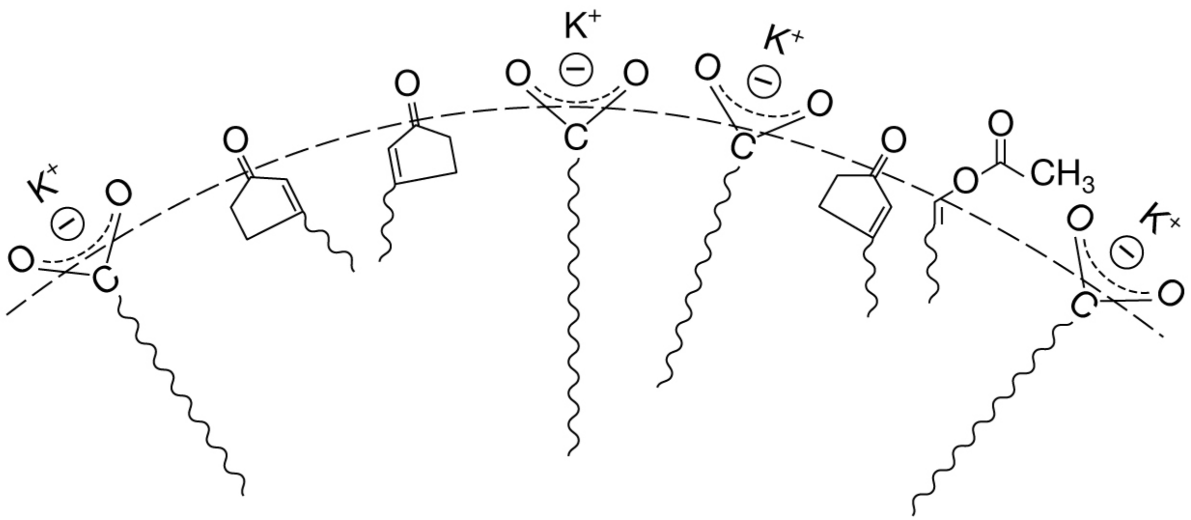
Templation in water with the help of an organized assembly

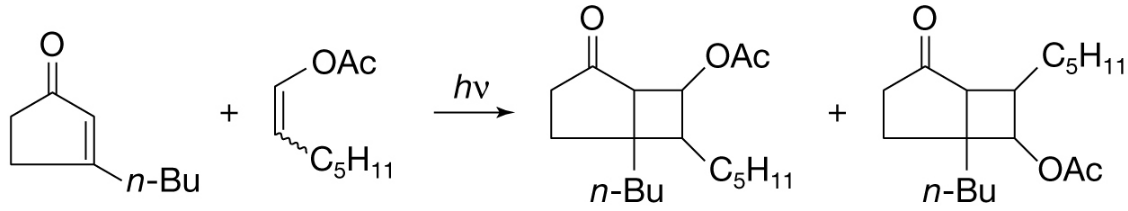




	19	20
C_6H_6	91%	9%
C_6H_{12}	96%	4%
KDC Micelle	2%	98%

Templation in water with the help of an organized assembly





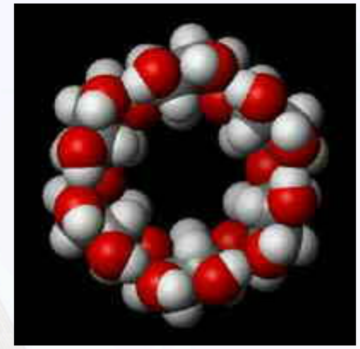
18 21 22 23

	22	23
CH_3OH	0%	100%
C_6H_{12}	0%	100%
KDC Micelle	70%	30%

A comparison of cavity dimensions of cyclodextrins and cucurbit[n]urils

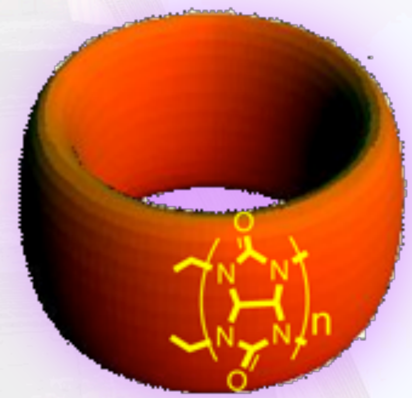
Type of CD	Cavity Diameter Å
α-CD	4.7–5.3
β-CD	6.0–6.5
γ-CD	7.5–8.3

α-D-glucopyranoside unit



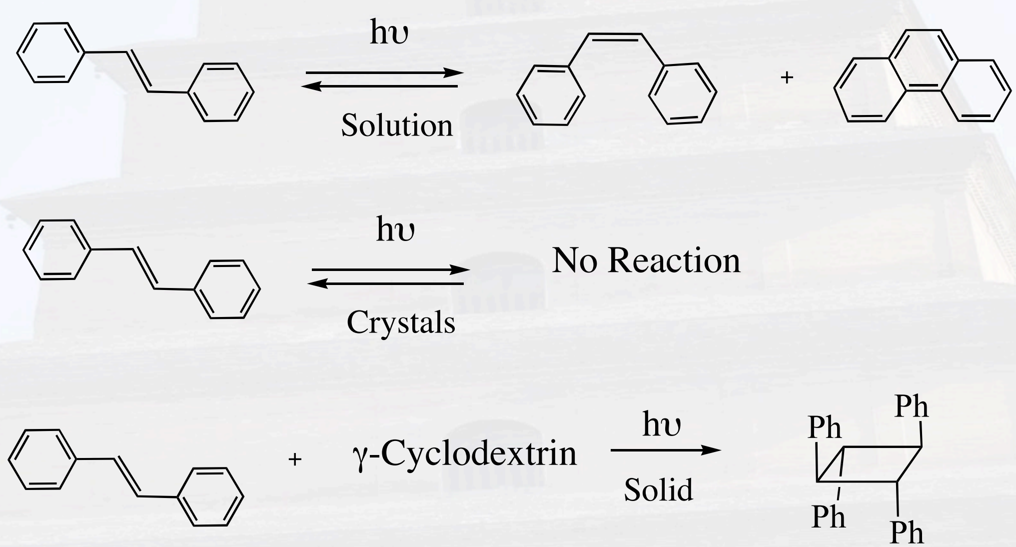
Cyclodextrins

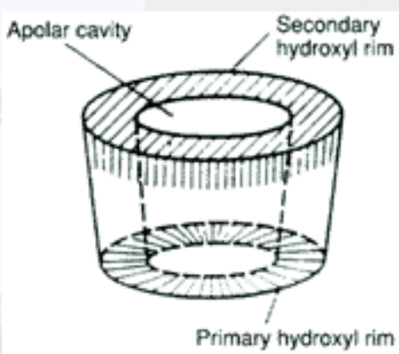
	CB[5]	CB[6]	CB[7]	CB[8]
portal diameter (Å)	2.4	3.9	5.4	6.9
cavity diameter (Å)	4.4	5.8	7.3	8.8
cavity volume (Å3)	82	164	279	479
outer diameter (Å)	13.1	14.4	16.0	17.5
height (Å)	9.1	9.1	9.1	9.1



