

Chapter 13

Supramolecular Photochemistry

Controlling photocycloadditions through pre-organization and templation

Concept

Examples

1

2

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.

The Concept of Reaction Cavity and Free Space

Reaction cavity

Boundary

Guest

Free Space

Cohen and Schmidt

530

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Photochemistry in Organized and Confining Media: A Model

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Role of Weak Interactions

Cation- π

π - π

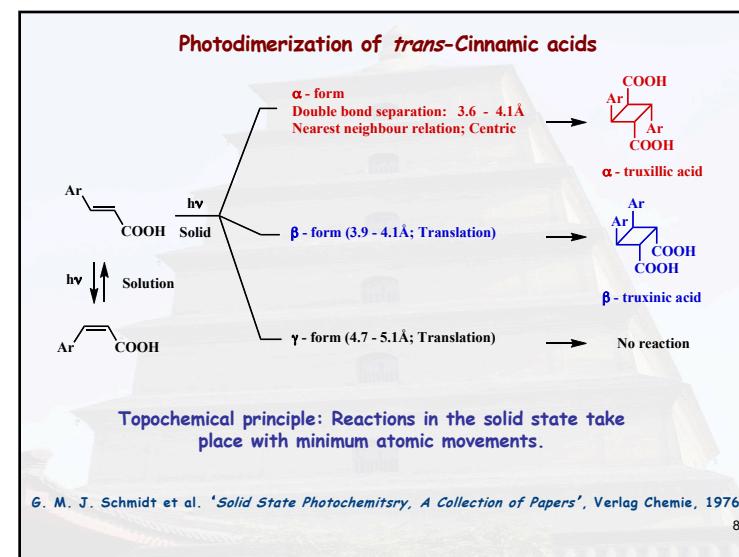
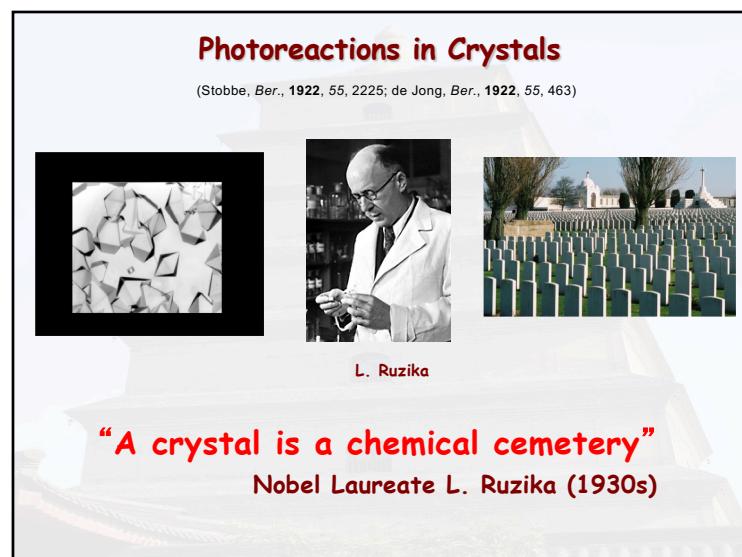
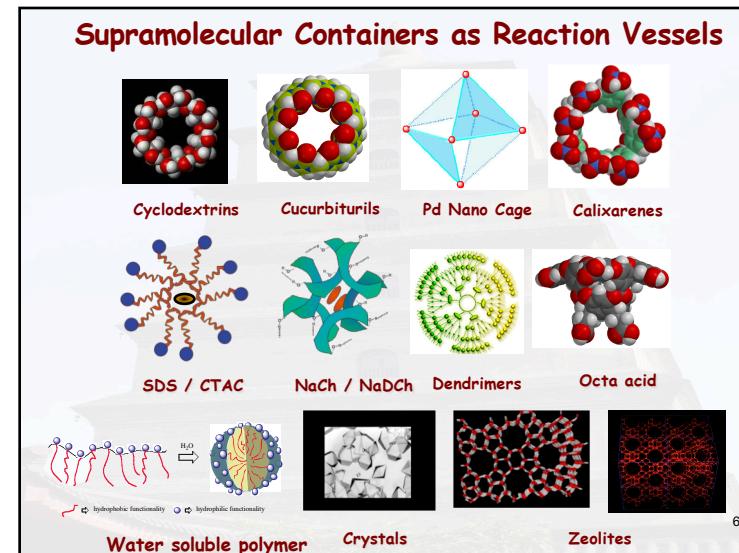
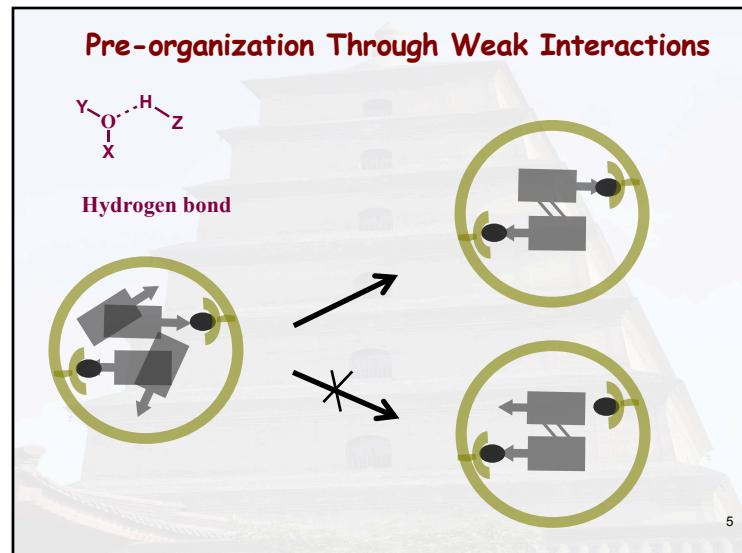
$C-H-\cdots\pi$

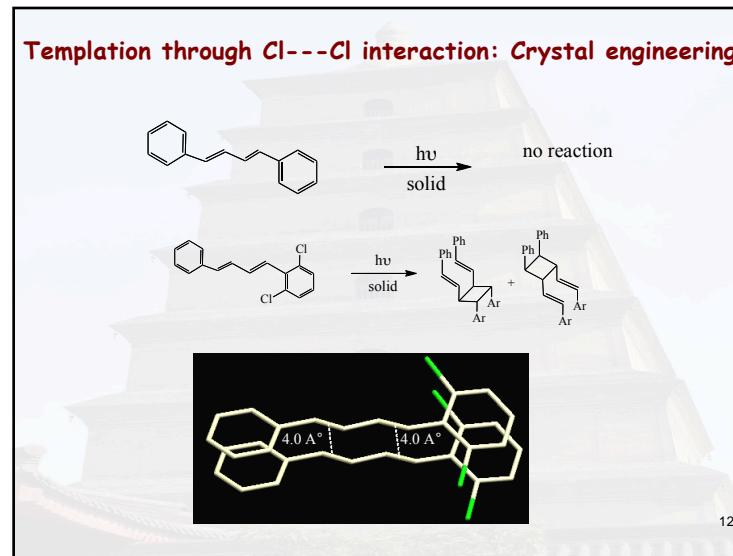
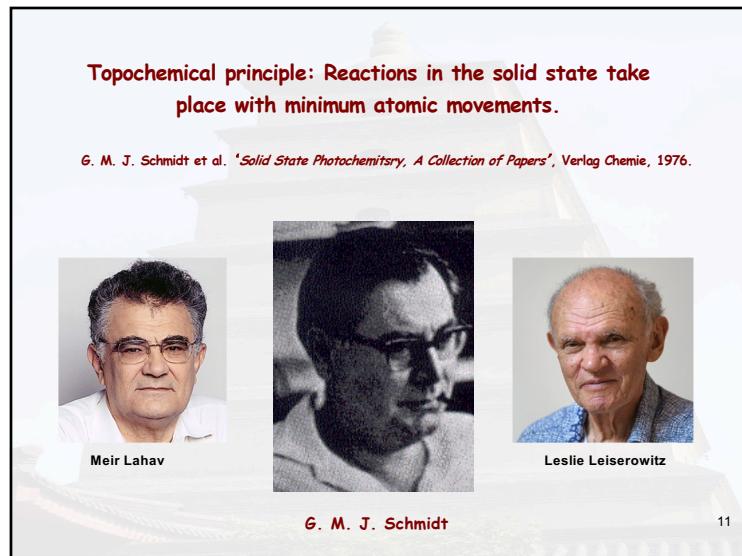
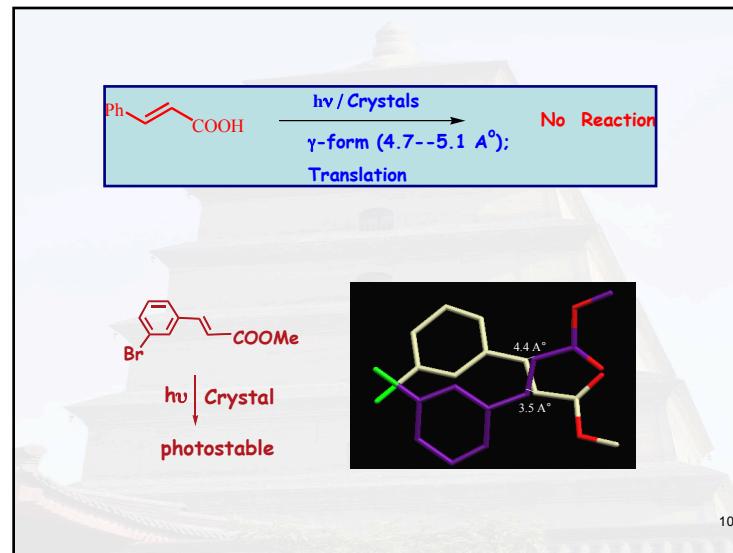
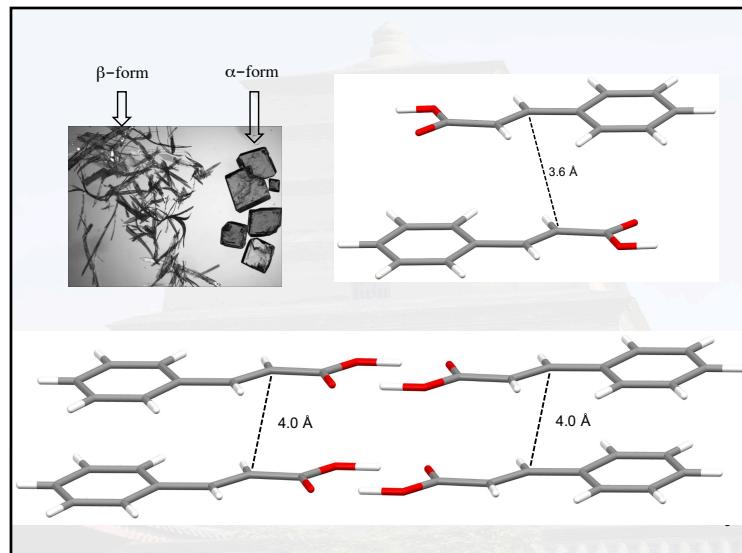
Hydrogen bond

