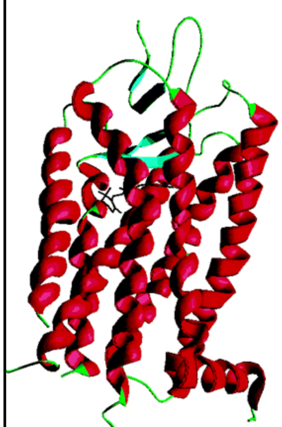
Medium Matters
Dynamics of Excited Molecules in Confined Spaces



Medium Matters

- Solubilizes the substrates in water
- Organizes the substrates through weak interactions
- Restricts the freedom by confining the substrate

How can we achieve such a high level of selectivity in <u>photo</u>chemical reactions in a laboratory?

Container Chemistry

Confinement and pre-organization exploited

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

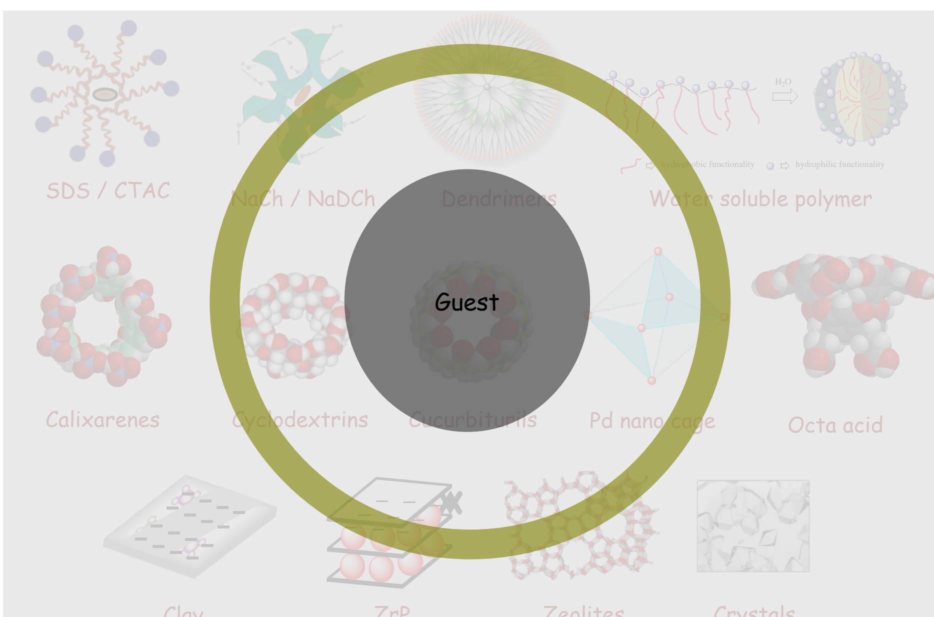
(most organic compounds are liquid)

Solution: Use water soluble hosts to solubilize organic molecules

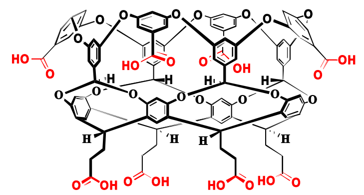
(use solid hosts to adsorb liquids)

Use confining hosts to achieve selectivity

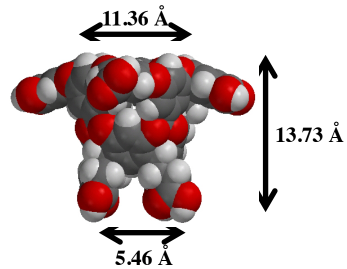
Photochemistry in a Container

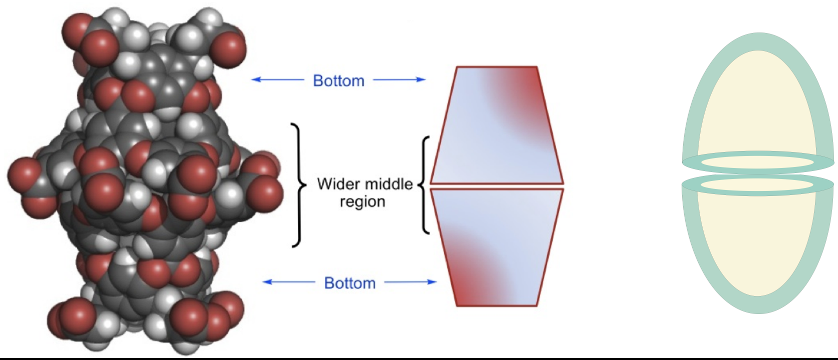


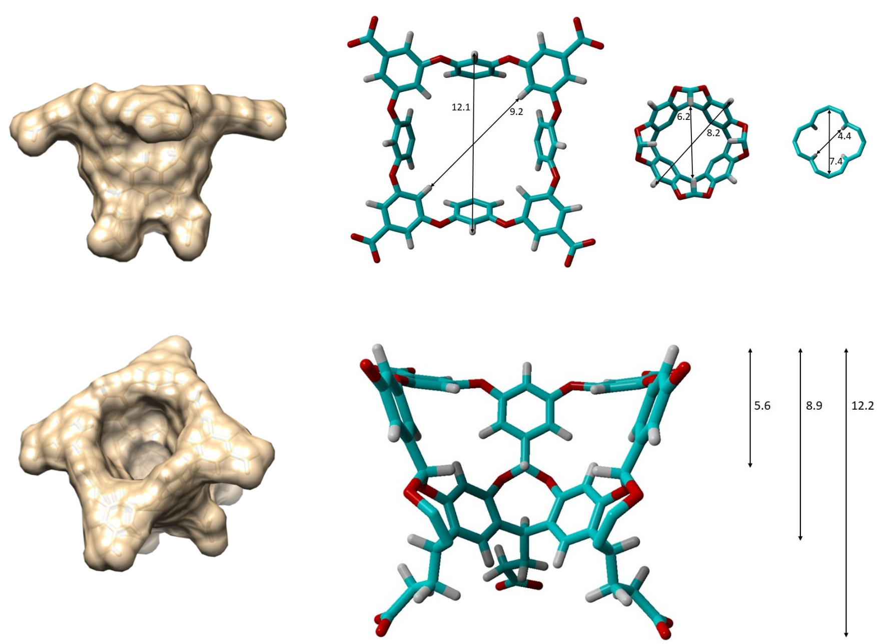
The host octa acid



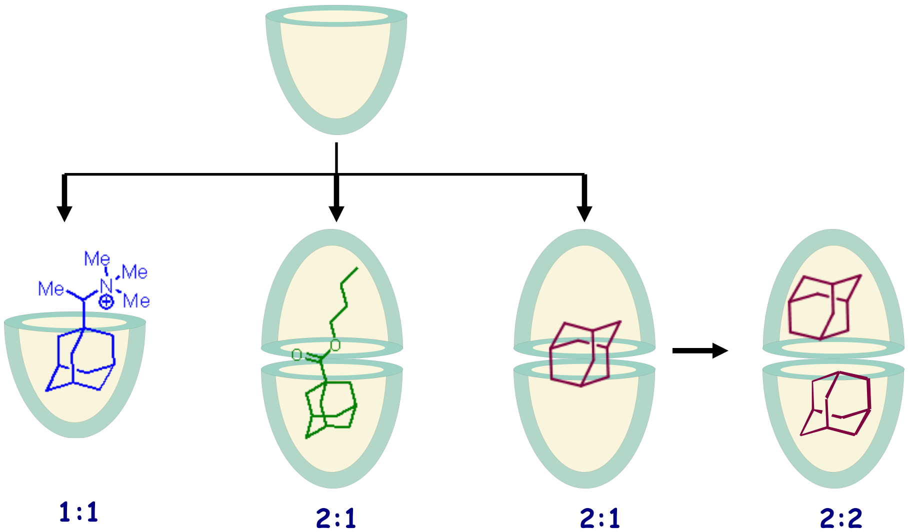
C. L. D. Gibb, and B. C. Gibb, *J. Am. Chem. Soc.*, 2004, *126*, 11408.



