Photochemistry in Confined Spaces





Medium is the Message

Medium Matters (UI) Solution Gas phase (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?

Container Chemistry

- Objective: To carry out product <u>selective</u> 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 selectivity

Supramolecular Containers





NaCh / NaDCh



Dendrimers





 \checkmark hydrophobic functionality \bigcirc \Rightarrow hydrophilic functionality

Water soluble polymer



Calixarenes



Cyclodextrins



Cucurbiturils



Pd nano cage



Octa acid



Zeolites



Crystals

The Medium is the Message

Understanding Media: The extensions of man Marshall McLuhan, 1962.













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SDS / CTAC



Crystals



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Zeolites



Octa acid

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.

Photoreactions in Crystals







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.



Pre-organization with a guest: Non reactive molecule made to react









MacGillivray et. al., JACS, 2000, 122, 7817.

Single Template Does Not Work for Several Olefins



Reactive Olefins



Templates

Thiourea as a Template: Importance of hydrogen bonding









CSD entry: AMILIR

CSD entry: AMILOX

























An overview of photochemistry of stilbazoles in thiourea co-crystals



Stilbazole not oriented suitably for photodimerization







Stilbazole + HCl











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

Type of CD C	avity Diam	eter Å			
a-CD	4.7–5.3	_	α-D-glu	copyranoside	e unit
β-CD	6.0–6.5	_			
γ-CD	7.5–8.3				
	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	



Cyclodextrins



Glycouril unit

Templation with cucurbiturils

Syn head-head





trans-Cinnamic acids that are photo inactive in solid state (y-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







Interior dia ~ 30 Å Hydrophobic interior Water soluble







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





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









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



Encapsulation of aromatics within octa acid







Manipulating photophysics and photochemistry through confinement



Photochemistry within a water-soluble organic capsule, V. Ramamurthy, *Acc. Chem. Res.*, 48, 2904, **2015**.

Room Temperature Phosphorescence



Diffusion controlled self-quenching and oxygen-quenching in solution

Prevention of self quenching with the help of containers







	$\tau^{o}_{T}(\mu s)^{a}$	ΟΑ		
Guests		H:G ^c	$ au_{\mathrm{T}}(\mu s)^{\mathrm{b}}$	k_{q,O_2} (M ⁻¹ s ⁻¹)
Fenchthione	154	2:2	187	(1.6±0.4)×10 ⁶
Camphorthione	46.3	2:2	65	(2.4±0.1)×10 ⁷
Adamantanethione	43.3	2:2	17.2	(2.8±0.1)×10 ⁷

a: exptraolated to infinite dilution in perflurodimethylcyclohexane b: at 10^{-5} M of thione and 10^{-5} M of OA

Asymmetric Photoreactions Within Chirally Modified Zeolites



Stilbene derivatives form 1:2 complex with OA Host



¹H NMR titration and integration suggest dimethyl stilbene forms a 1:2 complex with the host

Fluorescence enhanced and lifetime lengthened within OA capsule



C-H--- π Interaction Controls the Isomerization within OA

$H_{3}C$ $\downarrow hv$ $S_{1} \text{ or } T_{1}$		
H ₃ C CH ₃	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 Unsubstituted Phenyl group

$H_{3}C$ hv $S_{1} \text{ or } T_{1}$ $H_{3}C$	Solution CDCl ₃ / Hexane	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	

Location of methyl groups on the aryl ring makes a difference

$H_{3}C$			
Chemical shift δ of CH ₃ within Octa acid	- 2.3 ppm	- 1.6 ppm	0.8 ppm
Pseudo-photostationary state –Singlet (Cis: Trans)	20:80	85:15	85:15

The same photo-stationary states were also obtained starting from corresponding *cis* isomers in octa acid

Enhancement of fluorescence intensity of a GFP chromophore by encapsulation within OA









GFP, Roger Tsien



Torsional Rotation vs Pyramidalization







Azobenzenes form Complexes Similar to Stilbenes with OA





Photoisomerization of 4-MAB@OA₂ by UV-Vis:



Photoisomerization of 4,4'-DMAB@OA₂ by UV-Vis:





Torsional Rotation vs Pyramidalization







Zeolites

$M_x(AIO_2)_x$ (SiO₂)_y.ZH₂O



Entrance dia 7.4 Å Cage dia. 11.8 Å



Presence of exchangeable cations and well-defined confined space

Chiral inductor approach





Chiral induction: Solution vs. Zeolite







Chiral induction: Solution vs. Zeolite









Chiral induction within a modified zeolite



Cation Dependent Diastereomer Switch



Asymmetric Photoreactions Within Zeolites

Cation is the Key



- Chiral Induction Depends on
 - Nature of the Cation
 - Number of Cations (Si/Al ratio)
 - Water Content

Cation Effect Heavy Cations Enhance k_{isc} and k_p





Ability of zeolite supercage to induce spinorbit coupling depends on the cation

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

Room temperature phosphorescence of naphthalene included in MY zeolites



Room Temperature Phosphorescence from Diphenylpolyenes





Generation of Stable Organic Radical Cations at Room Temperature Within ZSM-5 Zeolites



Figure 2. Room temperature ESR spectra of the cation radicals of trans-stilbene, trans-stilbene-d₁₂ DPB, and DPOT included in Na-ZSM-5.

Absorption Spectra of Radical Cations



T. Shida, Electronic Spectra of Radical Ions, 1988

Absorption and Emission Spectra of Radical Cations



Generation of Stable Polythiophene Radical Cations at Room Temperature



Generation of Conducting Polymers

Heating TT with time











Table I.	Electronic	Absorption	Band Positions	for Oligomeric
Thiopher	les $(2 \leq n)$	≤ 9) Include	ed in Na-ZSM-	5°

oligomer chain length	$\hbar \omega_8$ (neutral)	2ħω ₀ (polaron)	ħω3 (bipolaron)	ħω ₁ (bipolaron)
2	300	407		
3	354	522		833
4	390	614	636	1046
6	434	775	600	1019
8			661	1383
9			761	1450



Importance of confined and well defined reaction space

> Role of weak interactions within a reaction cavity

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Supramolecular Photochemistry in Solution and on Surfaces: Encapsulation and Dynamics of Guest Molecules, and Communication Between Encapsulated and Free Molecules V. Ramamurthy, S. Jockusch and M. Porel, *Langmuir*, **2015**, *31*, 5554-5570 (Feature review article)

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Supramolecular Photochemistry Concepts Highlighted with Select Examples V. Ramamurthy and B. Mondal *J. Photochem. Photobiol. C: Photochem. Rev.*, **2015**, *23*, 68-102

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