van der Waals

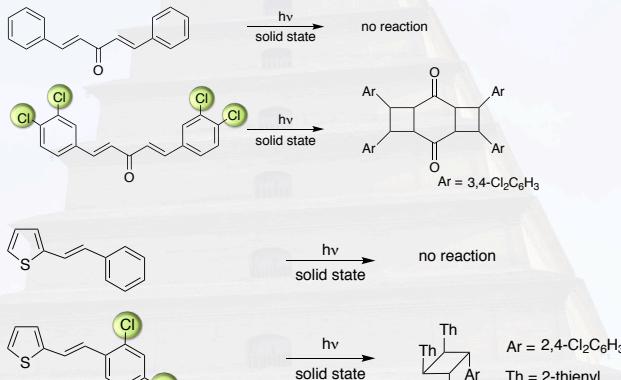
Charge transfer

4

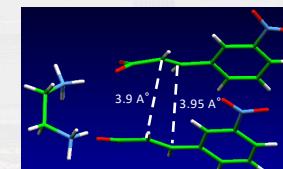
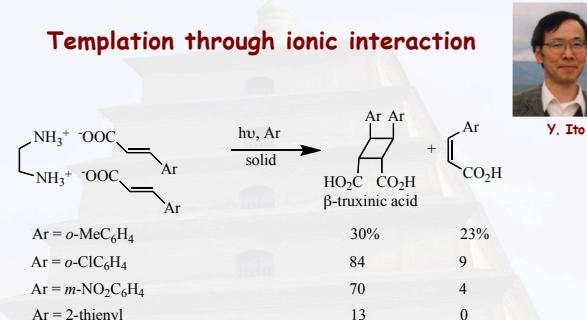




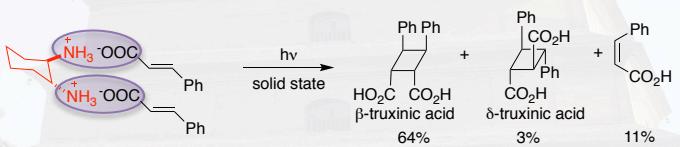
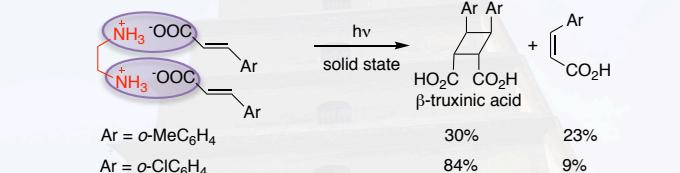
Temptation through Cl---Cl interaction



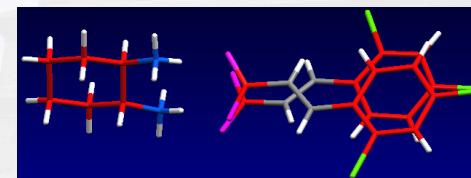
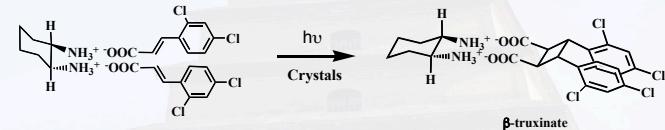
Temptation through ionic interaction

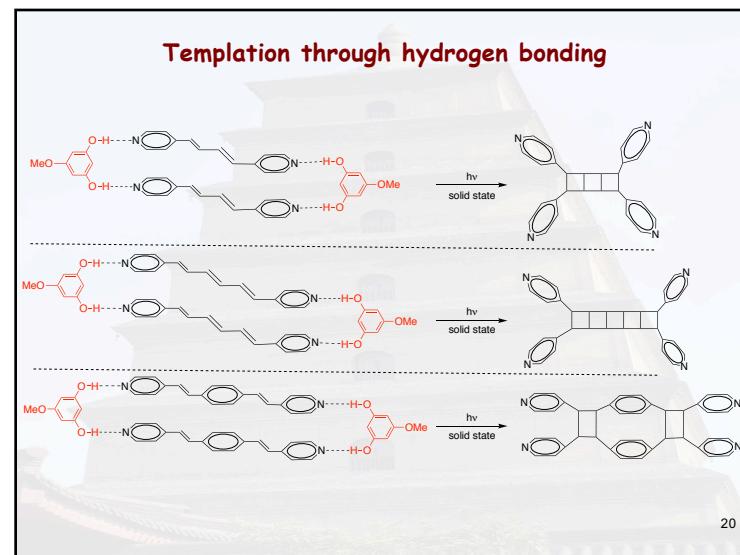
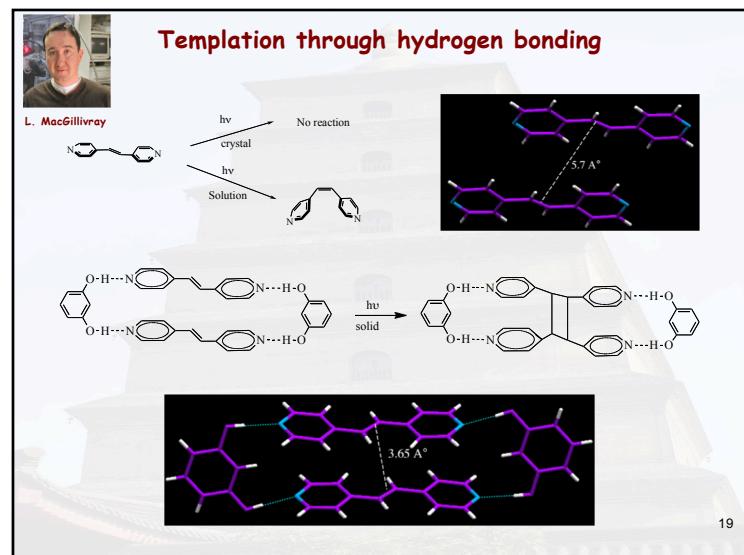
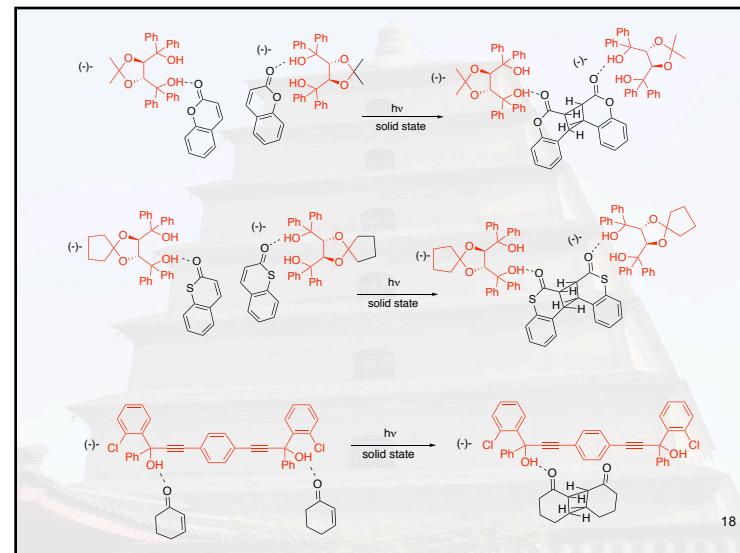
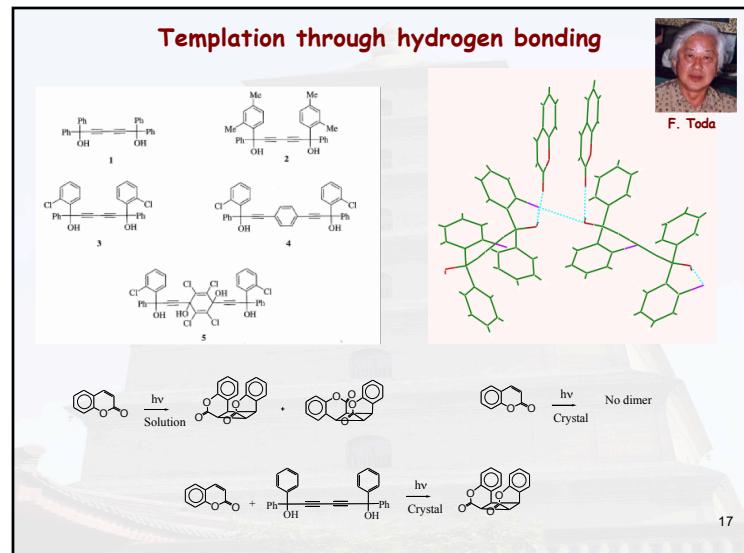