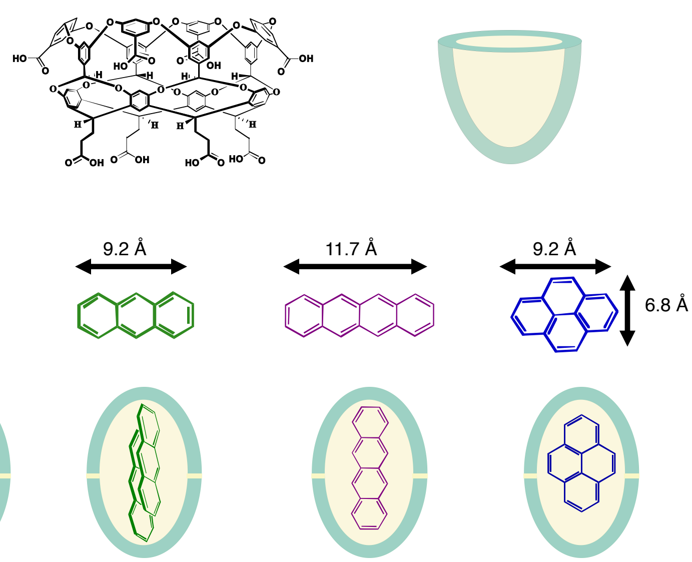




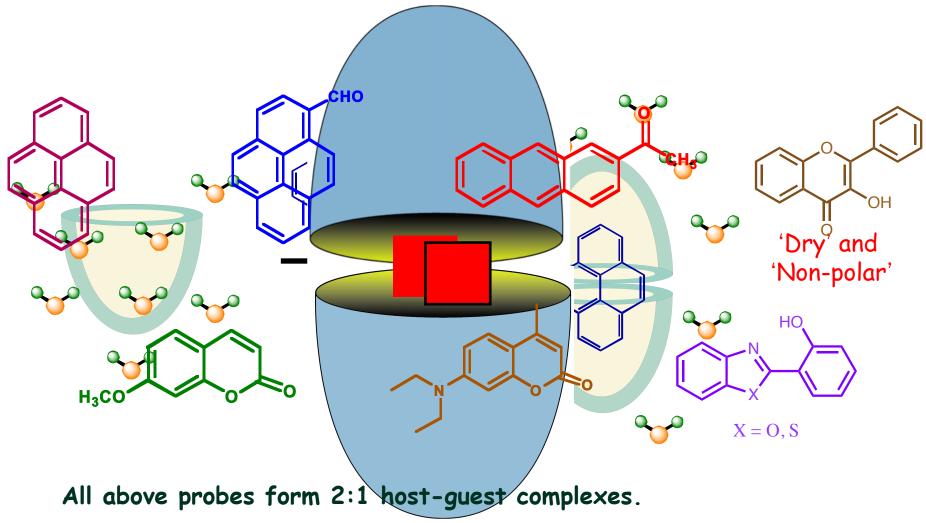
What type of and how many molecules may fit within a OA container?



Encapsulation of aromatics within octa acid

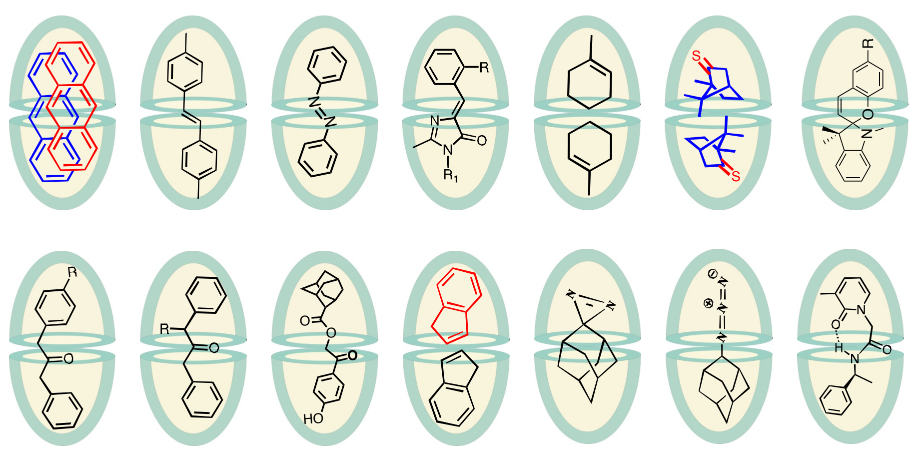


Probing the Micro-polarity of OA Capsule



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

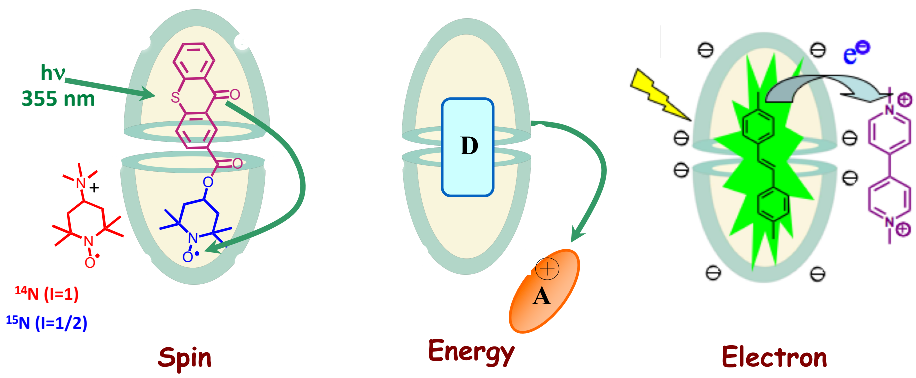
Effect of Confinement on Photophysics and Photochemistry



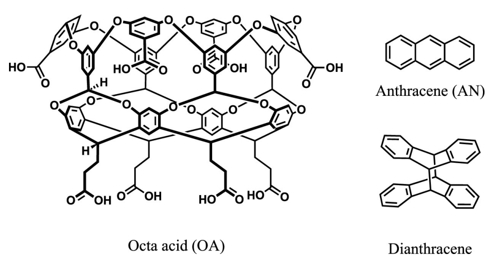
Photochemistry within a water-soluble organic capsule,
V. Ramamurthy, *Acc. Chem. Res.*, *48*, 2904, **2015**.

Communication between confined and free molecules

How good is the wall of a capsule at insulating a guest?