Glycouril unit

Templation with the help of an organic host: Cyclodextrins

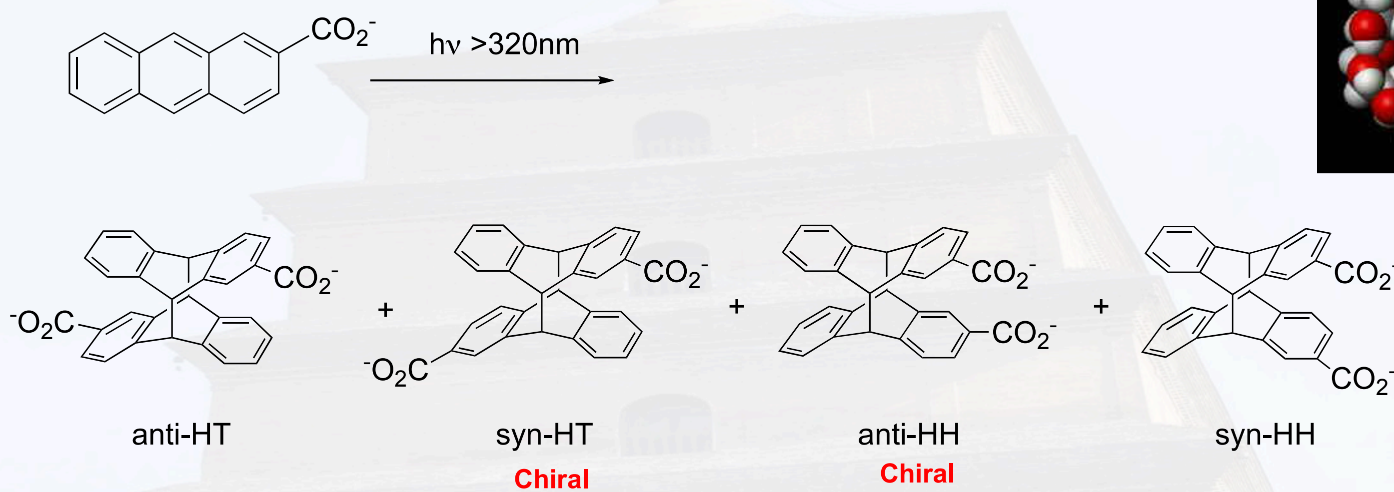


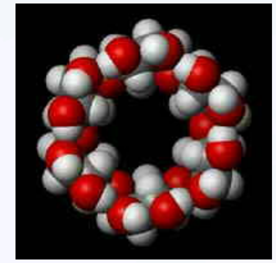


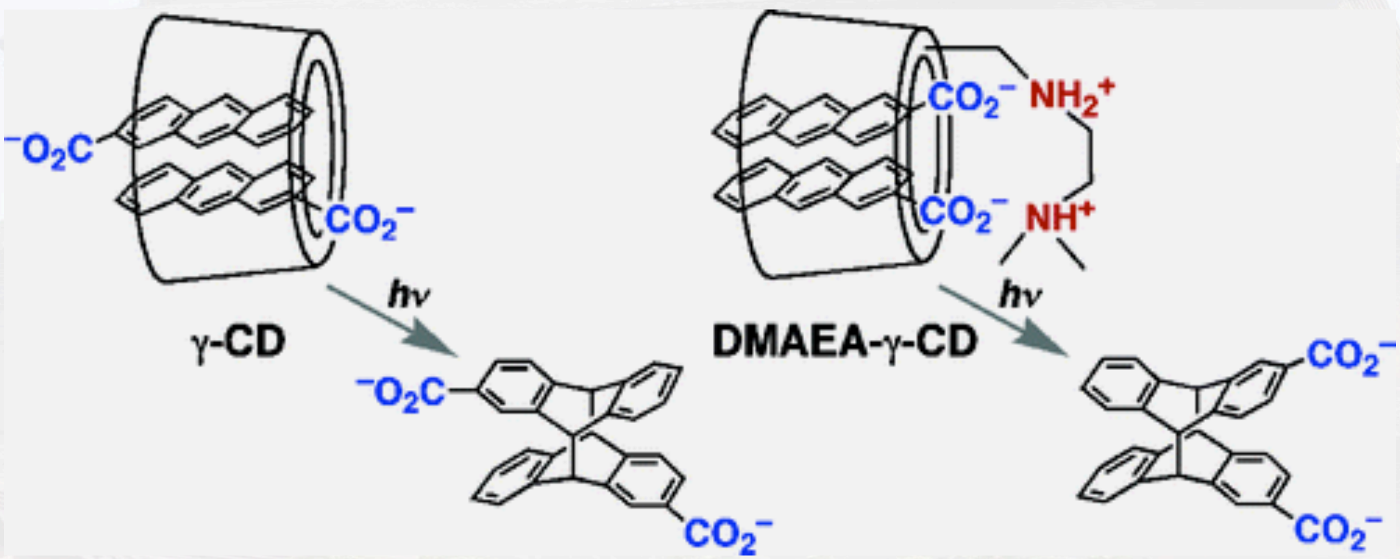
Oligosaccharides consisting of 6 or more a-1,4-linked D-glucose units

Volume (Å^3): 176 (α), 346 (β), 510 (γ)

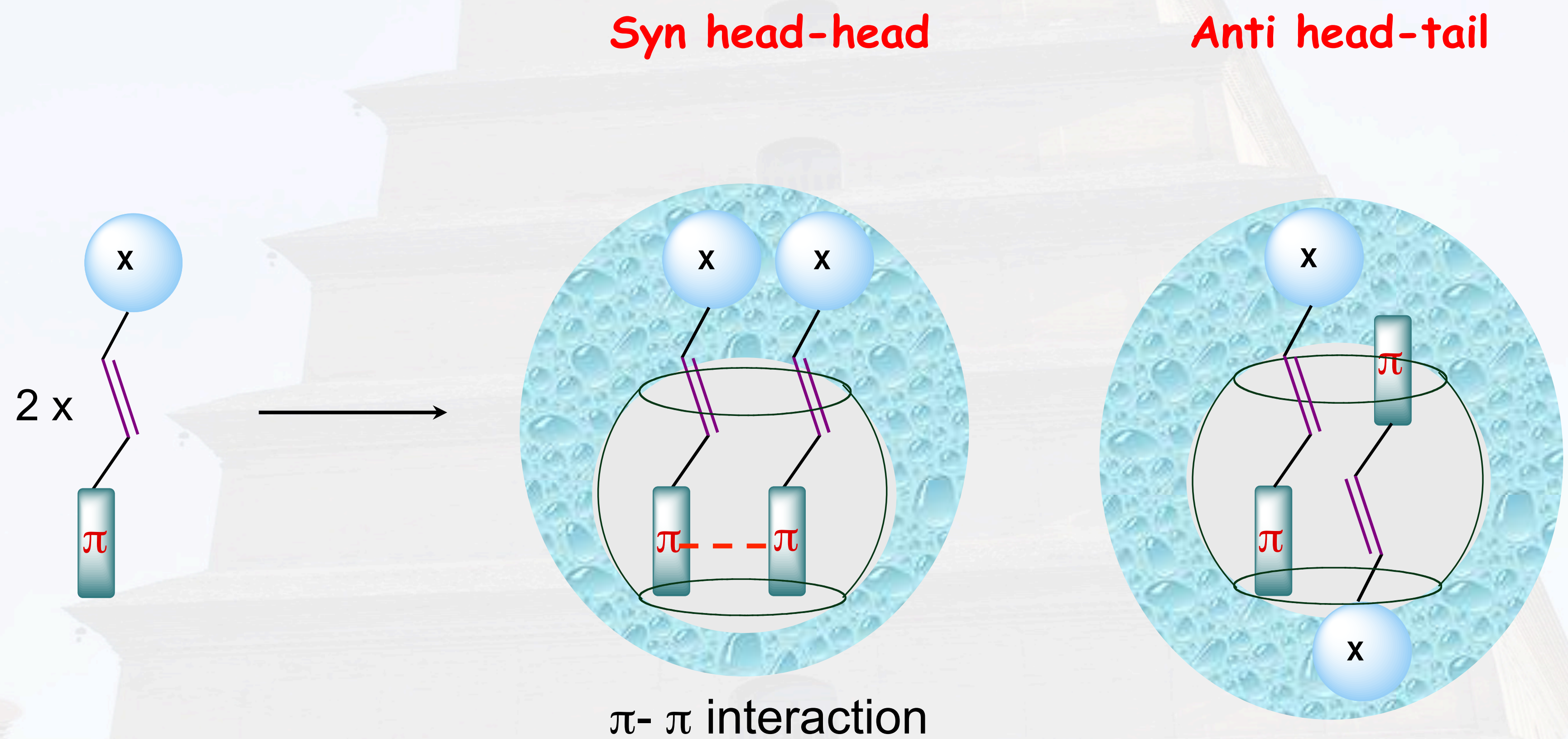
Dia at the larger end (Å):
8.8 (α), 10.8 (β), 12.0 (γ)


CO_2^-
hν >320nm
CO_2^-
^-O_2C
CO_2^-
^-O_2C
CO_2^-
CO_2^-
CO_2^-
CO_2^-
anti-HT
syn-HT
Chiral
anti-HH
Chiral
syn-HH