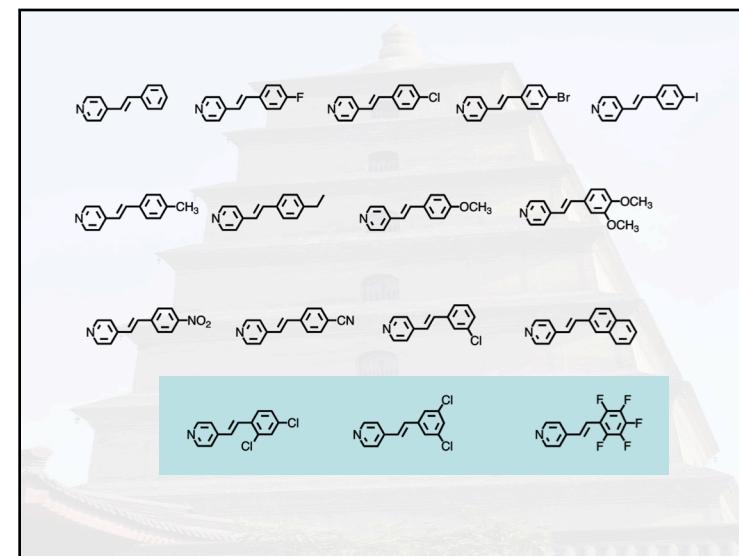
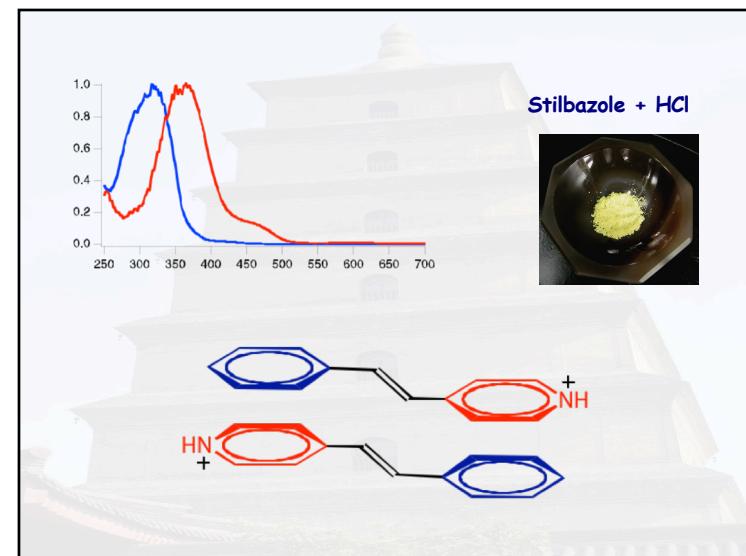
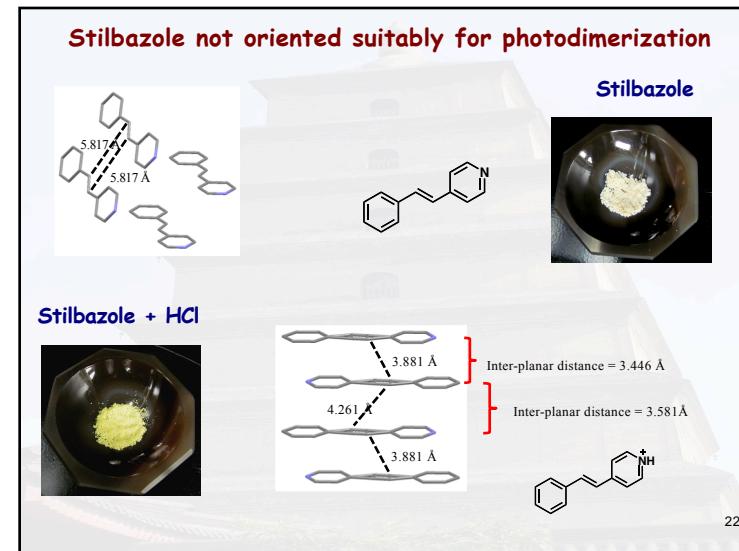
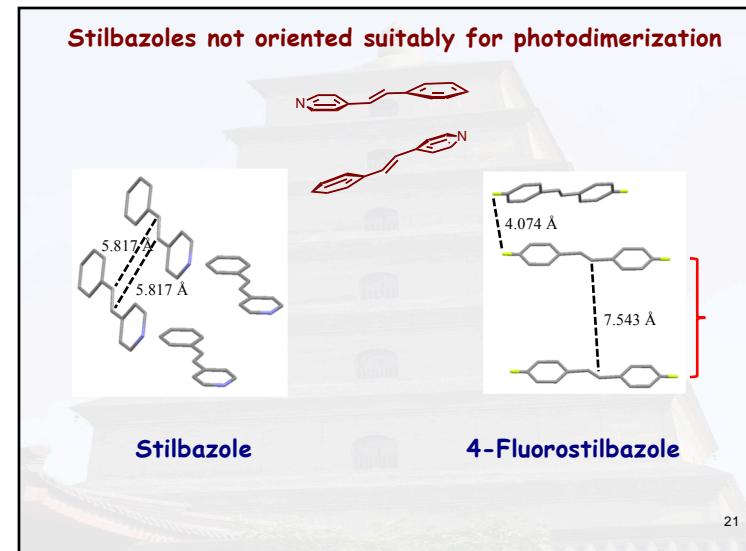
Temptation through ionic interaction

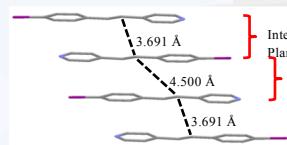


Temptation through ionic interaction

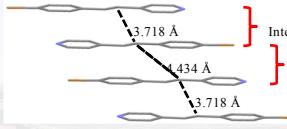
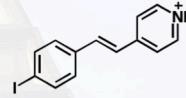




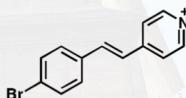
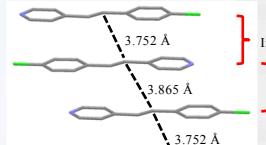


4-Halo Stilbazole.HCl Salt

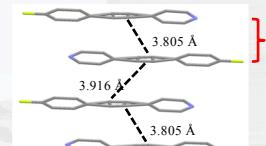
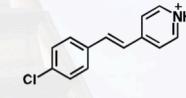
Inter-planar distance = 3.569 Å



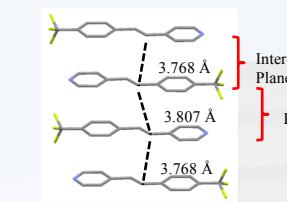
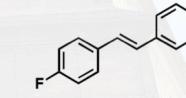
Inter-planar distance = 3.529 Å

**4-Halo Stilbazole.HCl Salt**

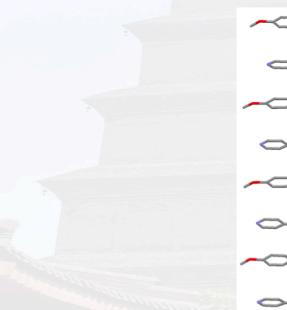
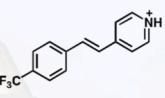
Inter-planar distance = 3.393 Å



Inter-planar distance = 3.425 Å



Inter-planar distance = 3.645 Å



Inter-planar distance = 3.819 Å



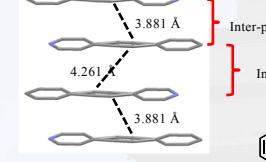
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Inter-planar distance = 3.739 Å

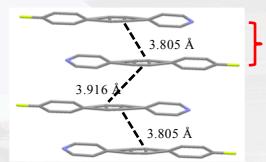
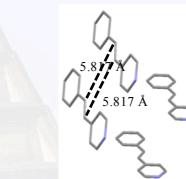
Inter-planar distance = 3.744 Å