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 (Invited Feature Article)



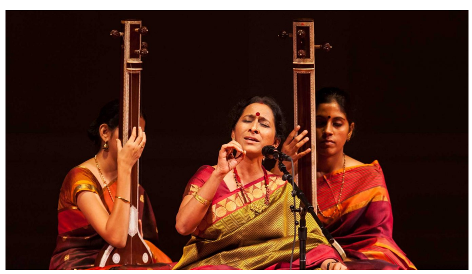
- **Excimer**
- **Host-Guest Complexation**
- **^{1}H NMR**
- **Steady state fluorescence spectroscopy**
- **Ultrafast spectroscopy**
- **Molecular modeling**
- **Quantum chemical calculations**

Struggle between basic and applied science

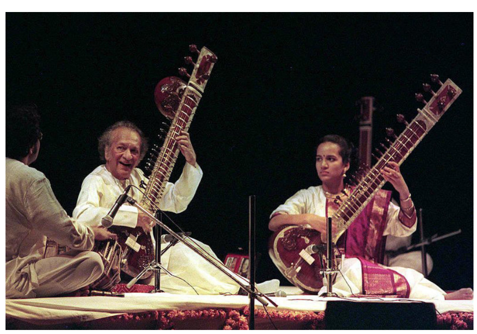
Making new knowledge is neither easy nor profitable in the short term. Fundamental research proves profitable in the long run, and, as importantly, it is a force that enriches the culture of any society with reason and basic truth.

Priestly Medal Address, 2011
"Dreaming The Future"
Ahmed H. Zewail,

Basic Science and Classical Music



Bombay Jayasree

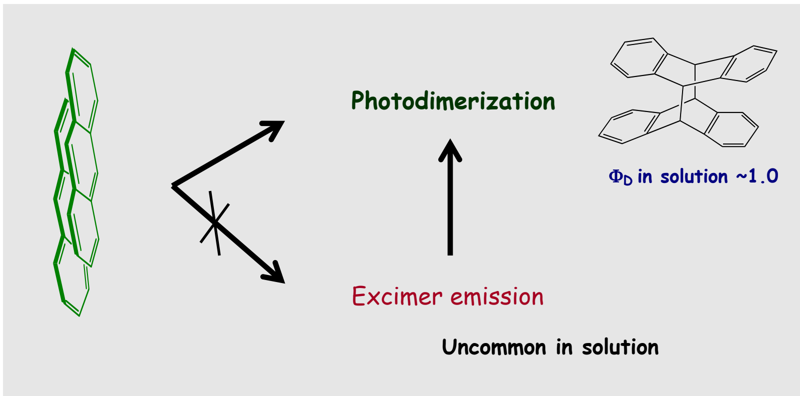


Ravi Shankar

Photochemistry and Photophysics of Anthracene in Isotropic Solution

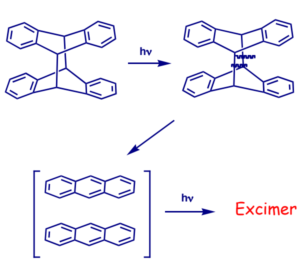
Excimer

Th. Forster and K. Kasper, *Elektrochem., Ber. Bunsenges. physik. Chem.* **1955**, *59*, 976



Anthracene Excimer

Rigid glass (methylcyclohexane) at 77° K



Chandross, E. A.; Ferguson, J. *J. Chem. Phys.* **1966**, *45*, 3546.

Excimer emission is weak in solution

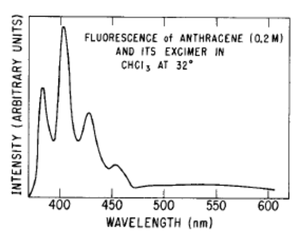
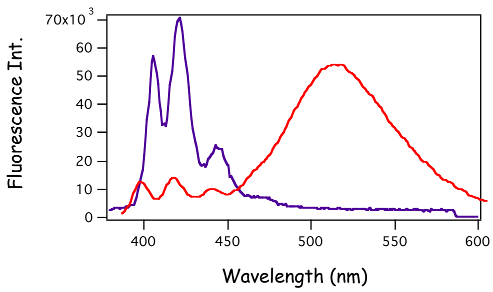


FIG. 1. Fluorescence of anthracene (0.2*M*) and its excimer in $CHCl_3$ at 32 °C.

McVey, J. K.; Shold, D. M.; Yang, N. C. *J. Chem. Phys.* **1976**, *65*, 3375.

Photophysics of OA-Anthracene Complex



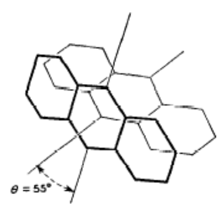
---- Anthracene in water

---- Anthracene in octa acid

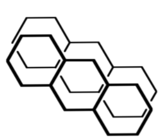
Sandwich pair emission- slow addition of host to the guest in borate buffer

Sireesha

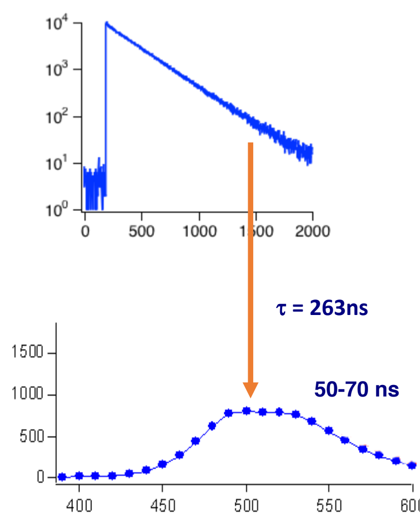
Photophysics of anthracene in octa acid: Lifetime studies



Stable excimer – 55^0 tilted τ 6-7 ns



Sandwich excimer – τ 210 - 225 ns

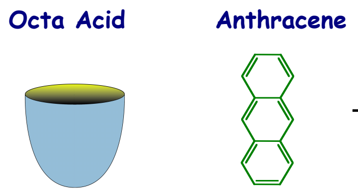


Time Resolved Emission Spectrum

Chandross, E. A.; Ferguson, J.; McRae, E. G. *J. Chem. Phys.* **1966**, *45*, 3546.

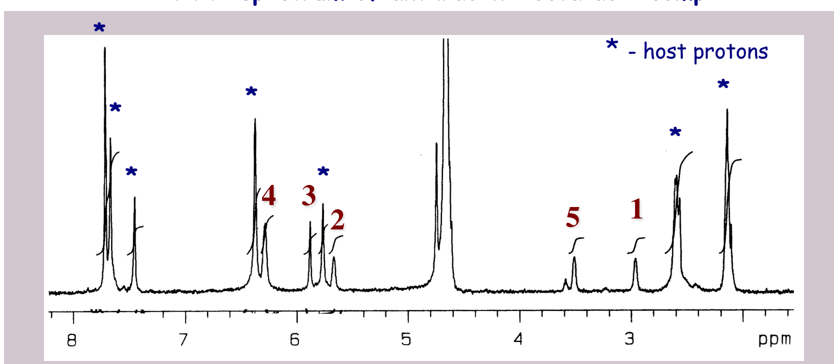
Fielding, P. E.; Jarnagin, R. C. *J. Chem. Phys.* **1967**, *47*, 427.