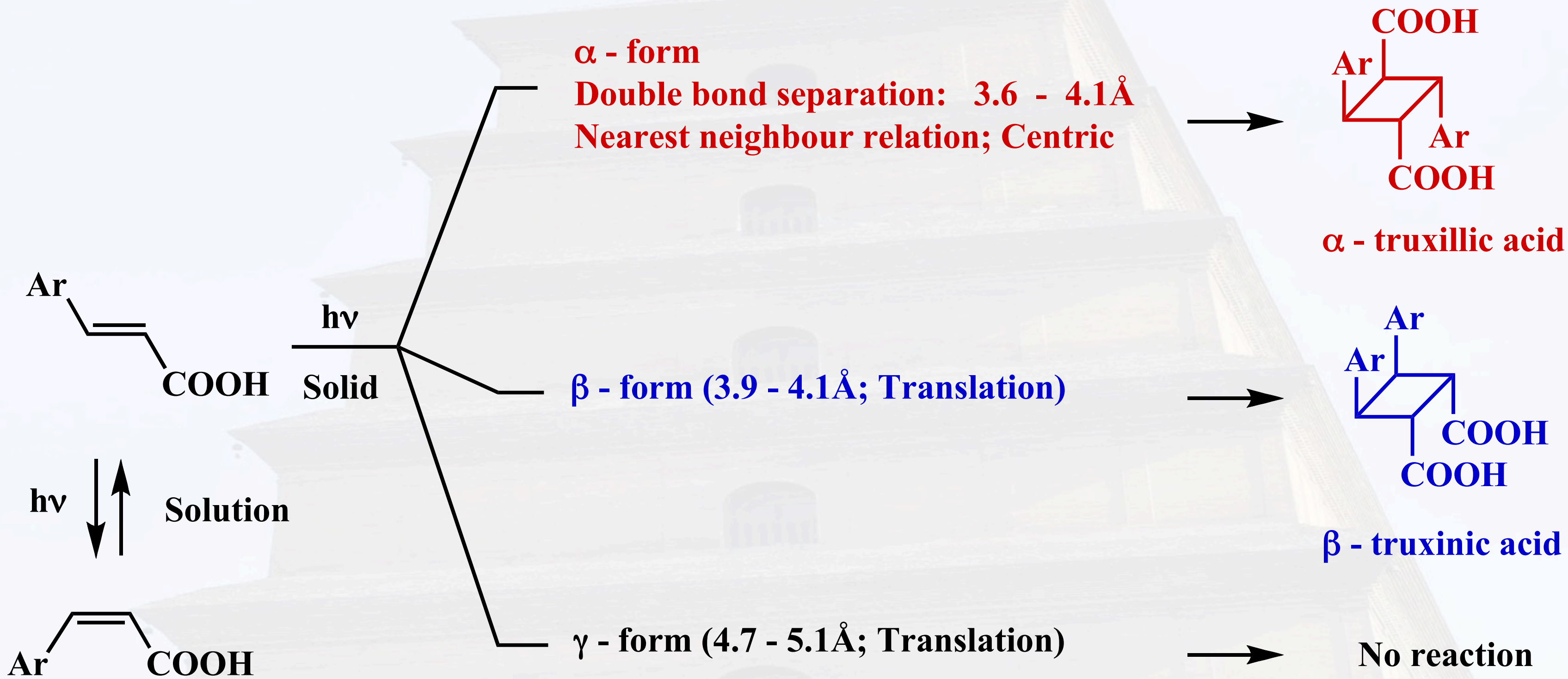



^-O_2C
CO_2^-
CO_2^-
NH_2^+
CO_2^-
NH^+
hν
γ-CD
DMAEA-γ-CD
hν
^-O_2C
CO_2^-
CO_2^-
CO_2^-

Templation with cucurbiturils



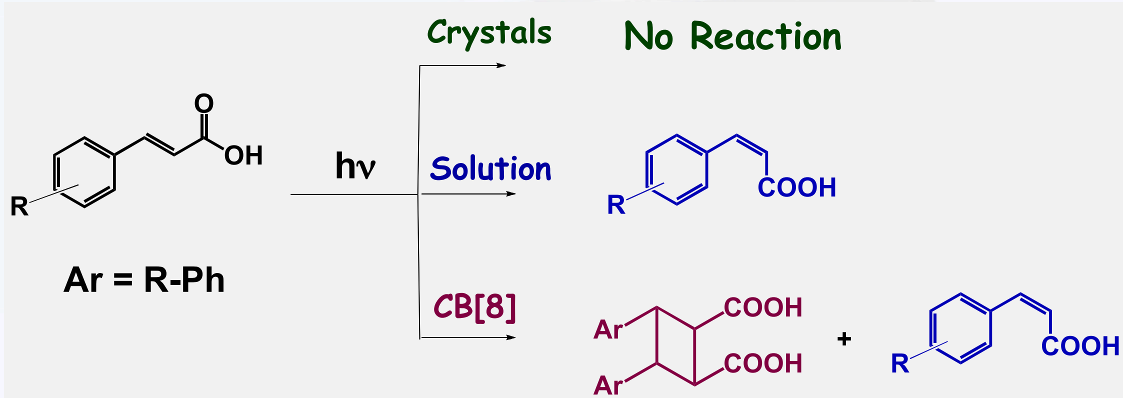
Photodimerization of *trans*-Cinnamic acids

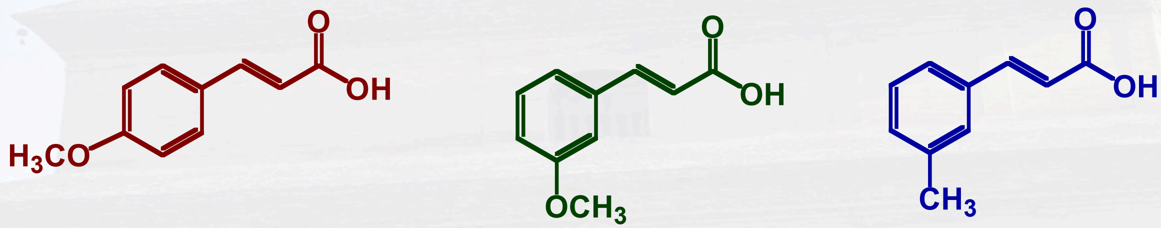


Topochemical principle: Reactions in the solid state take place with minimum atomic movements.

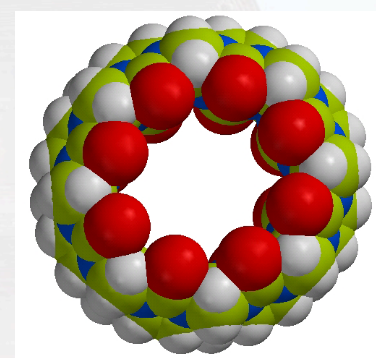
G. M. J. Schmidt et al. '*Solid State Photochemitsry, A Collection of Papers*', Verlag Chemie, 1976.

trans-Cinnamic acids that are photo inactive in solid state (γ-form)

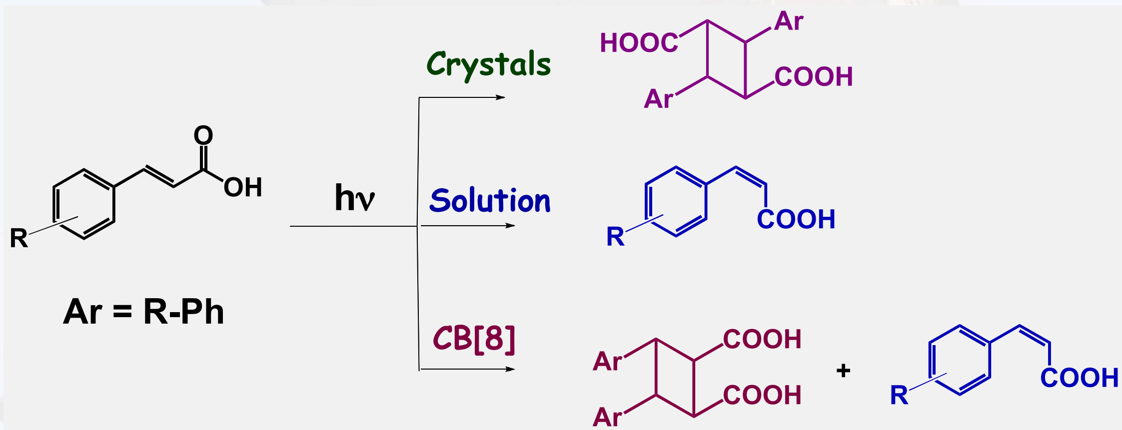


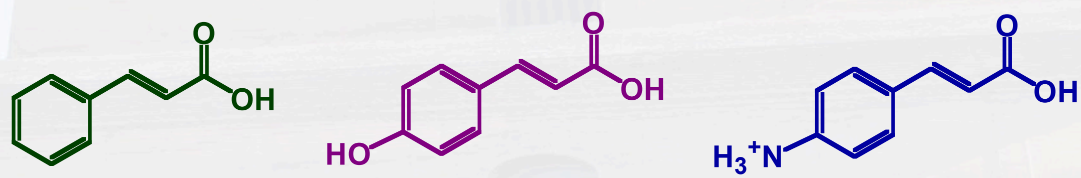


Ar	Solid state	% of dimer in CB[8]	% of cis isomer
R=4-OCH_3	--	72	28
R=3-OCH_3	--	72	28
R=3-CH_3	--	83	17