Inter-planar distance = 3.726 Å

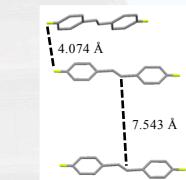
Inter-planar distance = 3.660 Å



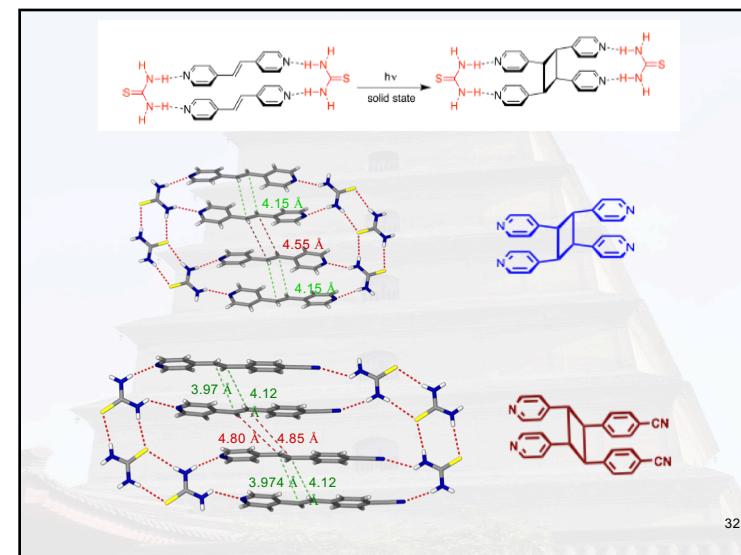
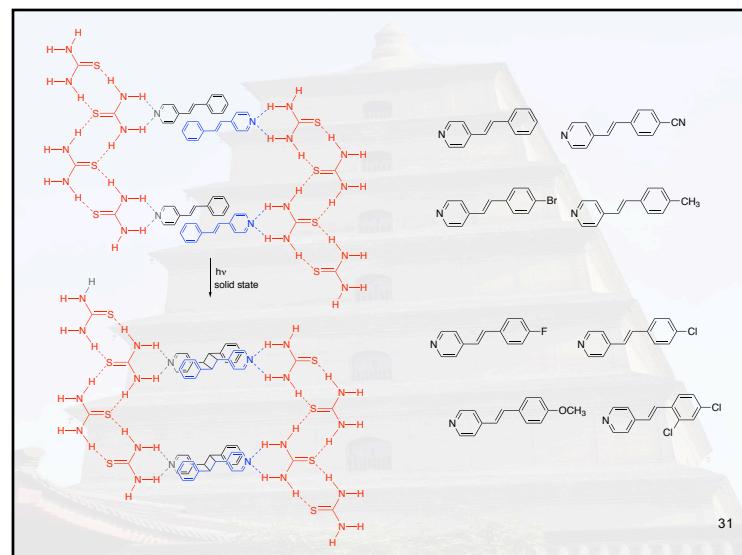
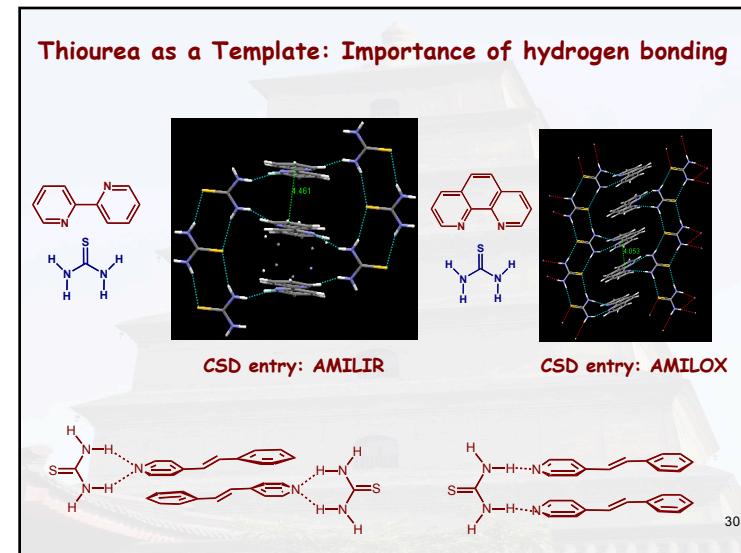
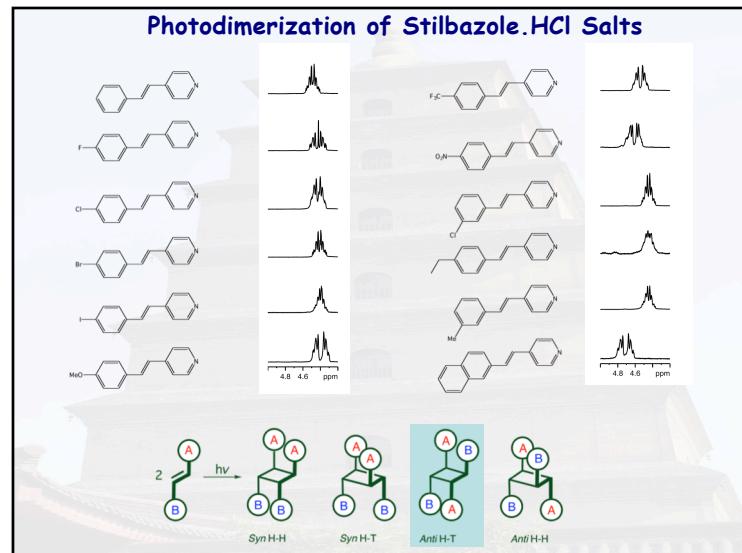
Inter-planar distance = 3.581 Å

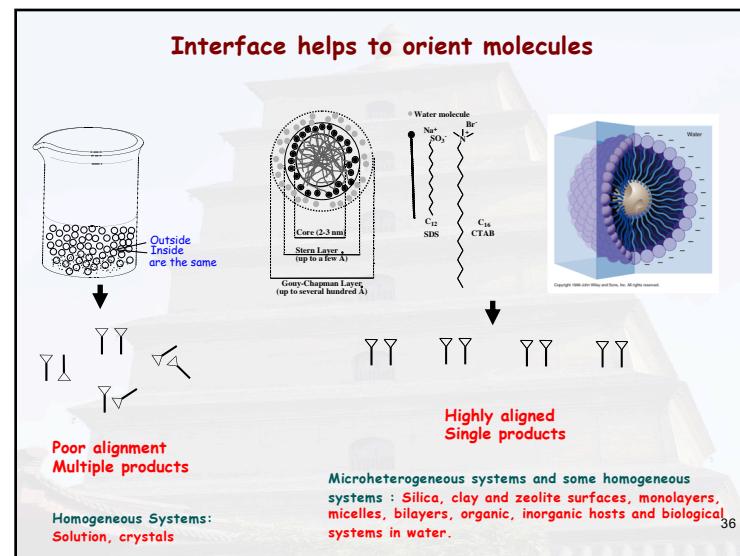
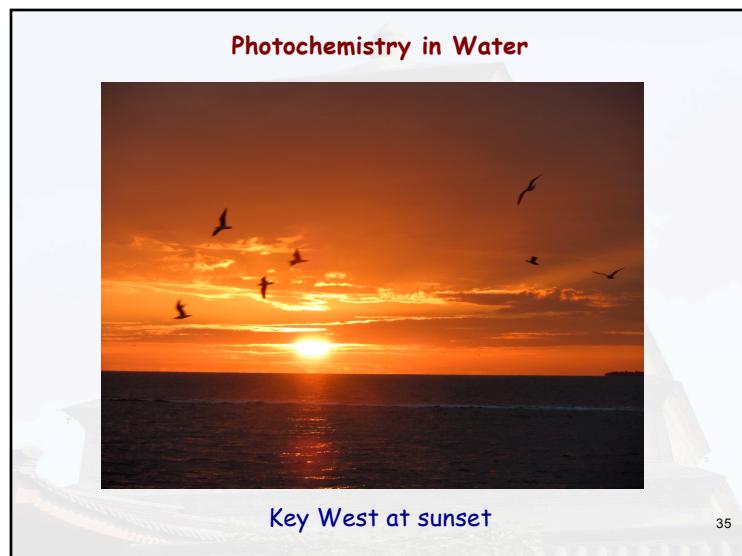
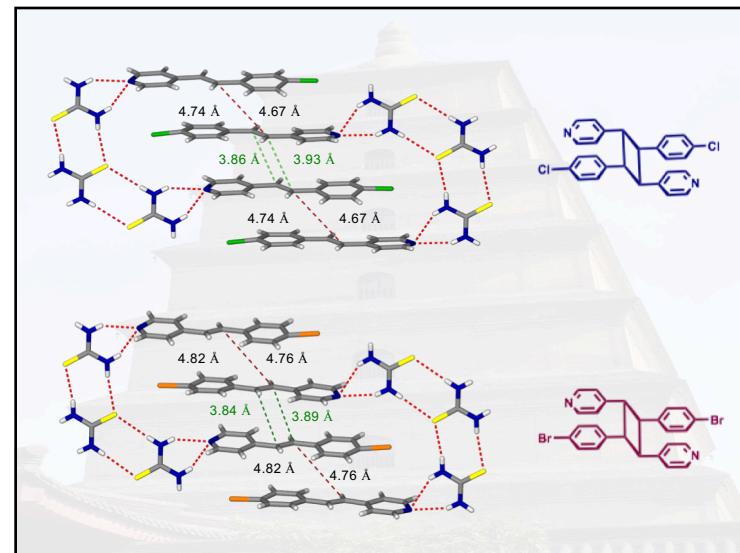
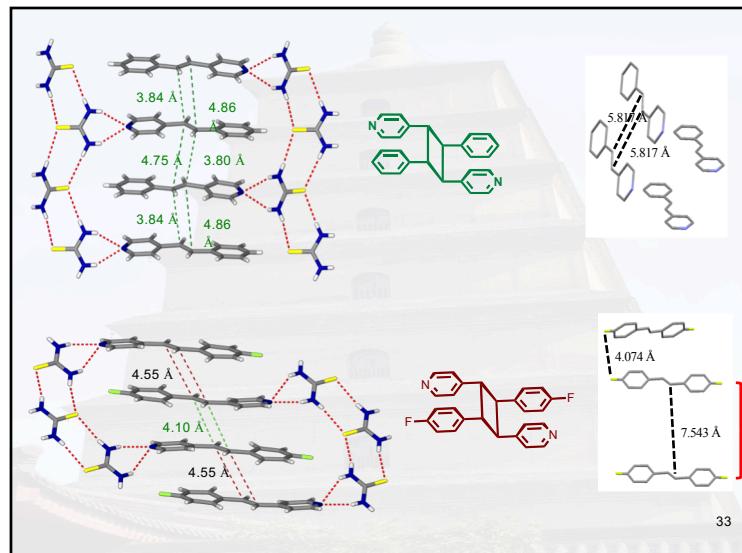


Inter-planar distance = 3.425 Å



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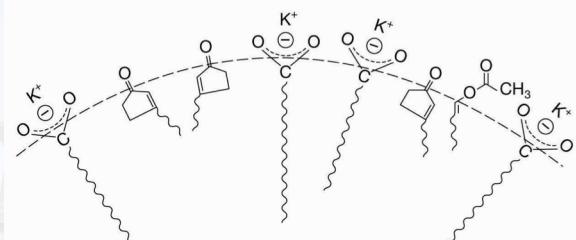




Temptation in water with the help of a micelle

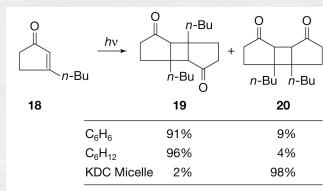
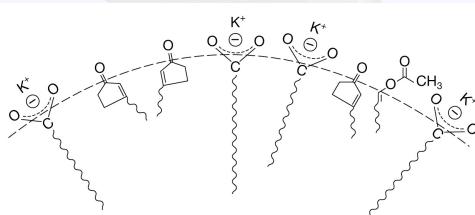


P. de Mayo

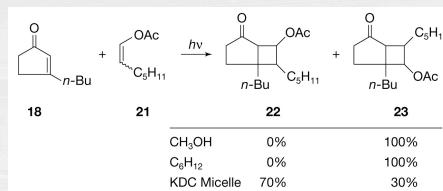
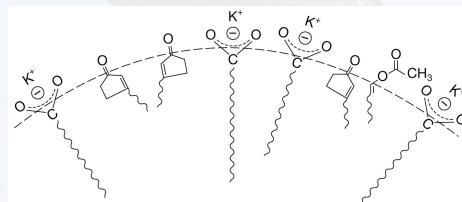


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Temptation in water with the help of an organized assembly