Encapsulation of anthracene within octa acid

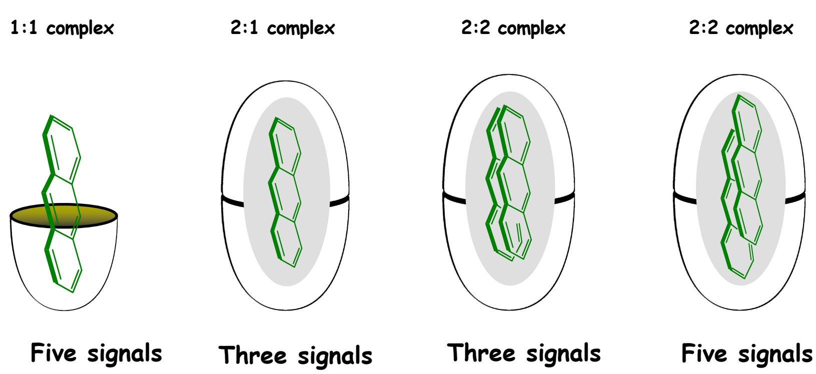


Based on integration 1:1 (H:G) stoichiometry inferred

^{1}HNMR spectrum of anthracene-octa acid complex



What is the nature of the complex?

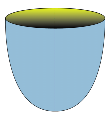


Signal integration is consistent with 1:1 or 2:2 complex

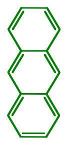
Five NMR signals

OA-Anthracene complex

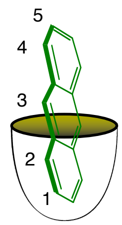
Octa Acid

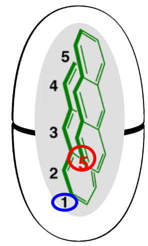


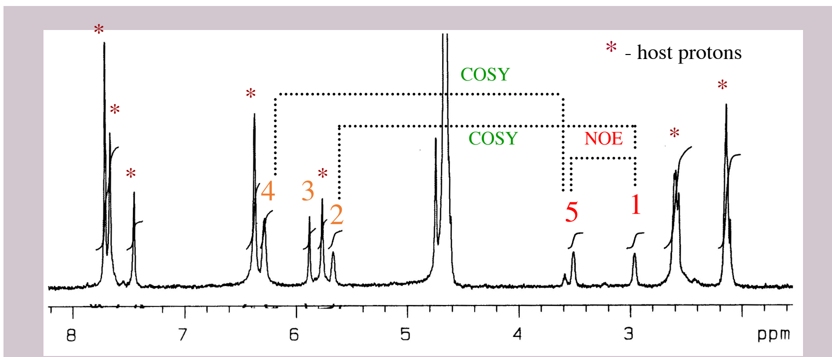
Anthracene



Five Signals

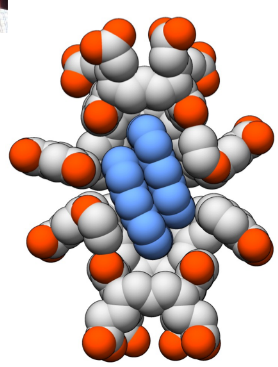


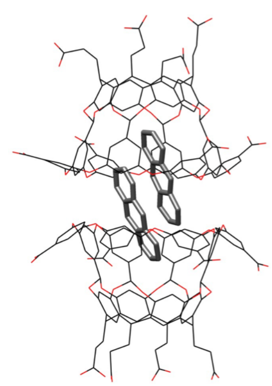




Molecular Modelling

(Prof. Rajeev Prabhakar and Dr. Garuav Sharma, Uni. Miami)





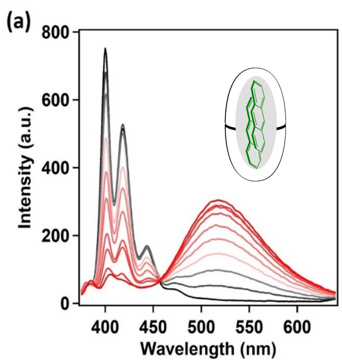
An-An (π-π) = 3.2 Å
An-OA = 3.5 Å
Van der wall radius of carbon = 1.7 Å
Anthracene moved up by = 1.9 Å

Gaussian09
Autodock Vina 1.5.6
GROMACS
Yasara/Chimera

Monomer (1:0) to Excimer (2:2) to Monomer (1:2)

Addition of OA (0 – 5.0 μM; AN 5.0 μM)

Addition of OA (5 – 50 μM) AN 5.0 μM)

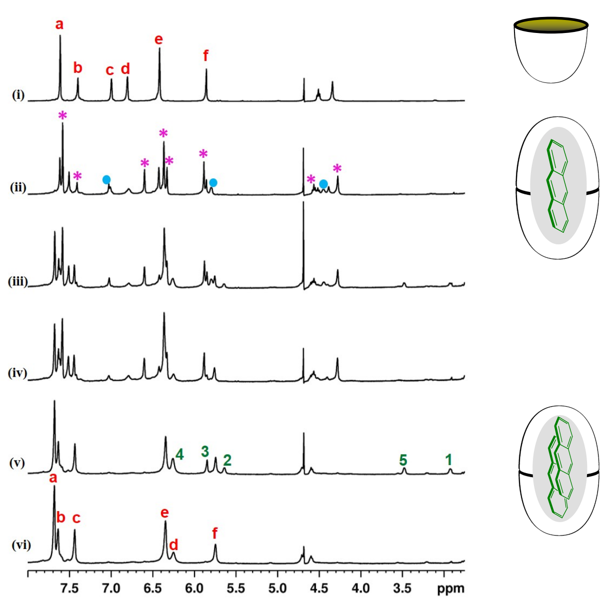


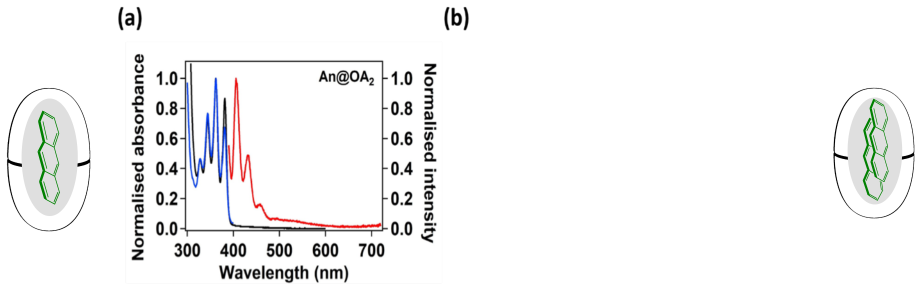
(a) From bulk anthracene monomer (black) to $An_2@OA_2$ complex (red).

(b) From $An_2@OA_2$ (red) to $An@OA_2$ complex (green) upon addition of excess octa acid.

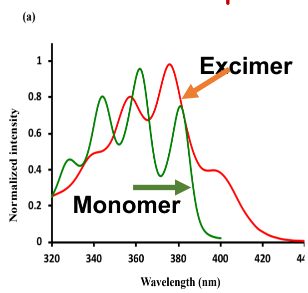
Three types of anthracenes: An aggregates, $An@OA_2$, $An_2@OA_2$

Are there two types of anthracene monomer emission?