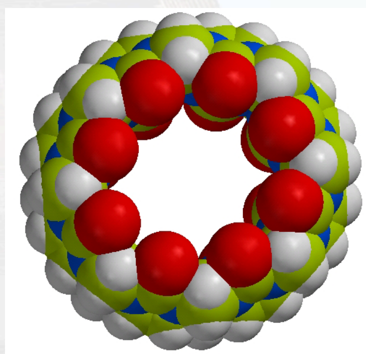


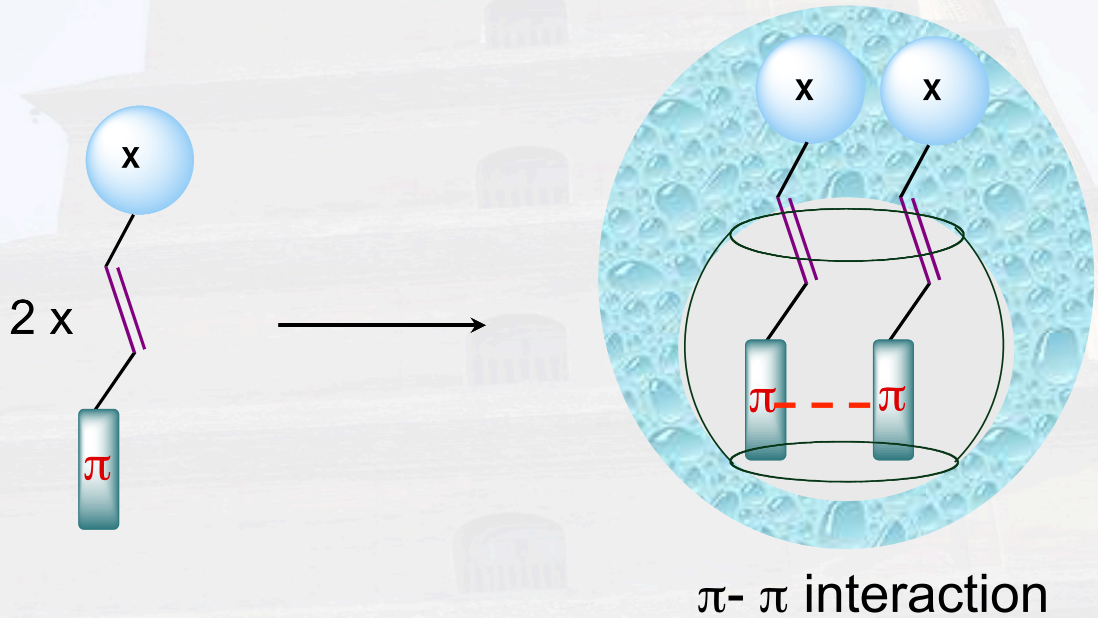
trans-Cinnamic acids that yield *anti* H-T dimer upon irradiation in solid state (α-form)

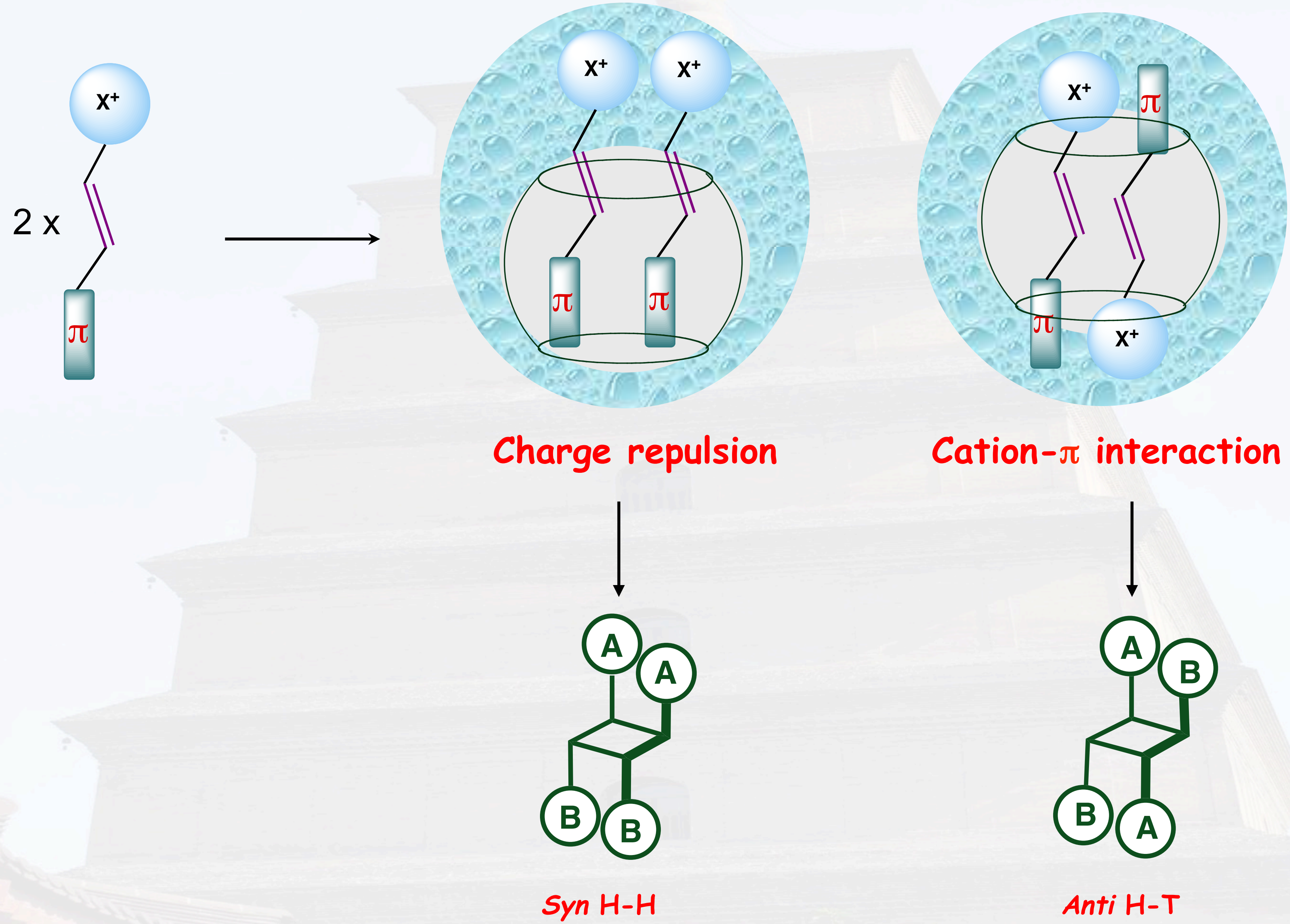




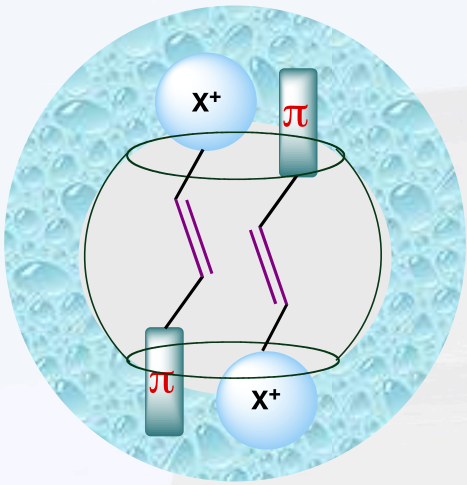
Ar	Solid state % of anti H-T dimer	% of Syn H-H dimer in CB[8]	% of cis isomer
R=H	100	54	46
R=4-OH	100	38	62
R=4-NH_3^+	100	88	12



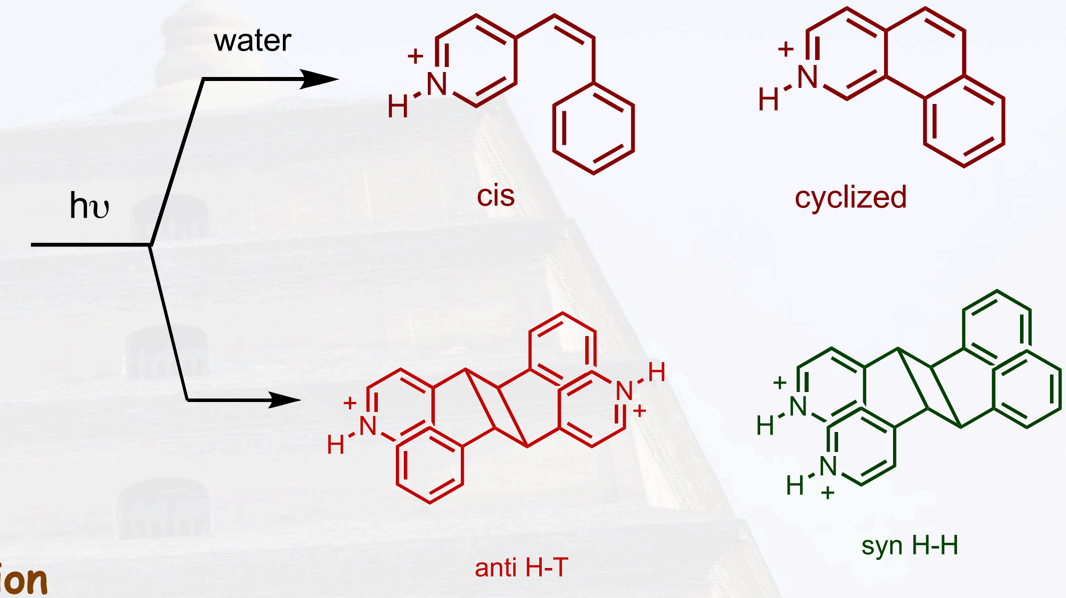

x
2 x
π
x
x
π
π
π- π interaction

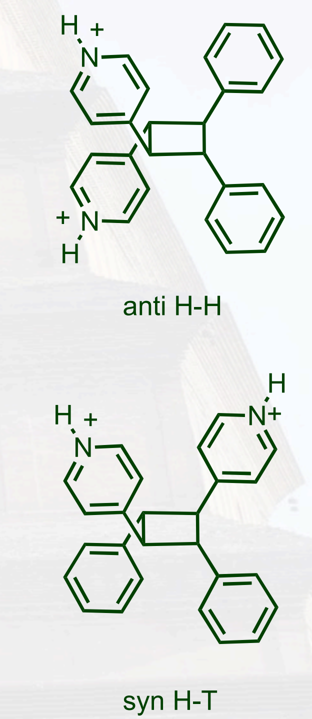


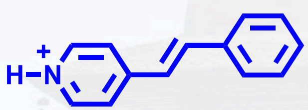
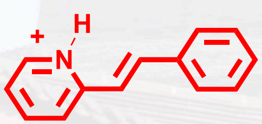
2 x
X+
π
Charge repulsion
Cation-π interaction
A
B
Syn H-H
Anti H-T