Temptation in water with the help of an organized assembly

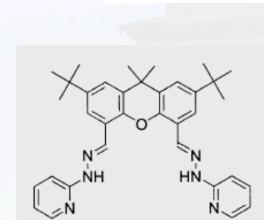
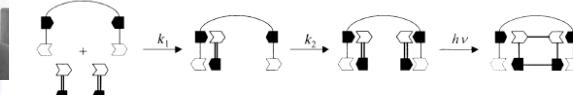


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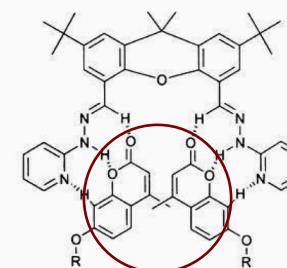


J. M. Lehn

Templation in solution through hydrogen bonding

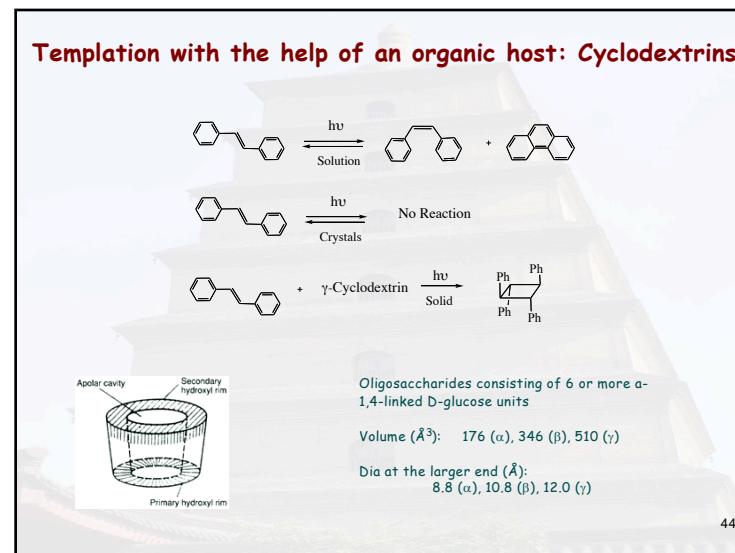
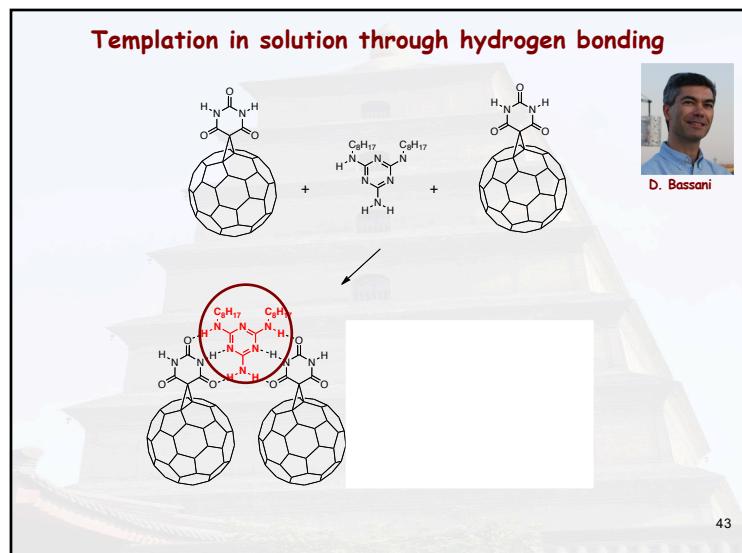
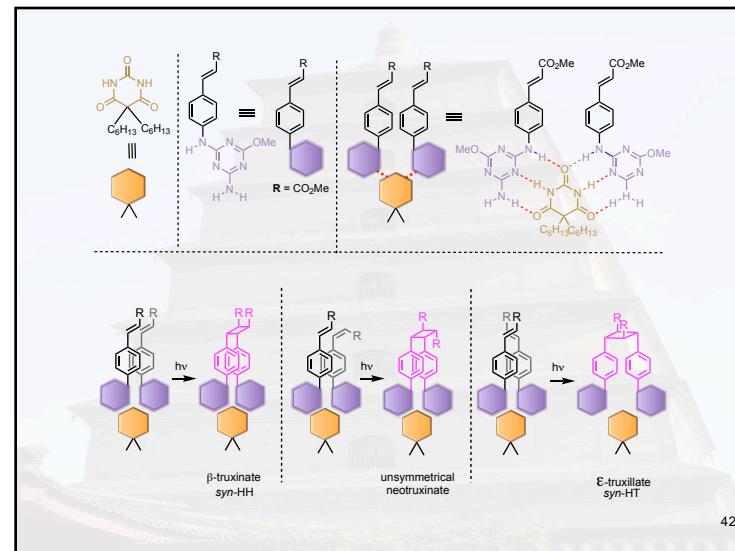
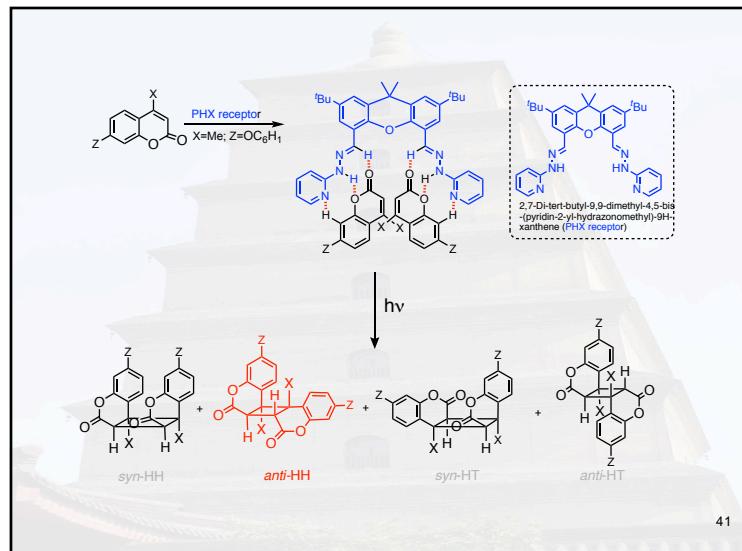


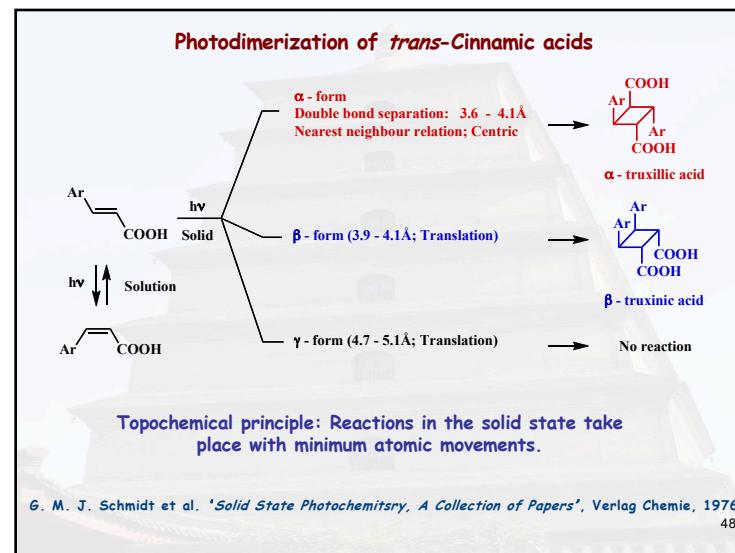
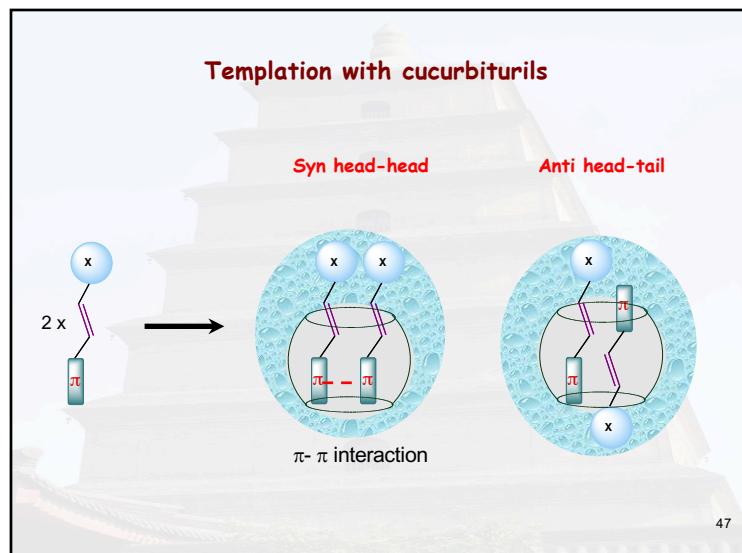
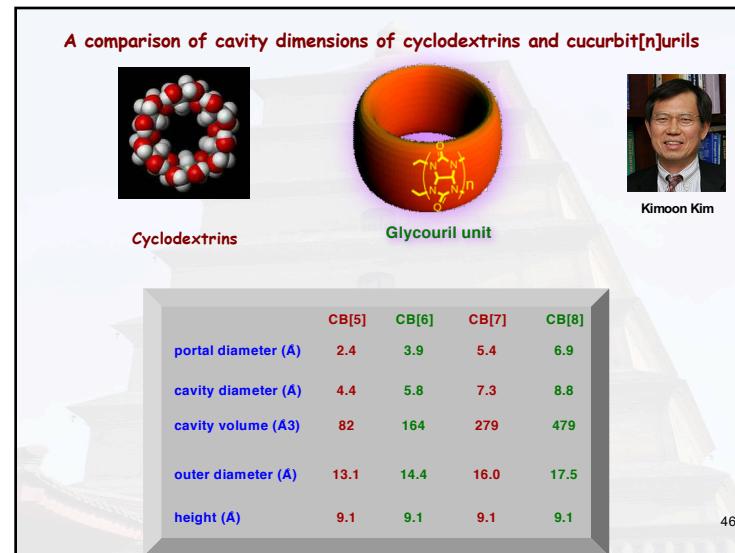
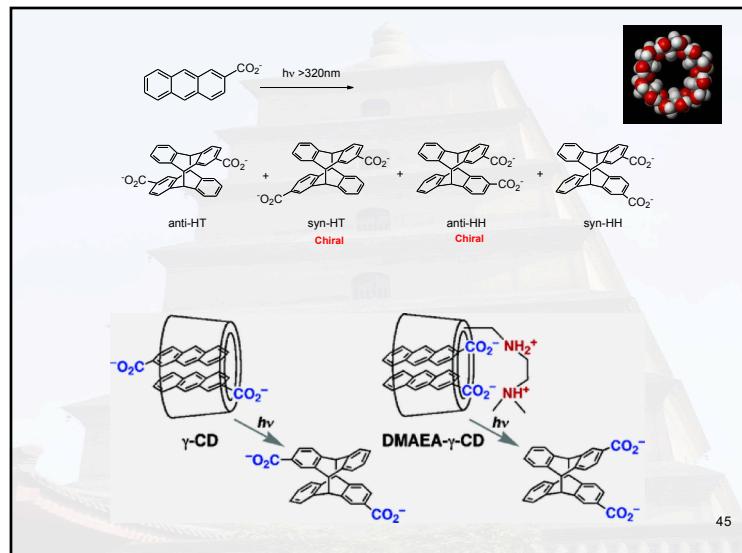
Host