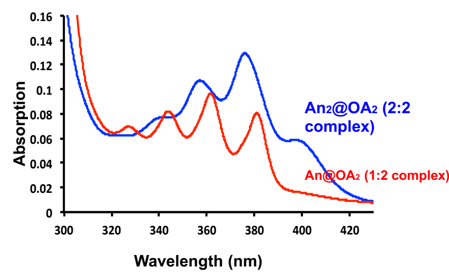




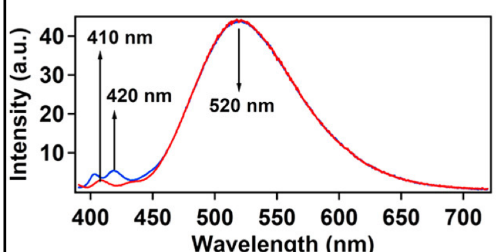
Excitation spectra

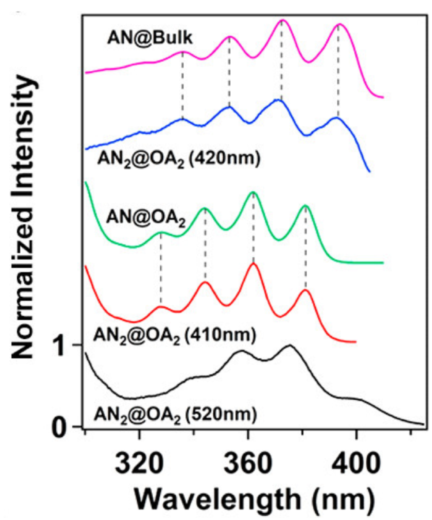


Absorption spectra



Origin of monomer, aggregate and excimer emissions

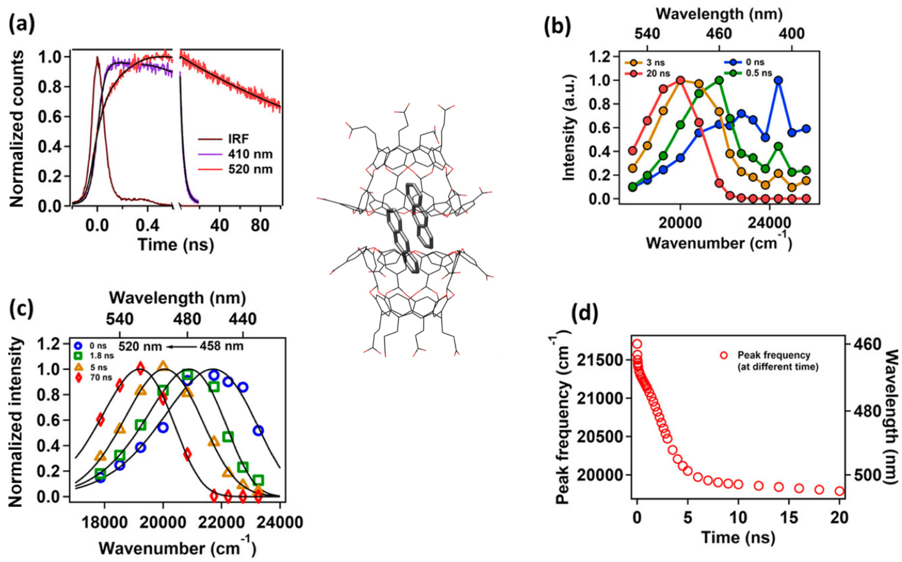




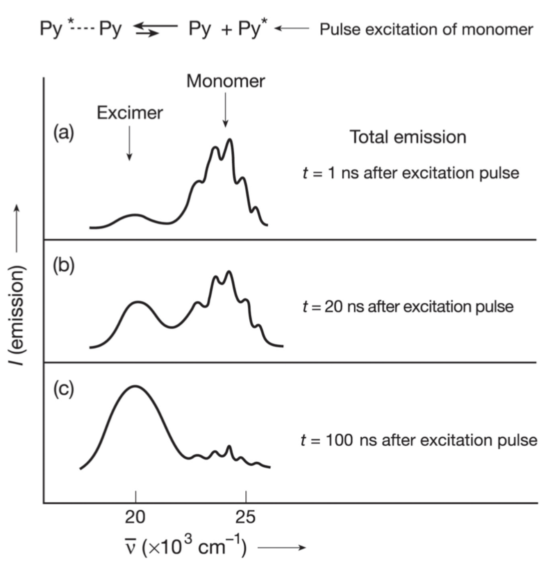
Dynamics of excimer formation

Time resolved emission spectra (TRES)

(Prof. Pratik Sen and Aritra Das, IIT-Kanpur)



Classic example of monomer–excimer equilibrium

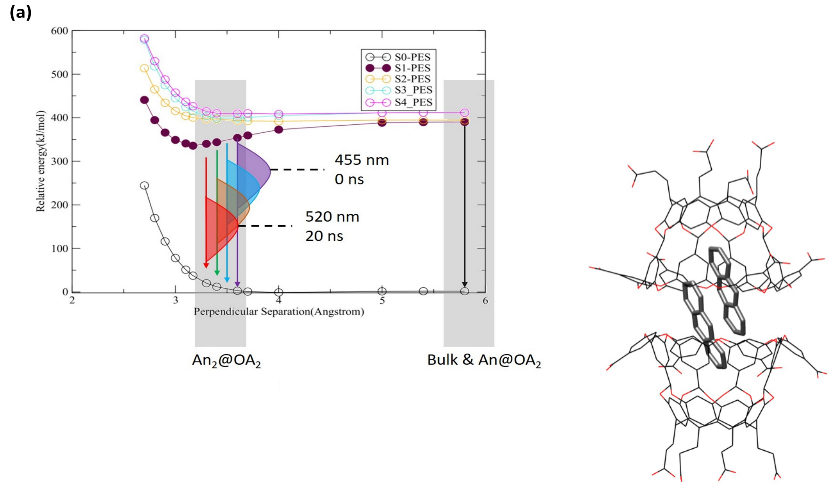


Th. Forster and K. Kasper, *Elektrochem., Ber. Bunsenges. physik. Chem*. **1955**, *59*, 976

Th. Forster, *Angew. Chem. Internat. Edit*., **1969**, *8*, 333.