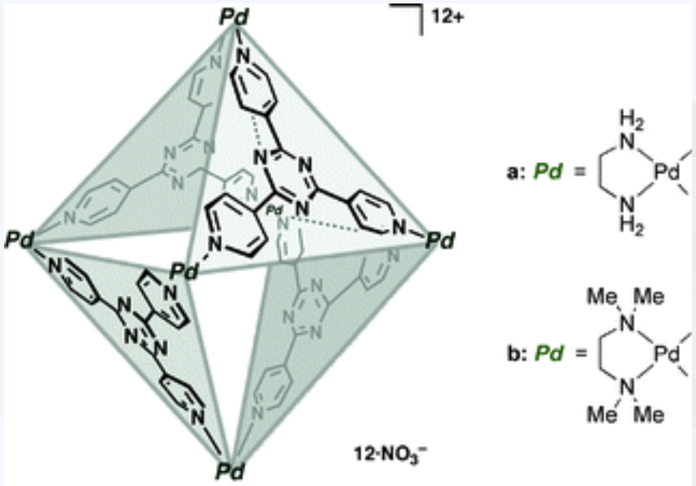


Cation-π interaction
Minimized ionic repulsion

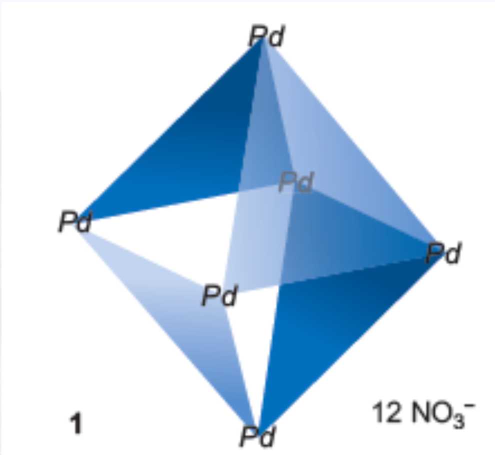


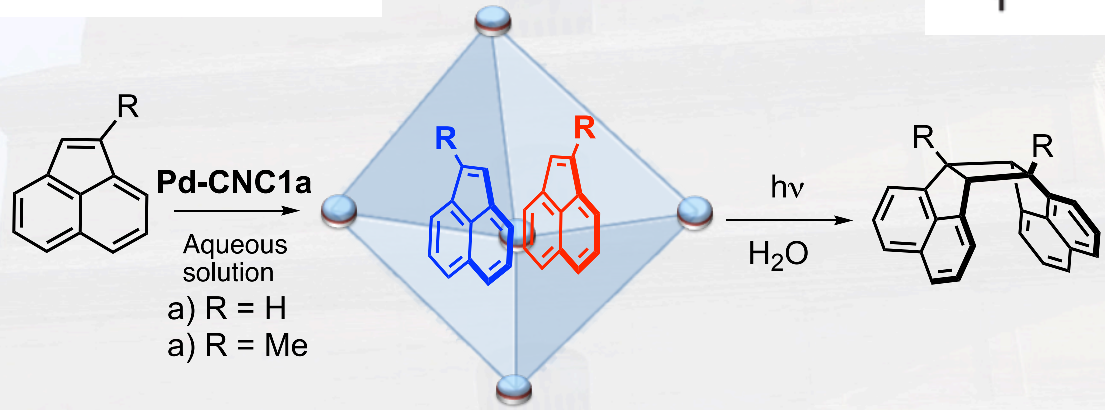


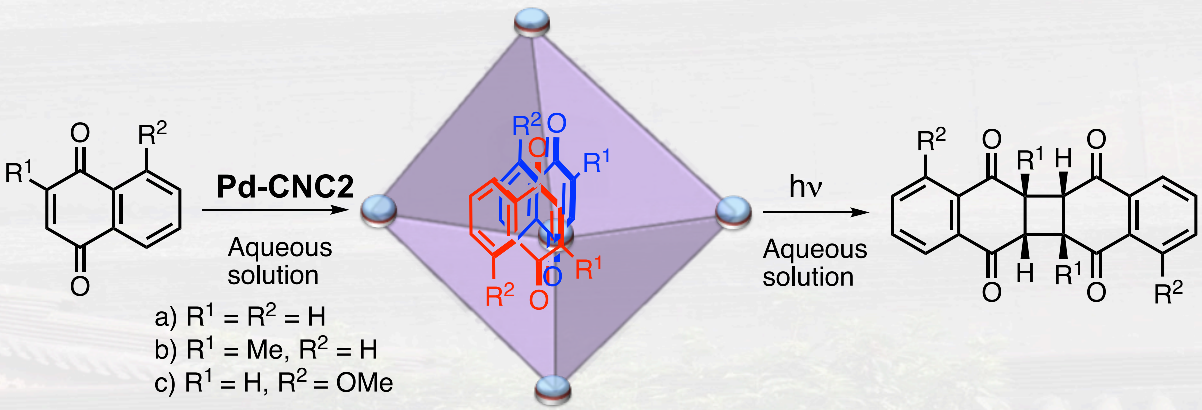
Guest	Medium	*anti* H-T	*syn* H-T	*cis*
	Water	03	02	95
	CB[8]	90	05	05
	Water	02	02	96
	CB[8]	82	00	18