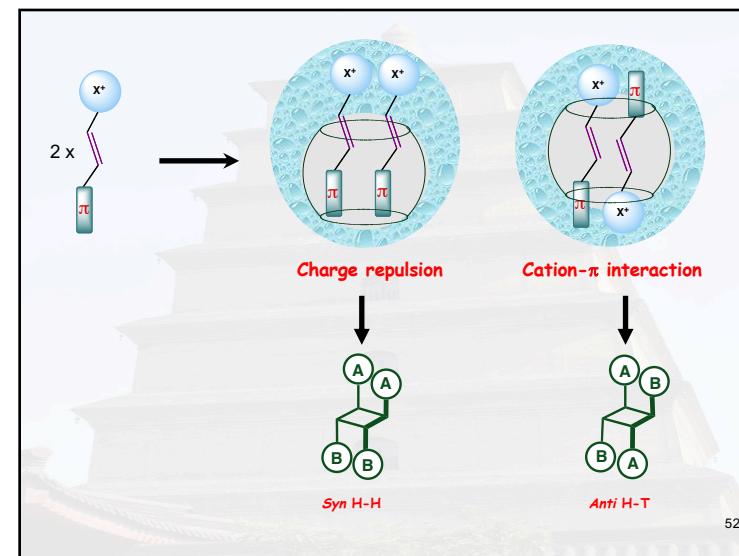
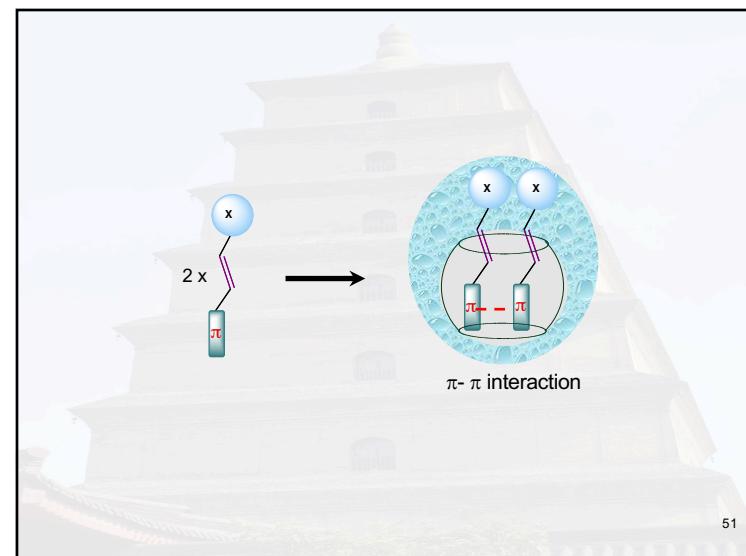
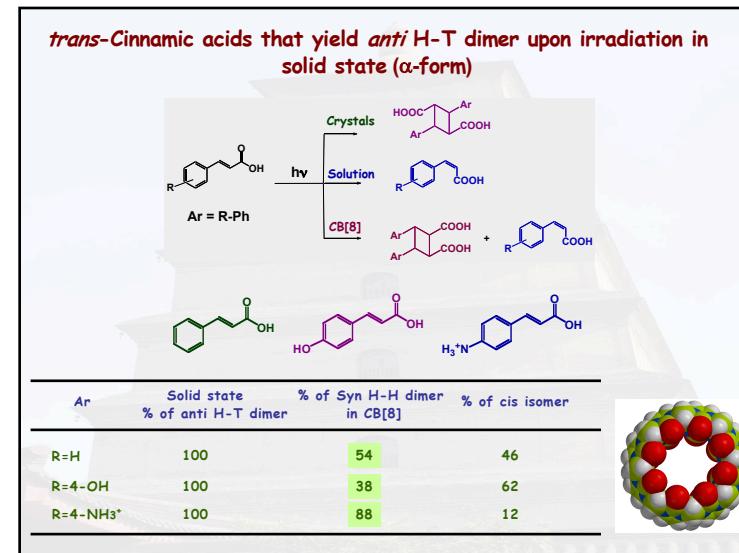
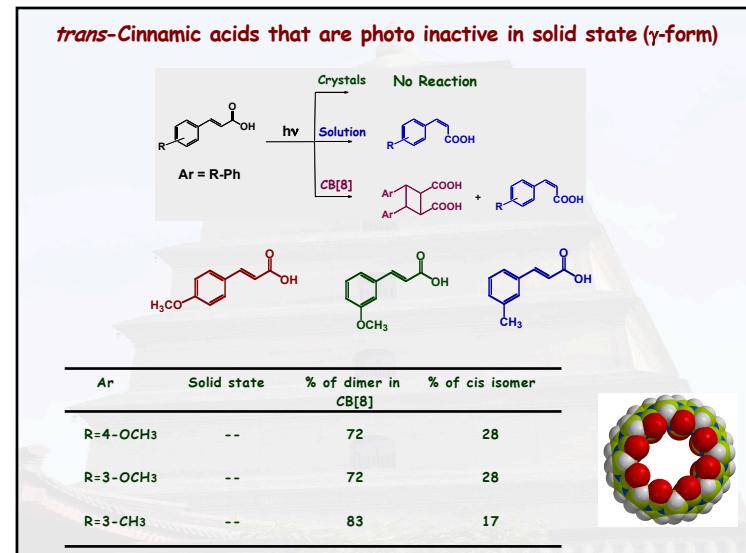


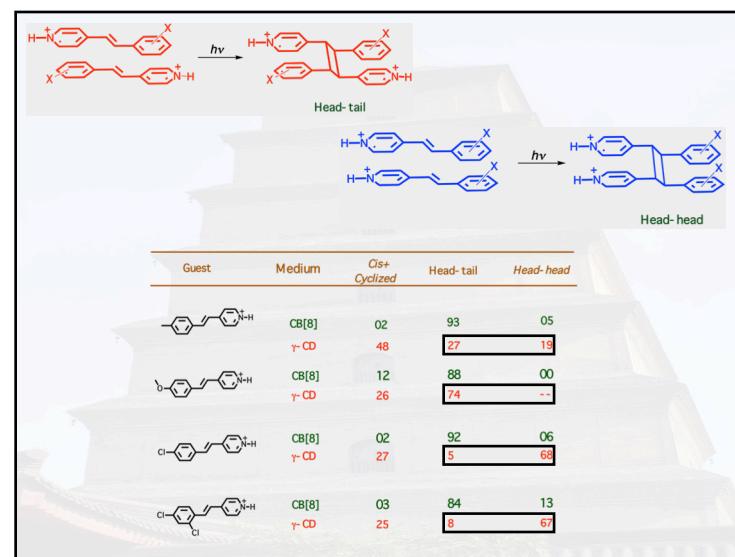
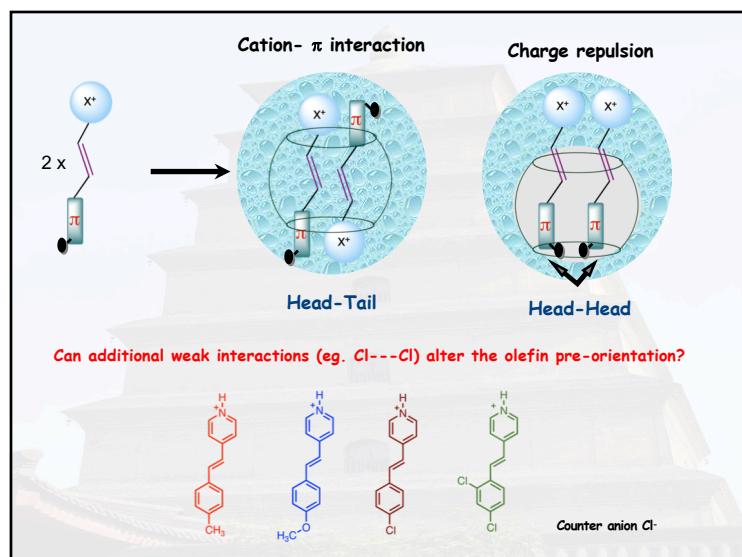
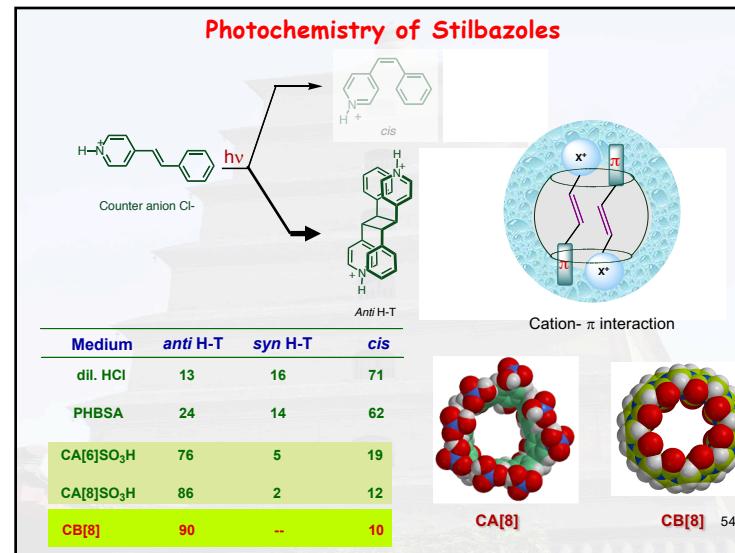
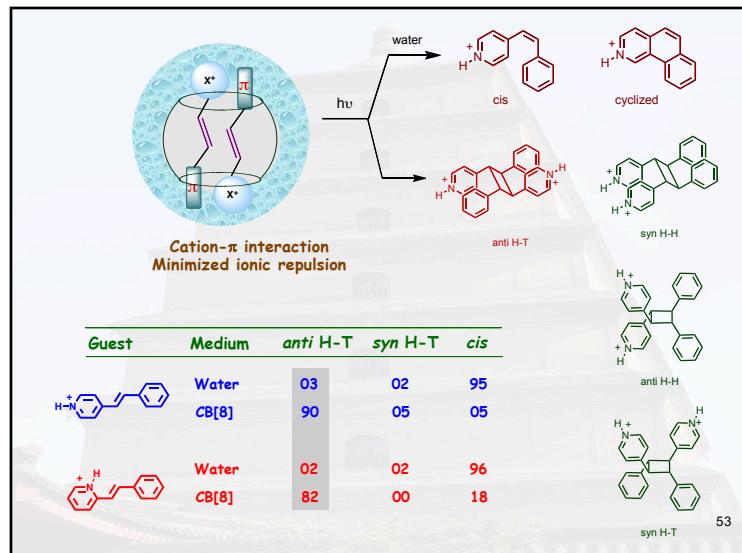
Guest templated by host