K. Yoshihara, T. Kasuya, A. Inoue and S. Nagakura, *Chem. Phys. Lett*., **1971**, *9*, 469.

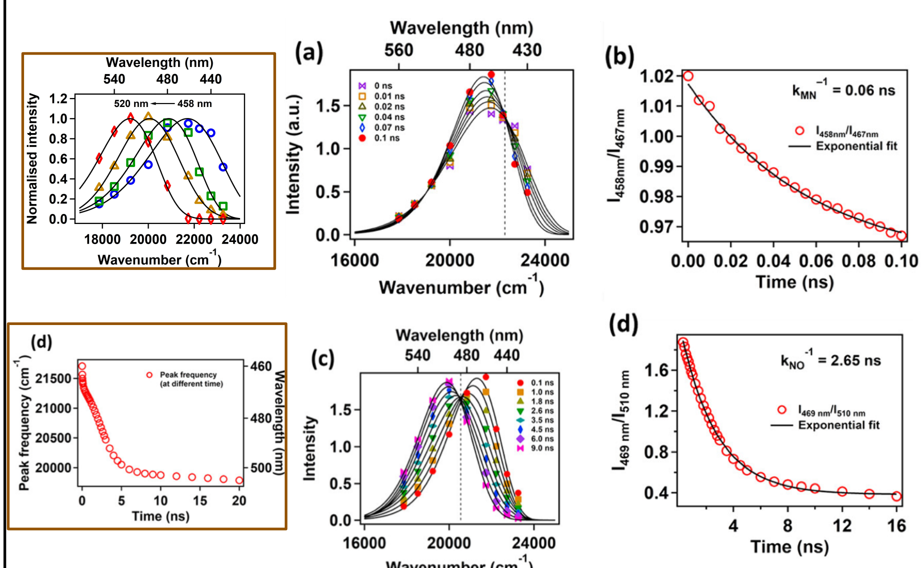
N. J. Turro, V. Ramamurthy and J. C. Scaiano, *Modern Molecular Photochemistry of Organic Molecules*, **2010**, p. 255



(a) Potential energy scan for the two anthracene monomer approaching each other against the perpendicular distance in between them, (b) some representative TRES at different wavelength along the excimer emission band, (c) time-dependence of the emission intensity at 520 nm.

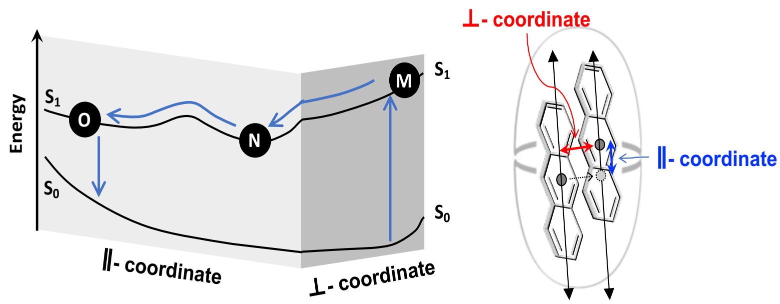
Time-resolved area normalized emission spectra (TRANES)

Dynamics of excimer formation

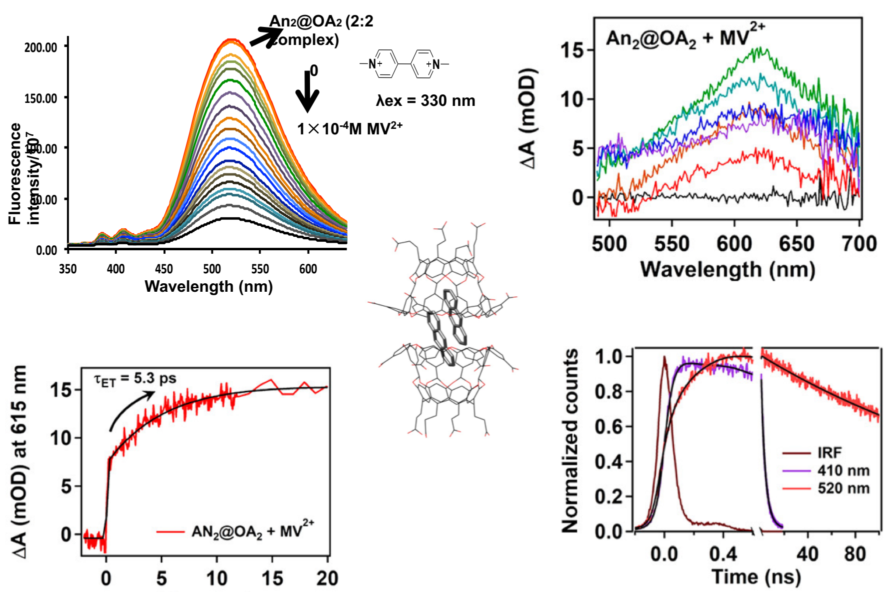


Two iso-emissive points indicate the overall process of energy relaxation occurs through **two steps**.

A pair of anthracene molecules struggles to tunnel through a capsular cave



Kinetic model based on the result of TRES, TRANES and the theoretically calculated PES.

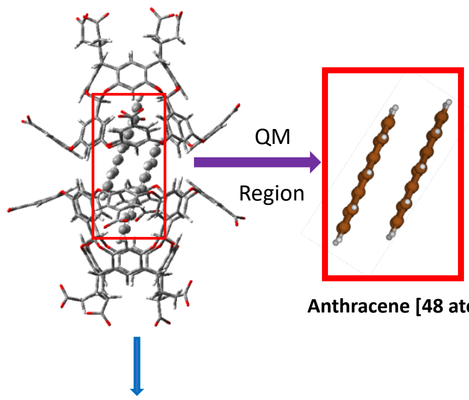


Rise time for excimer: 400 ps

QM/MM Approach

(Prof. Varadharajan Srinivasan and Shubhojit Banerjee, IISER-Bhopal)

- Combines two different descriptions: quantum and classical
- **MM Region**: OA cage does not participate electronically in (lowest) excited states and was treated by Amber Force Field.
- **QM Region**: Reactive regions are two anthracene molecules which were modelled as QM with CAM-B3LYP exchange-correlation (xc) functional along with the BJ-damped Grimme's D3 dispersion (CAM-B3LYP-D3BJ) and a 6-31G(d,p) basis set.
- The interaction between QM and MM region are
  - Electrostatic interactions
  - Van der Waals interaction

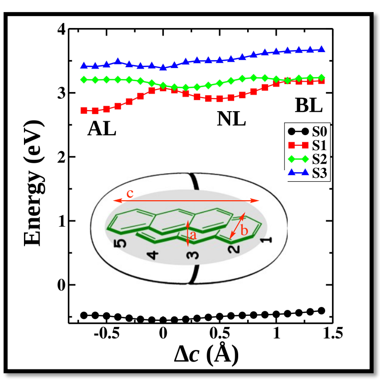


Anthracene [48 atoms]

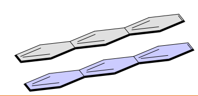
MM region: OA cage [368 atoms]

Gas-phase potential energy curve (PEC)

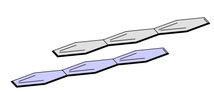
- To explain excimer, PEC was calculated with CAM-BLYP/6-31G** level of theory along with D3BJ dispersion correction.
- PEC is symmetric about sandwich like geometry with a avoided crossing between S_1 and S_2.