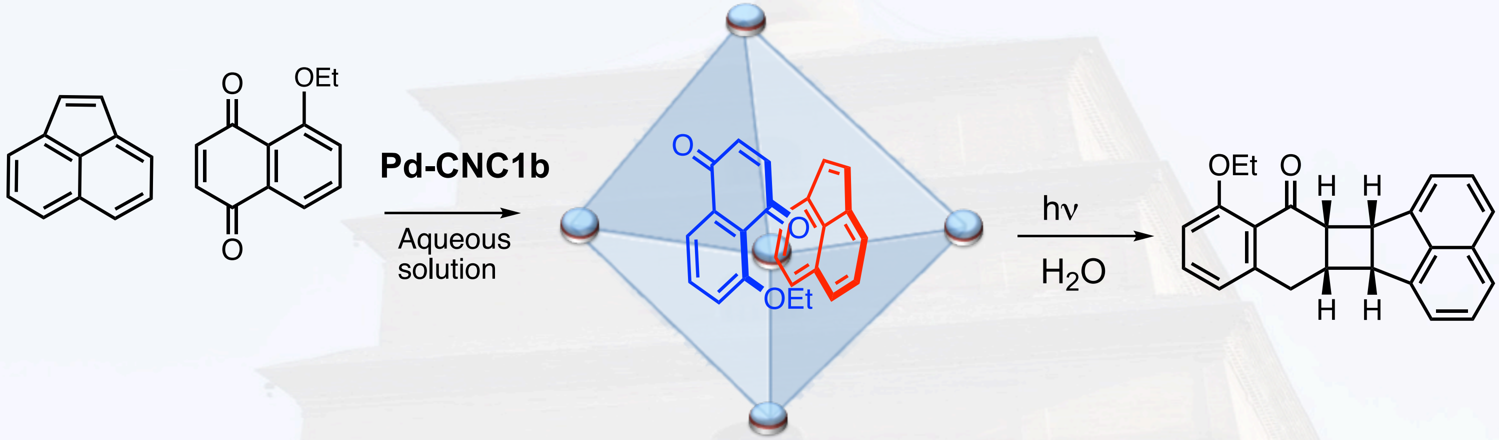


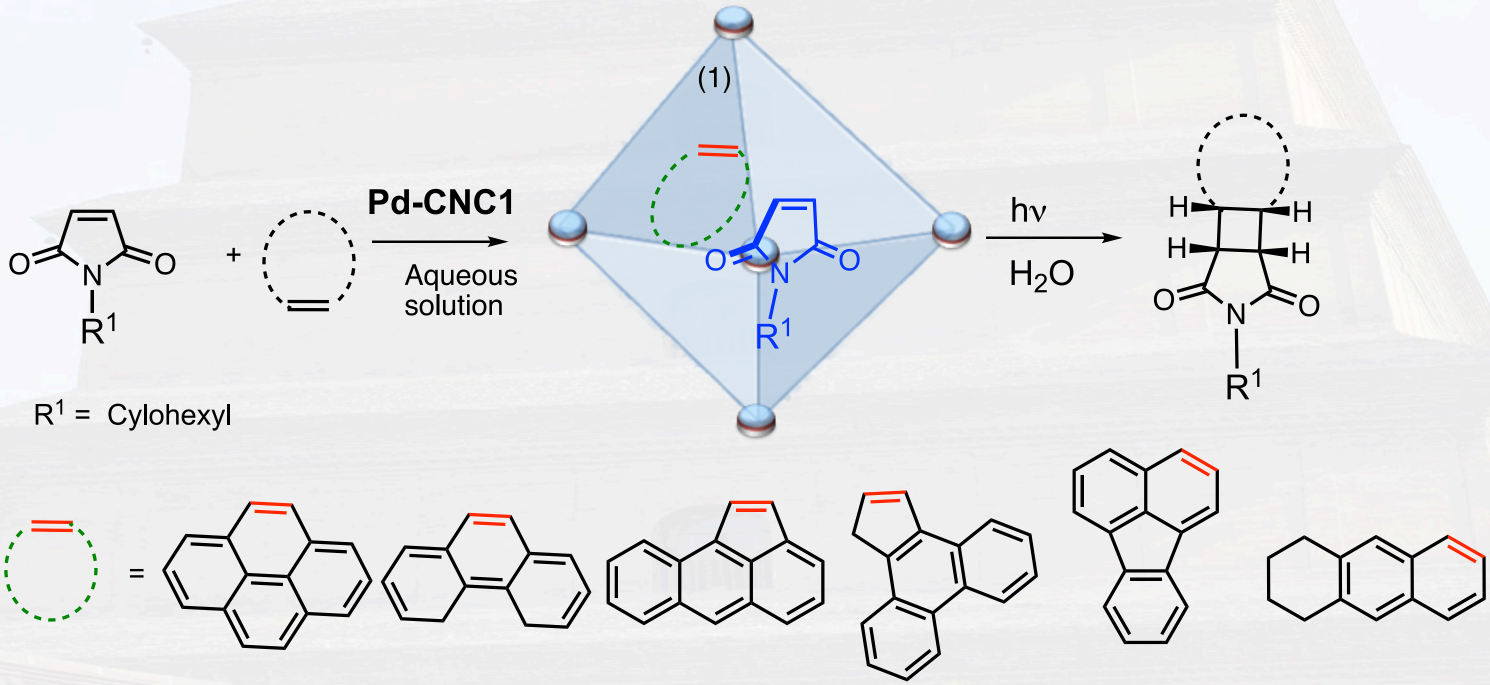
Interior dia ~ 30 Å
Hydrophobic interior
Water soluble



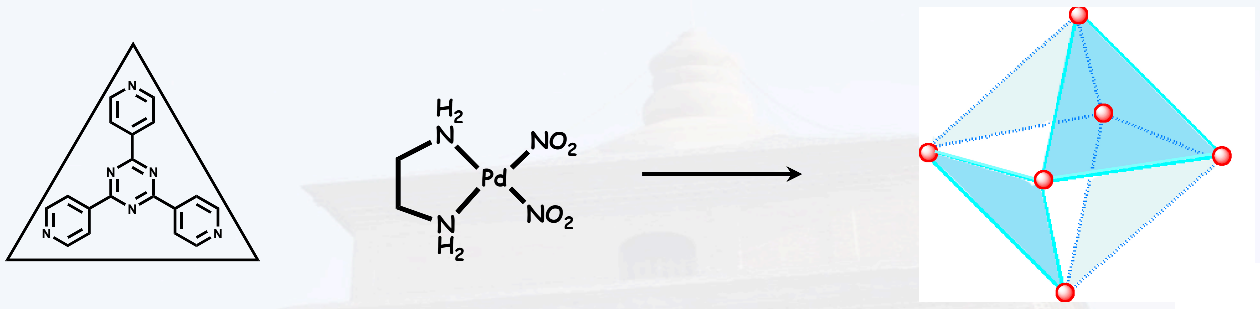


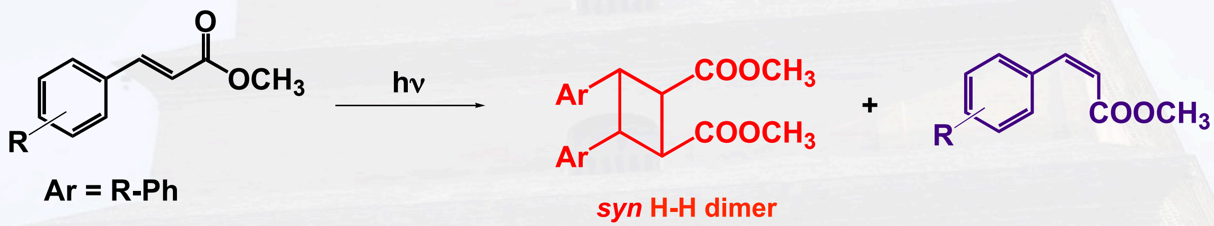


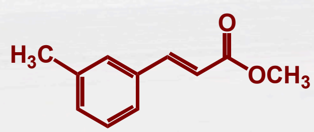
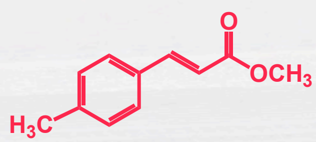
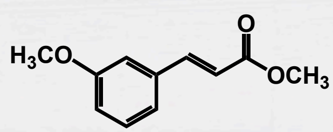
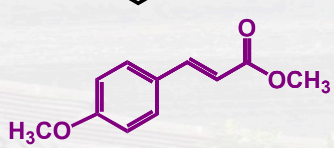


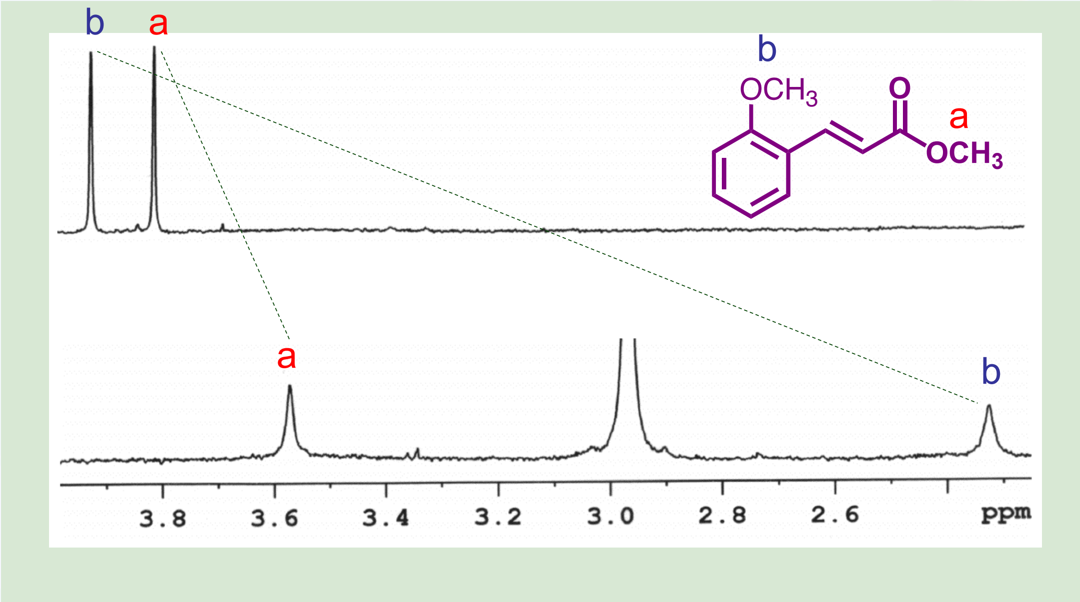


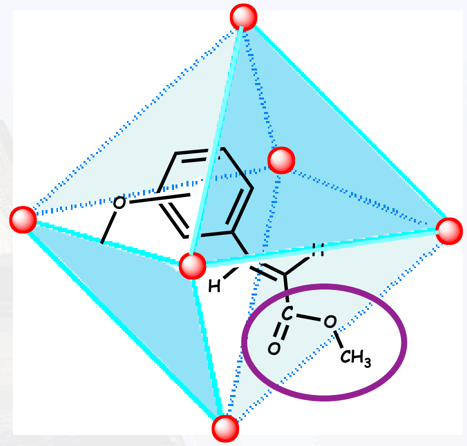
(Reactive double bond in red)