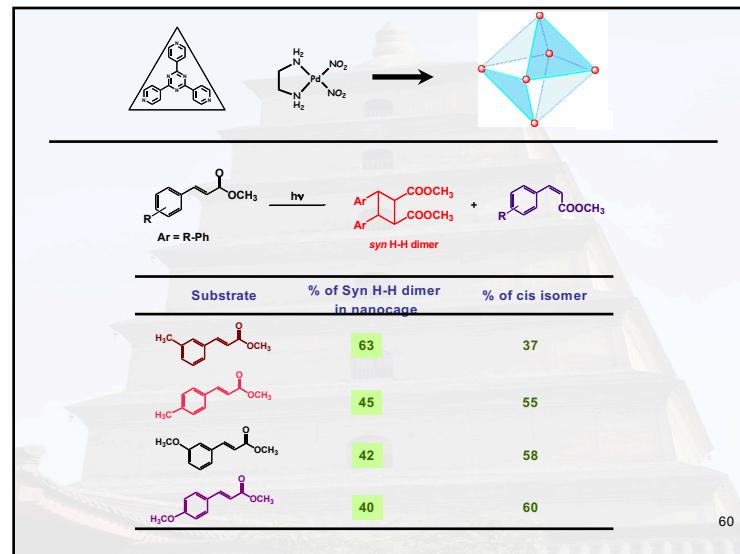
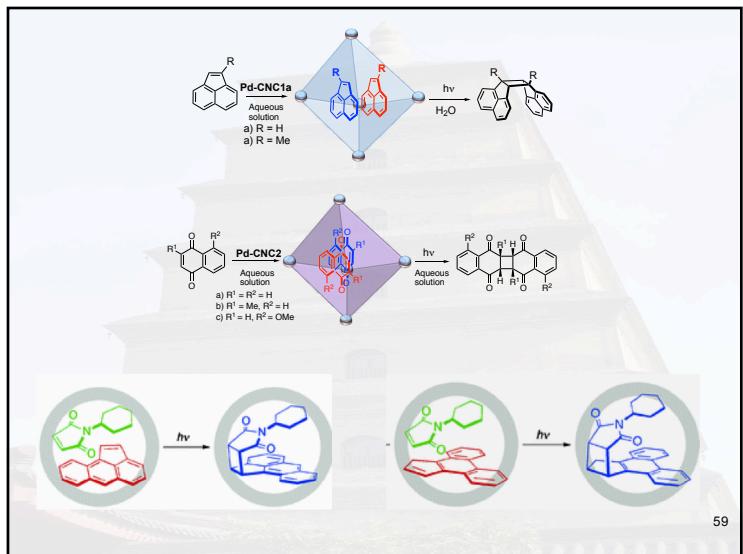
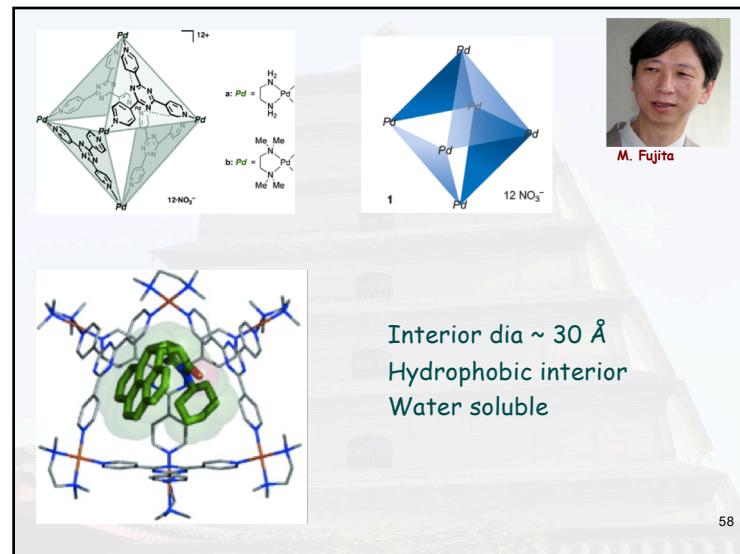
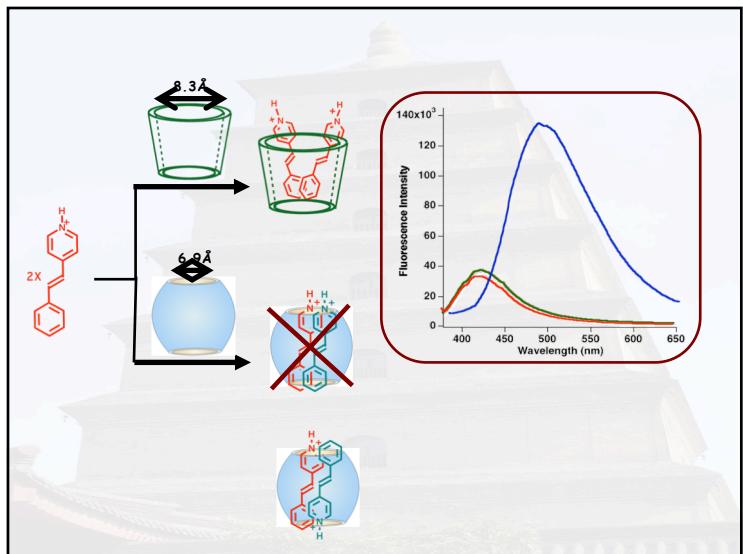
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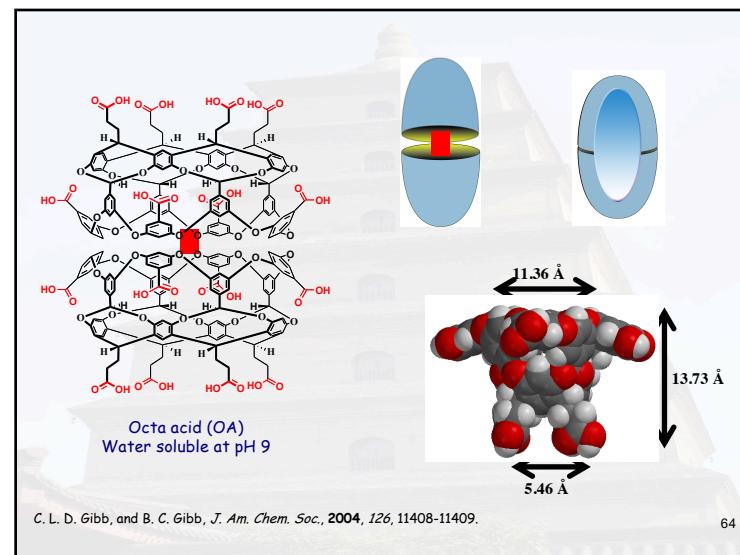
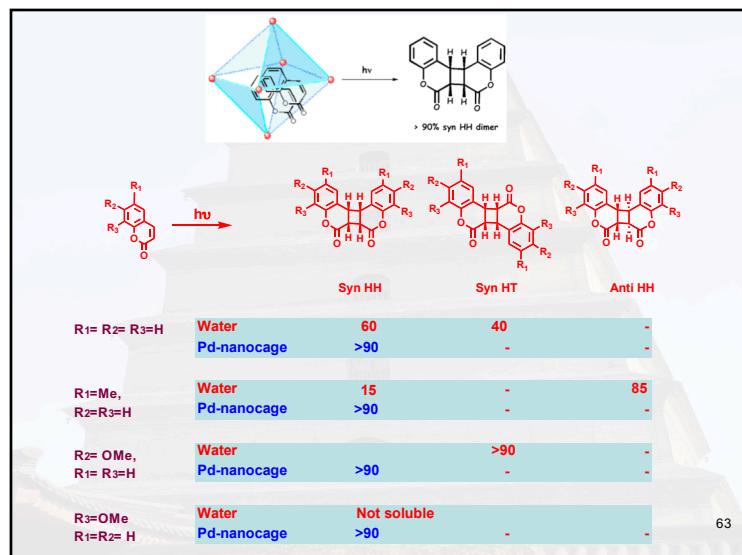
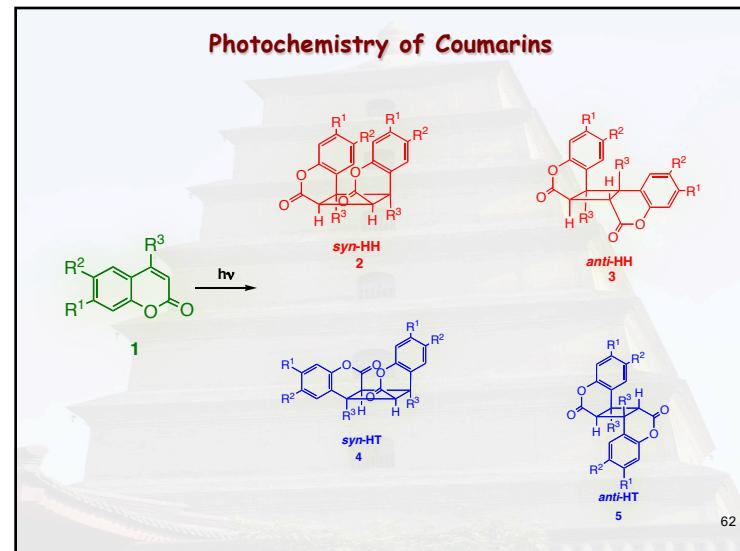
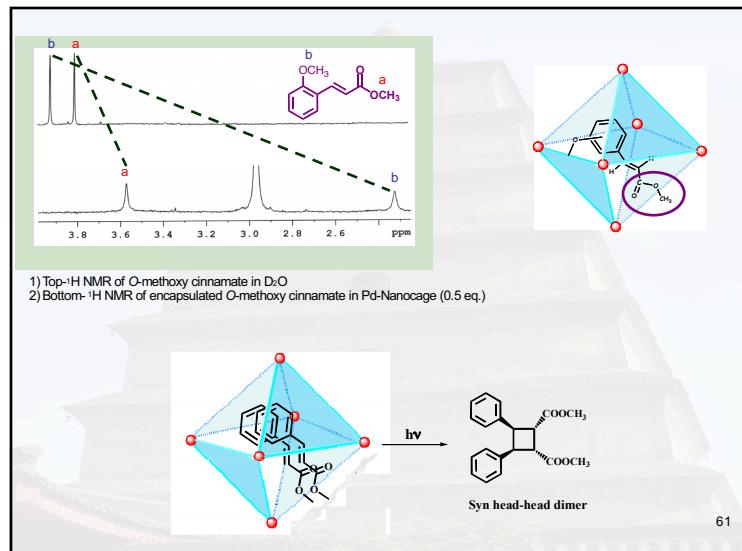