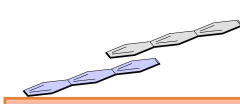
Gas-phase PEC along c-axis



Anthracene Like excimer (AL)

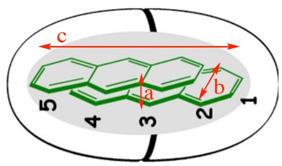


Naphthalene like excimer (NL)

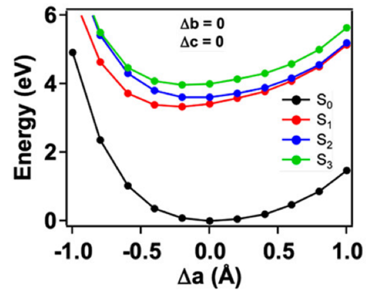


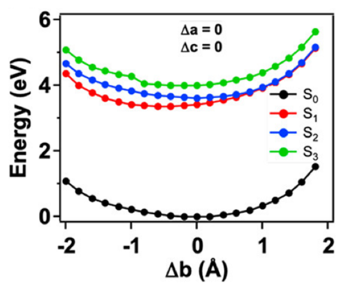
Benzene like excimer (BL)

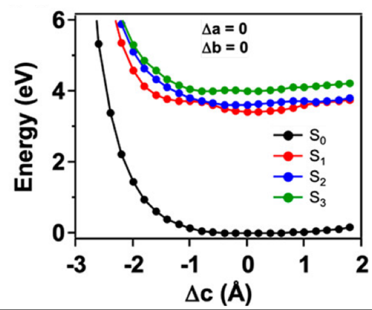
PEC along 'c' in confined phase



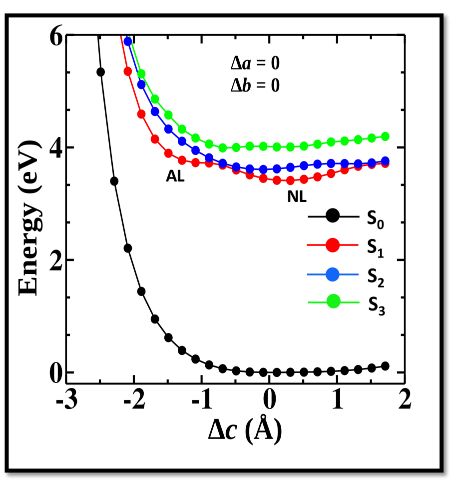
a = 3.544 Å
b = 1.003 Å
c = 2.089 Å







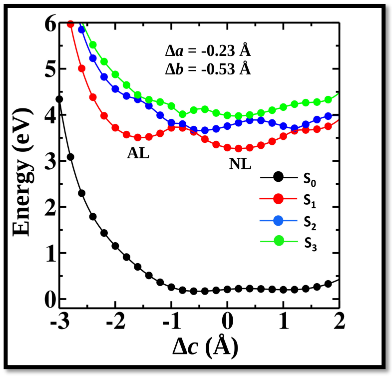
PEC along *c*-axis in confined phase



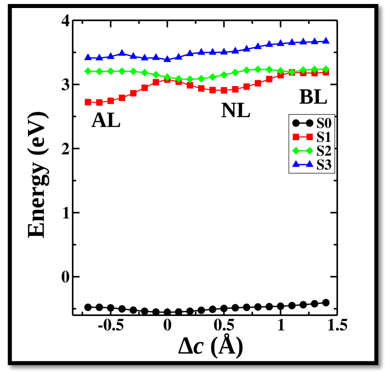
- Though in gas phase the PEC is symmetric about sandwich like geometry, but in confined environment clearly it's not the case.
- PEC curves upward after a certain point due to interaction with the capsule wall.
- In gas-phase, we can clearly see the three types of excimer among which AL one is the most stable. But inside octa-acid, NL excimer is more stable than AL excimer.