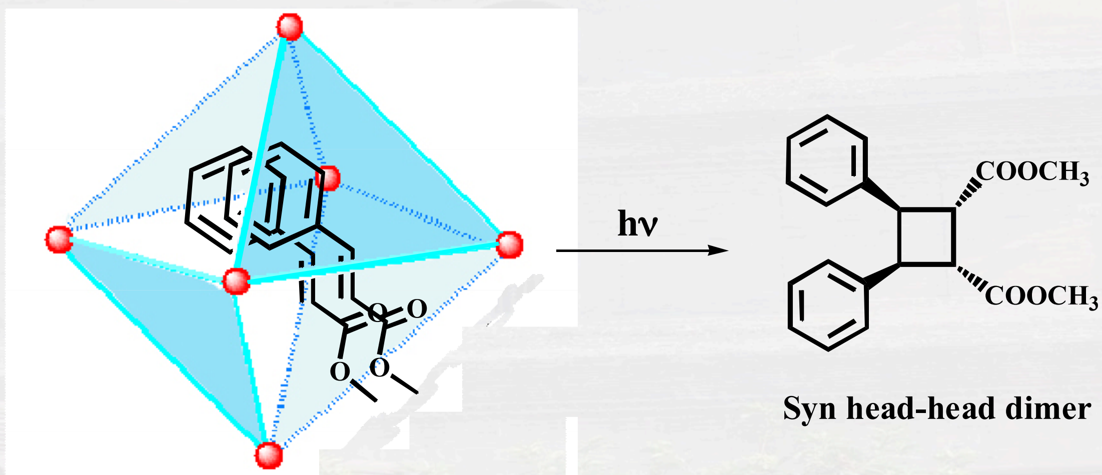


Substrate	% of Syn H-H dimer in nanocage	% of cis isomer
	63	37
	45	55
	42	58
	40	60



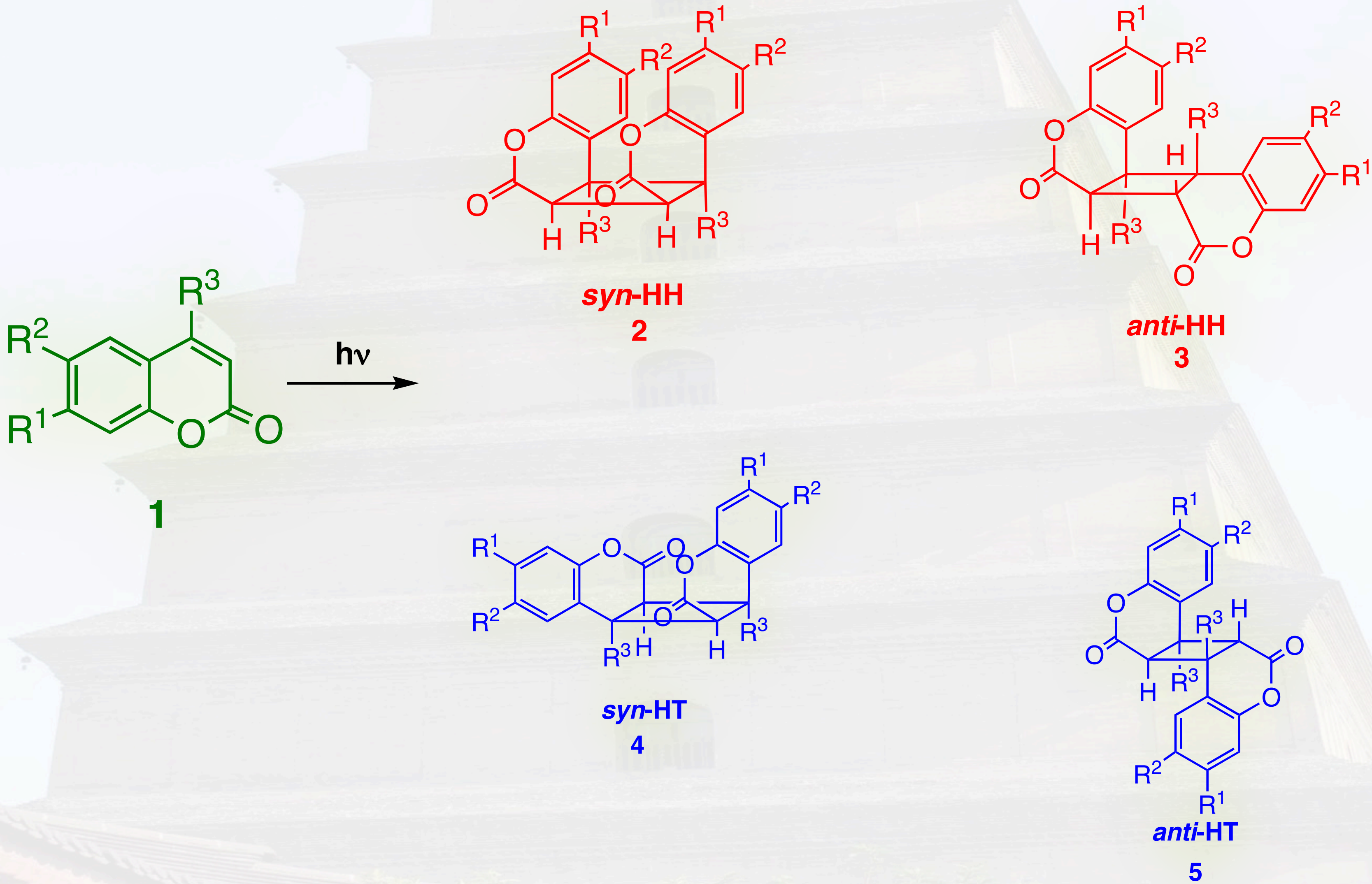


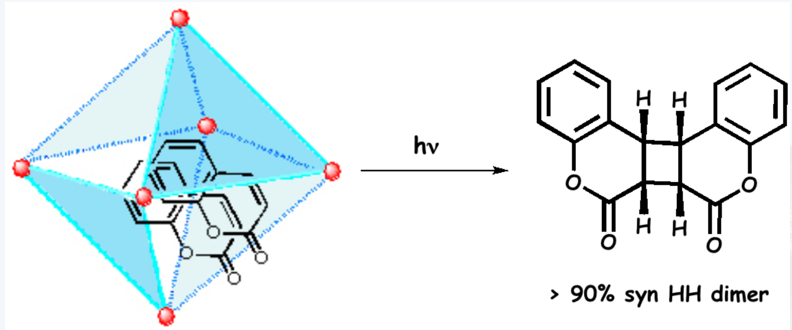
1) Top-[1]H NMR of *O*-methoxy cinnamate in D_2O
2) Bottom- [1]H NMR of encapsulated *O*-methoxy cinnamate in Pd-Nanocage (0.5 eq.)