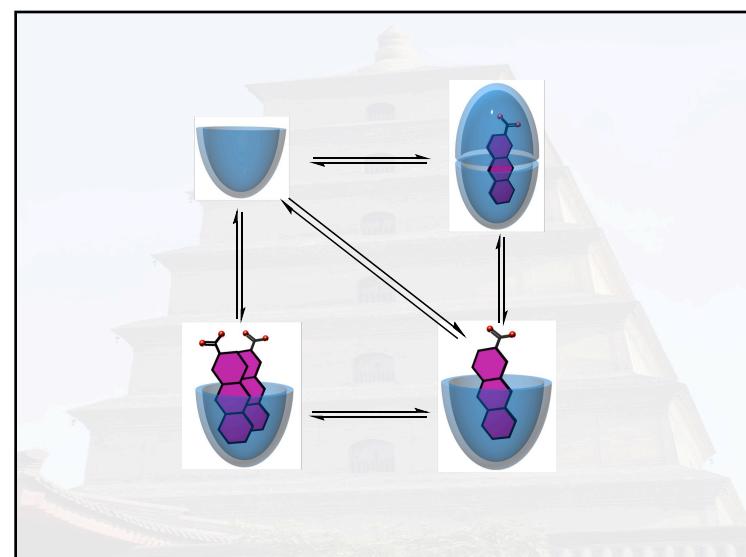
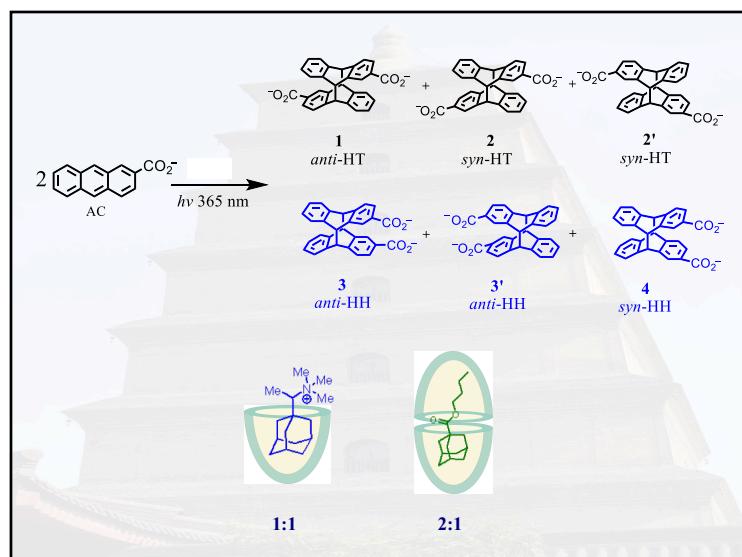
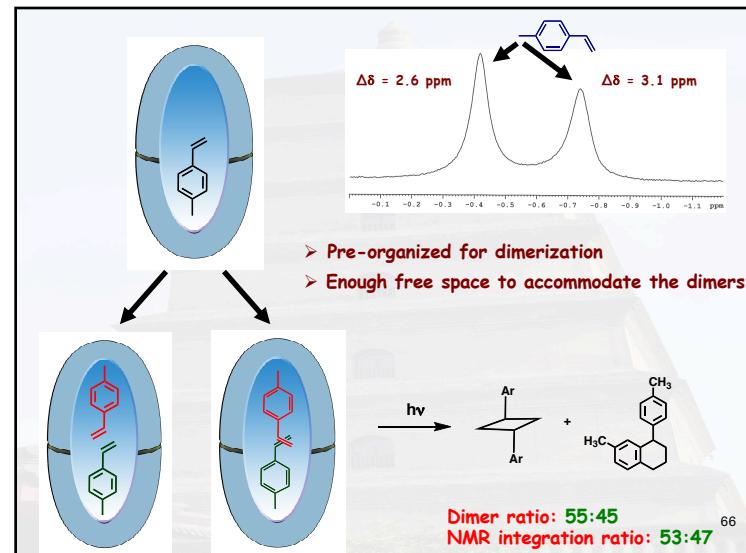
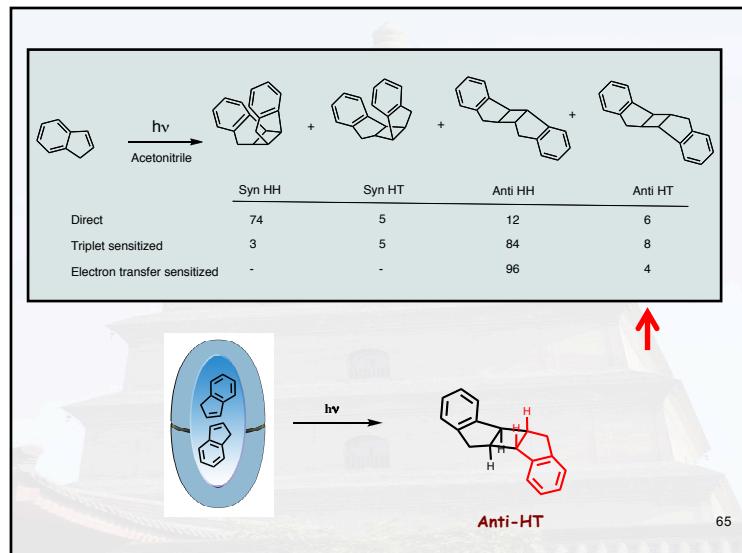


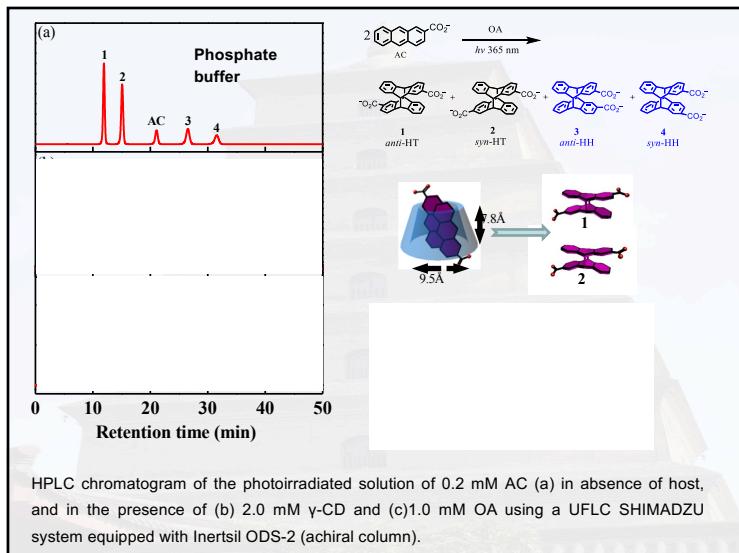












Photodimerization of 2-AC (0.2 mM)

host	host/guest ratio	CsCl/M	Relative yield (%)			
			1	2	3	4
None	0	0	42.0	36.0	13.8	8.2
γ -CD	10	0	42.9	44.7	7.3	5.2
OA	5	0	0	0	57.3	42.7
	2	0	0	0	57.8	42.1
	1	0	0	0	56.5	43.5
	0.5	0	0	0	56.4	43.6
	0.33	0	4.7	3.8	54.8	36.6
	0.25	0	8.7	7.4	47.5	36.4
	0.2	0	19.4	17.2	38.3	25.1
	5	6	0	0	44.8	55.2
	2	6	0	0	43.0	57.0
	1	6	0	0	40.0	60.0
	0.5	6	0	0	34.8	65.2
	0.2	6	0	0	29.3	70.7