Comparison of PEC in gas phase *vs* capsule

Capsule



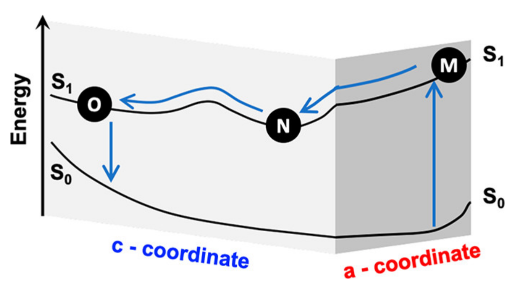
Gas phase

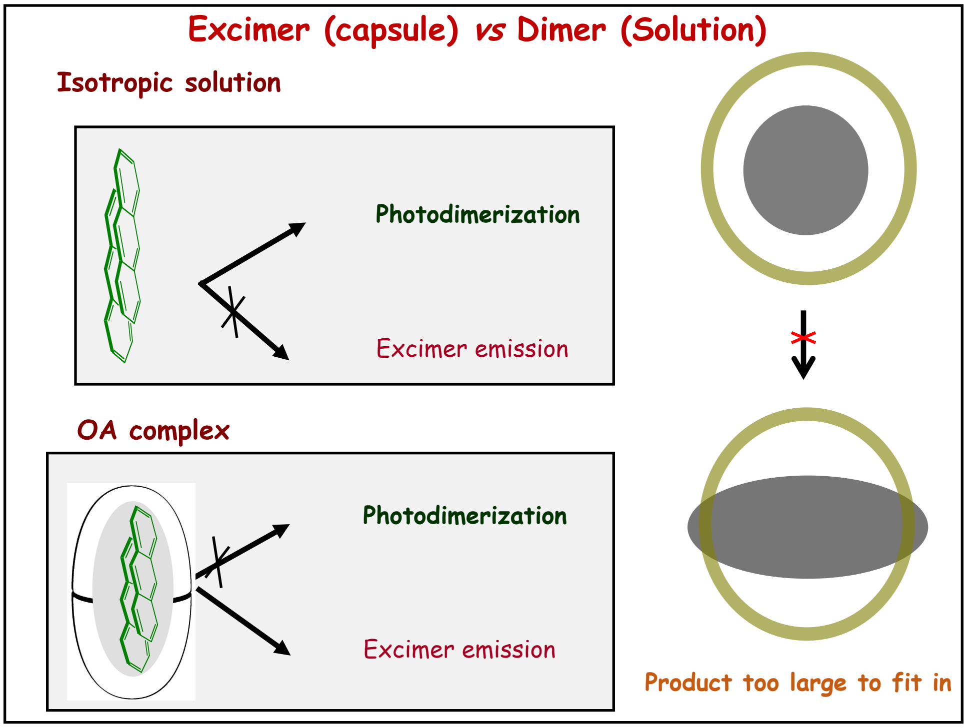


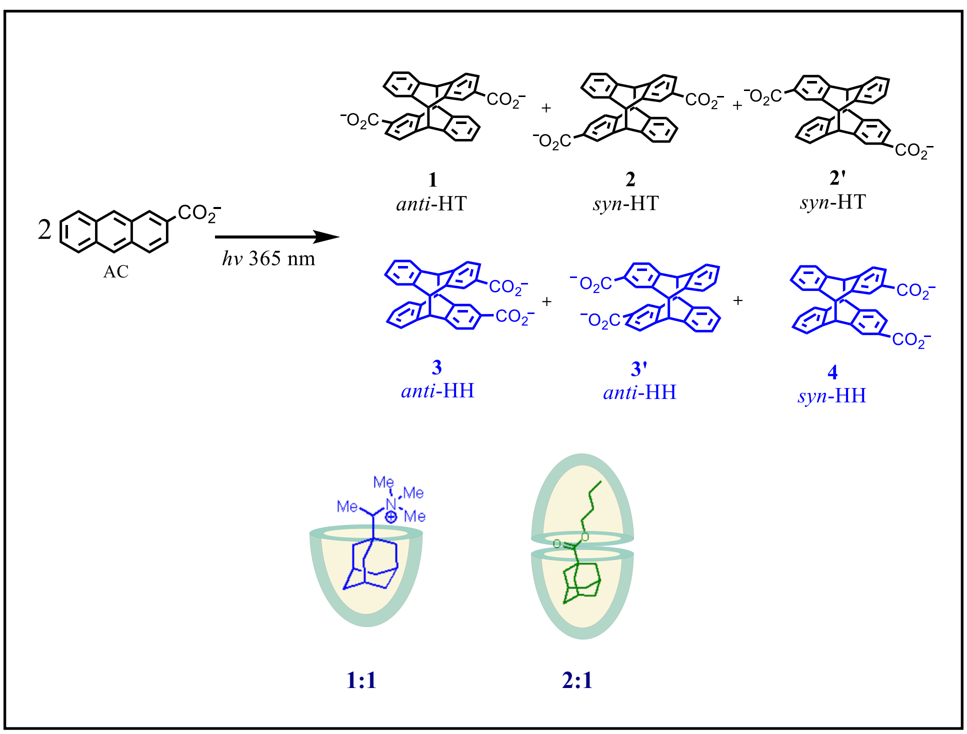
	AL	NL	Exp.
Emission maxima	441 nm	407 nm	520 nm

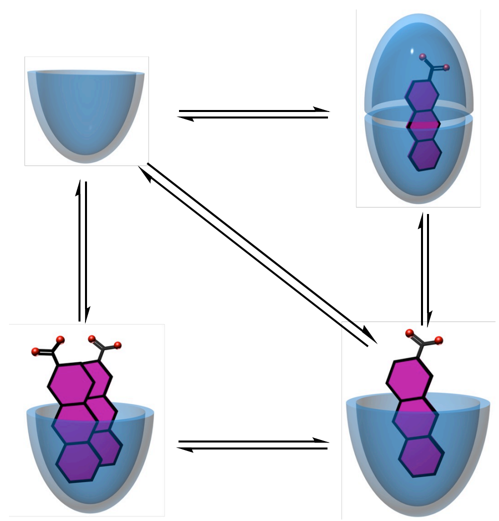
- For more accurate results, excited state (S_1) optimized structure along multiple co-ordinates will be required.

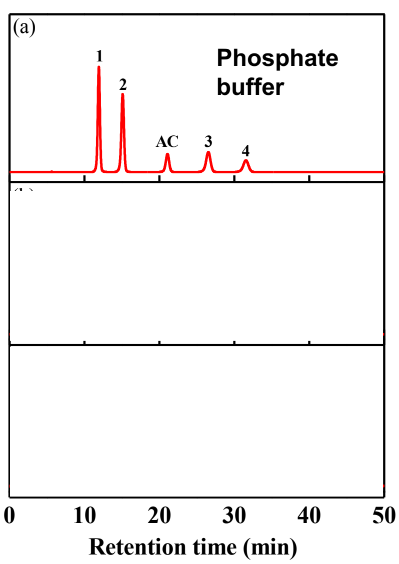
Mechanism of excimer formation within a confined space

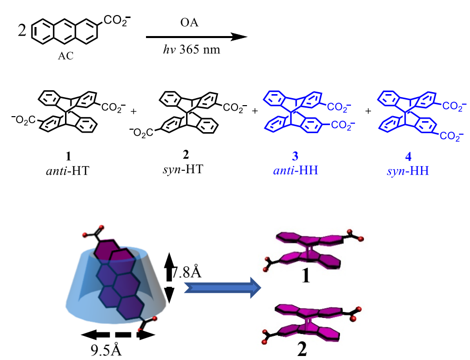



Excimer (capsule) vs Dimer (Solution)
Isotropic solution
Photodimerization
Excimer emission
OA complex
Photodimerization
Excimer emission
Product too large to fit in

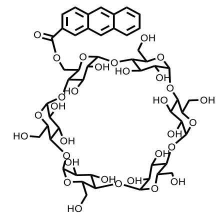

2
AC
hv 365 nm
1
anti-HT
2
syn-HT
2'
syn-HT
3
anti-HH
3'
anti-HH
4
syn-HH
1:1
2:1





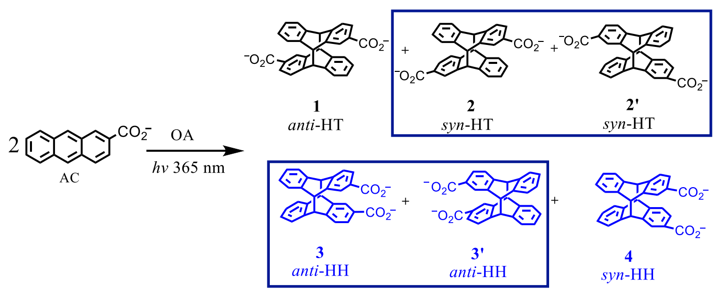


HPLC chromatogram of the irradiated solution of 0.2 mM AC (a) in absence of host, and in the presence of (b) 2.0 mM γ-CD and (c)1.0 mM OA using a UFLC SHIMADZU system equipped with Inertsil ODS-2 (achiral column).



6-O-(2-anthracenecarbonyl)- -CD
-CD-AC)

solvent	host	temp / °C	relative yield (%)					%ee	
			1	2	3	4		2	3
PBS	none	0.5	47.7	38.8	11.4	2.1		15.6	-26.0
	OA	0.5	6.1	4.4	52.7	36.8		51.8	-55.7



Dynamics of Anthracene Excimer Formation within a Water-soluble Nanocavity at Room Temperature

A. Das, A. Dano, A. Mohan Raj, G. Sharma, S. Banerjee, R. Prabhakar, V. Srinivasan, V. Ramamurthy and P. Sen, *J. Am. Chem. Soc.*, **2021**, 143, 2025-2036

Reversal of Regioselectivity During Photodimerization of 2-Anthracene carboxylic acid in a water-soluble organic cavitand

X. Wei, A. Mohan Raj, J. Ji, W. Wu, G. Veerakanellore, C. Yang and V. Ramamurthy, *Org. Lett*. **2019**, 21, 7868-7872

A Hydrophobic Nanocapsule Controls the Photophysics of Aromatic Molecules By Suppressing their Favored Solution Pathways

L. S. Kaanumalle, C. L. D. Gibb, B. C. Gibb, V. Ramamurthy, *J. Am. Chem. Soc.*, **2005**, *127*, 3674-3675.

Summary

- Depending on the guest, the OA forms 1:1, 2:1 or 2:2 complexes.
- In host-guest complexes, guest and host molecules are not stationary. They undergo several different types of motions.
- Weak interactions and confinement could be used to control ground state and excited state properties of molecules.
- New pathways unseen in solution may open up within confined spaces.
- Ultrafast experiments reveal that molecular dynamics are significantly altered within confined spaces.
- Communication between molecules across molecular wall is possible.


Sireesha


Mohan Raj


Ashwini


Pratik Sen


Aritra Das


V. Srinivasan


S. Banerjee


R. Prabhakar


G. Sharma


Bruce Gibb