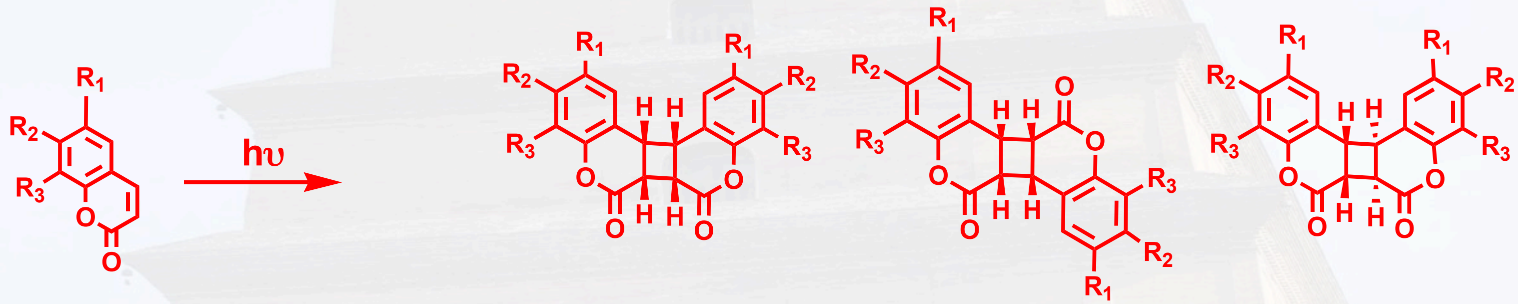


Syn head-head dimer

Photochemistry of Coumarins

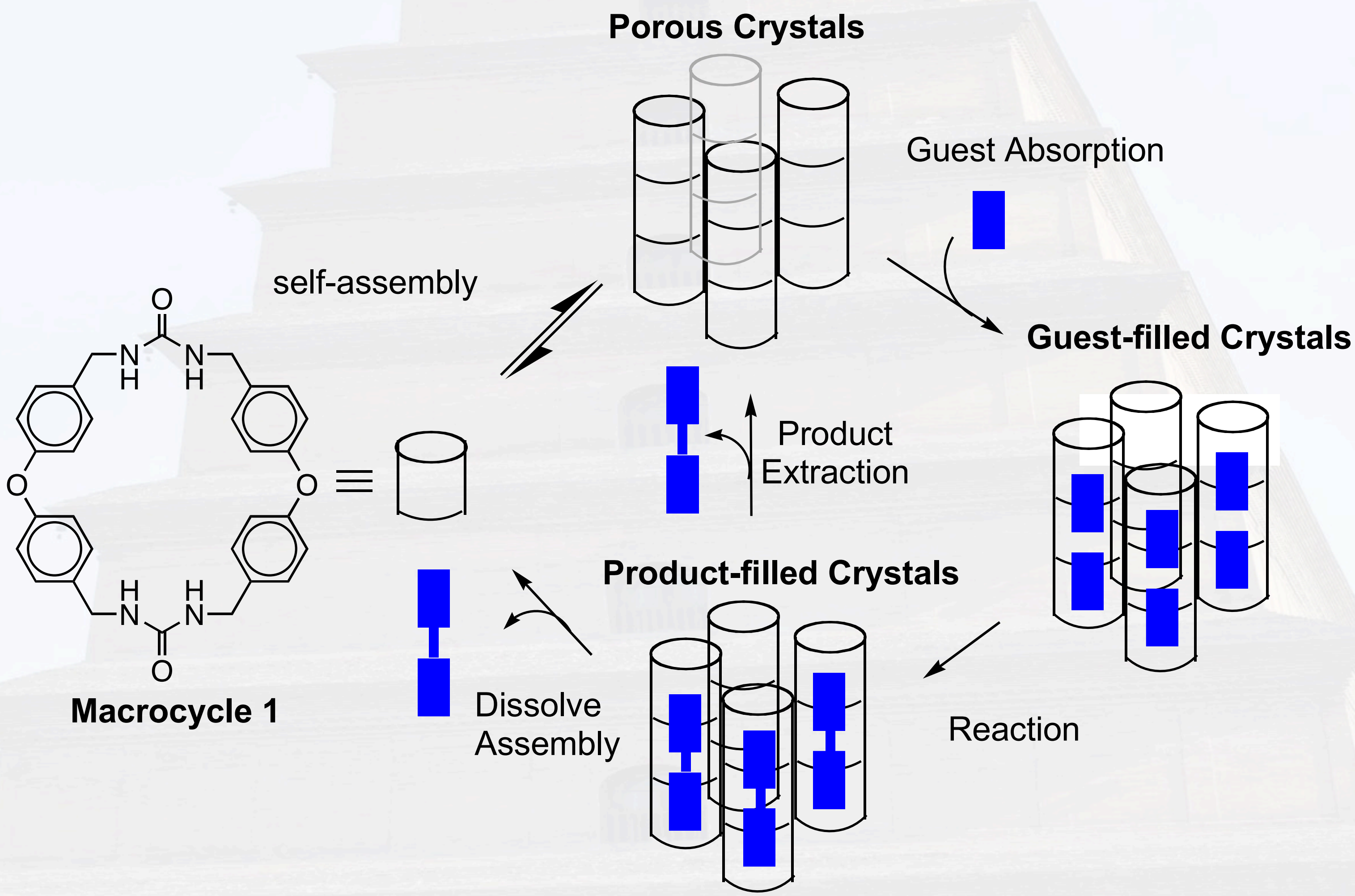




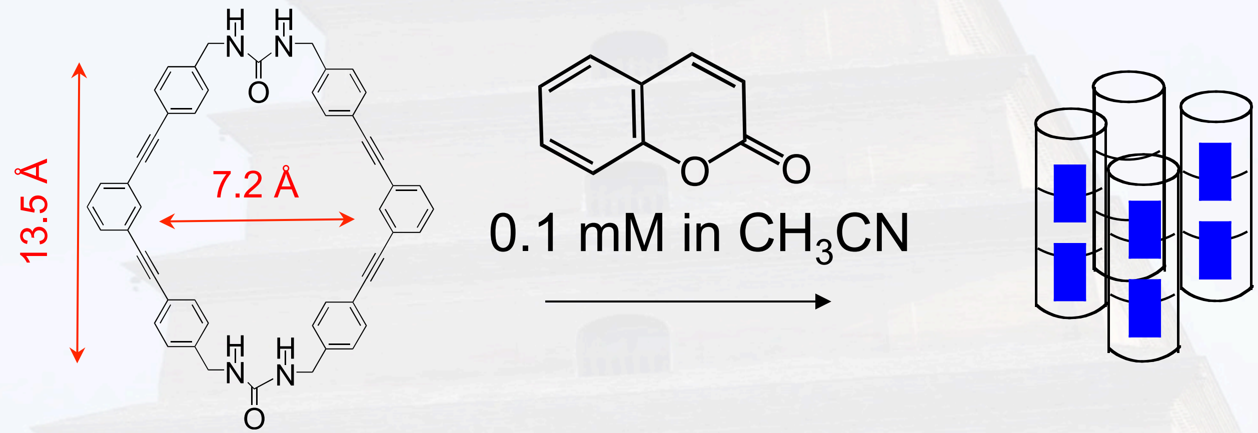


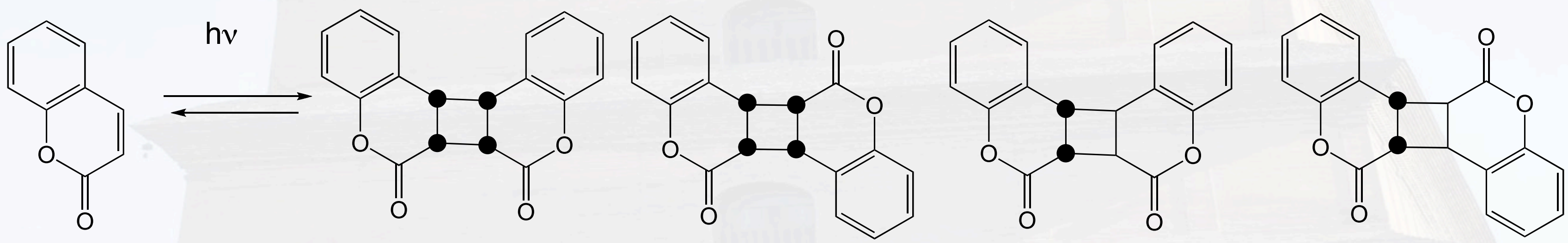
Substituents	Medium	Syn HH	Syn HT	Anti HH
$R_1 = R_2 = R_3 = H$	Water	60	40	-
	Pd-nanocage	>90	-	-
$R_1 = Me$, $R_2 = R_3 = H$	Water	15	-	85
	Pd-nanocage	>90	-	-
$R_2 = OMe$, $R_1 = R_3 = H$	Water		>90	-
	Pd-nanocage	>90	-	-
$R_3 = OMe$ $R_1 = R_2 = H$	Water	Not soluble		
	Pd-nanocage	>90	-	-

Channels as reaction vessels in the solid state



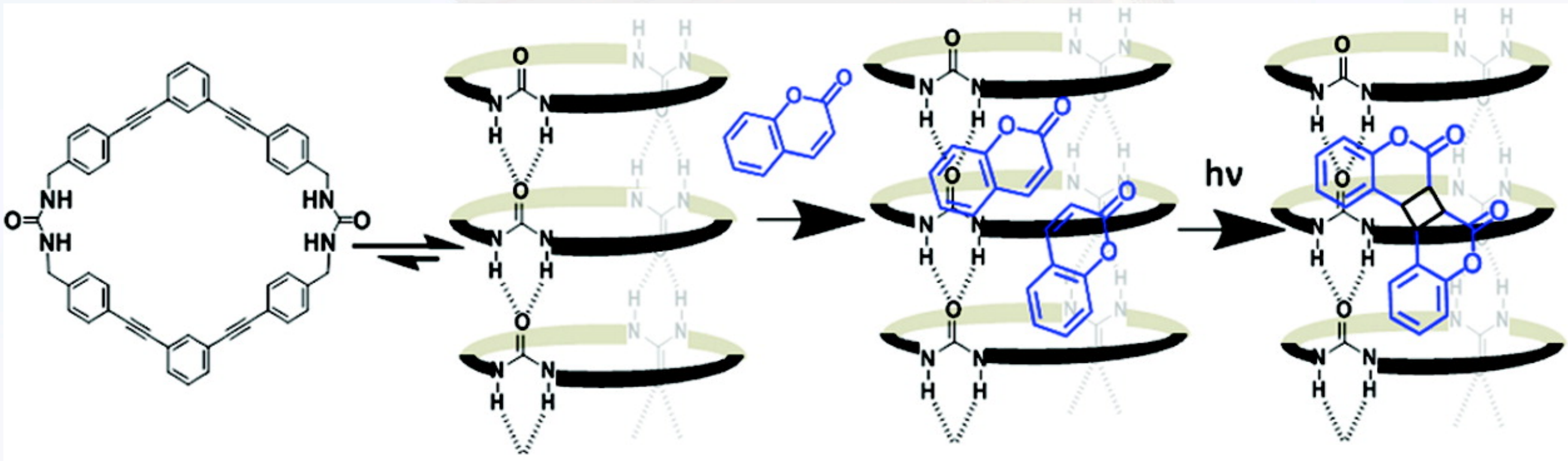
Back to photochemistry of coumarins





	***syn*-HH**	***syn*-HT**	***anti*-HH**	***anti*-HT**
$HOCH_2)_2$	59 %	19 %	22 %	-
solid	30 %	20 %	30 %	10 %
with host	< 1 %	-	**97 %**	< 1 %

Selective photodimerization of coumarin



anti-**HH** product fits well in host

syn-**HH** does not fit in channel.