

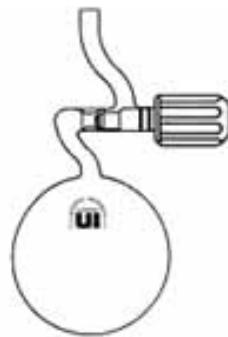


Photochemistry in a Capsule

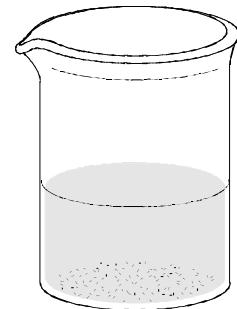


Controlling Photochemical Reactions With Confinement and
Weak Intermolecular Forces

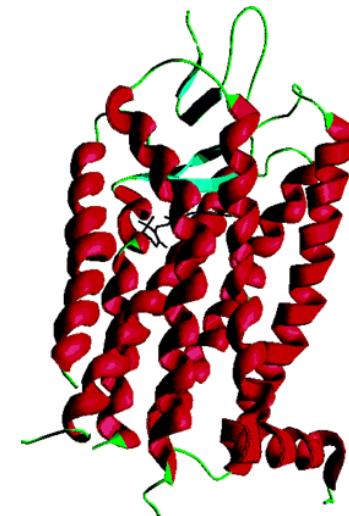
Medium Matters



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?

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

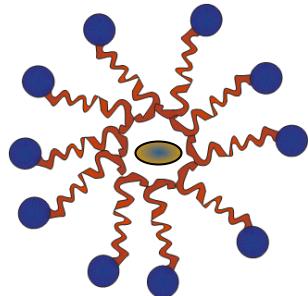
(Most organic compounds are liquid)

Solution: Use water soluble hosts to solubilize organic molecules

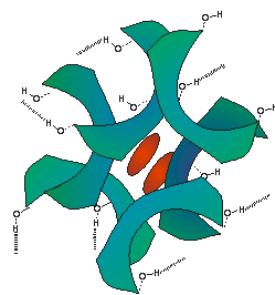
(Use solid hosts to trap liquid molecules)

Use confining hosts to achieve selectivity

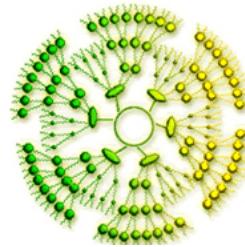
Supramolecular Containers



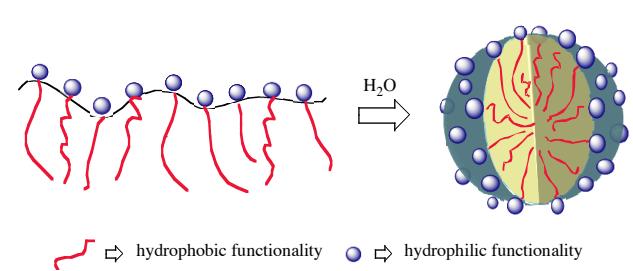
SDS / CTAC



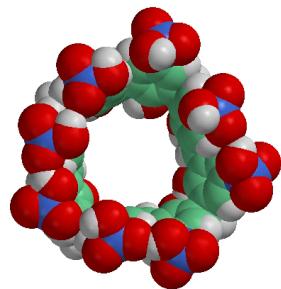
NaCh / NaDCh



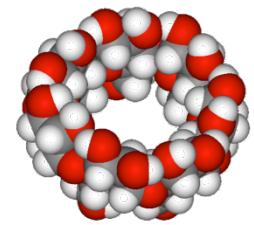
Dendrimers



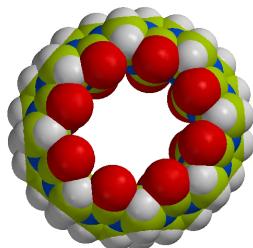
Water soluble polymer



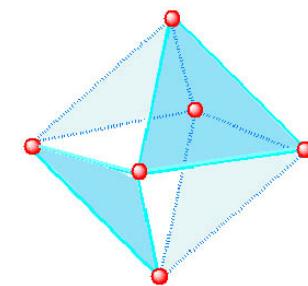
Calixarenes



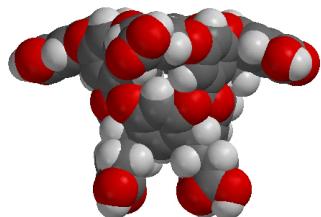
Cyclodextrins



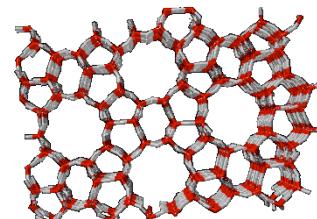
Cucurbiturils



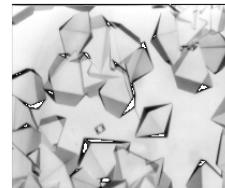
Pd nano cage



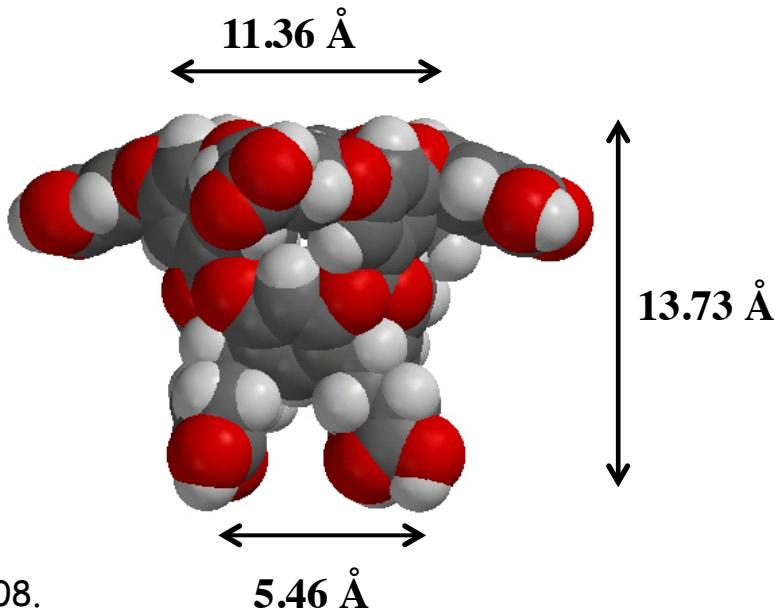
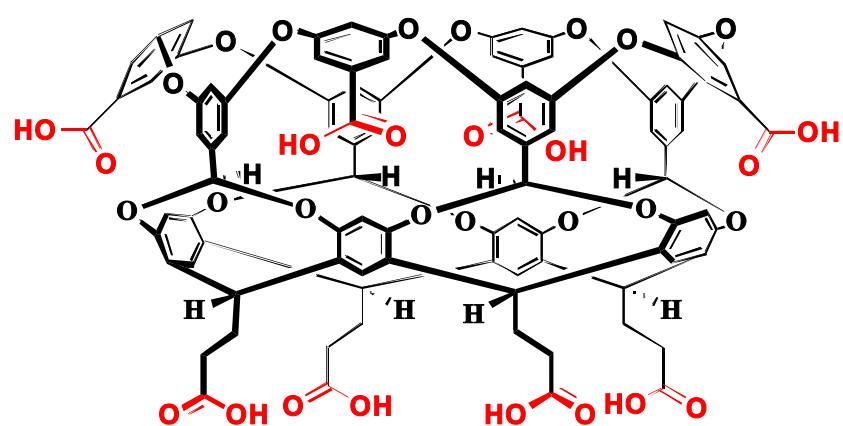
Octa acid



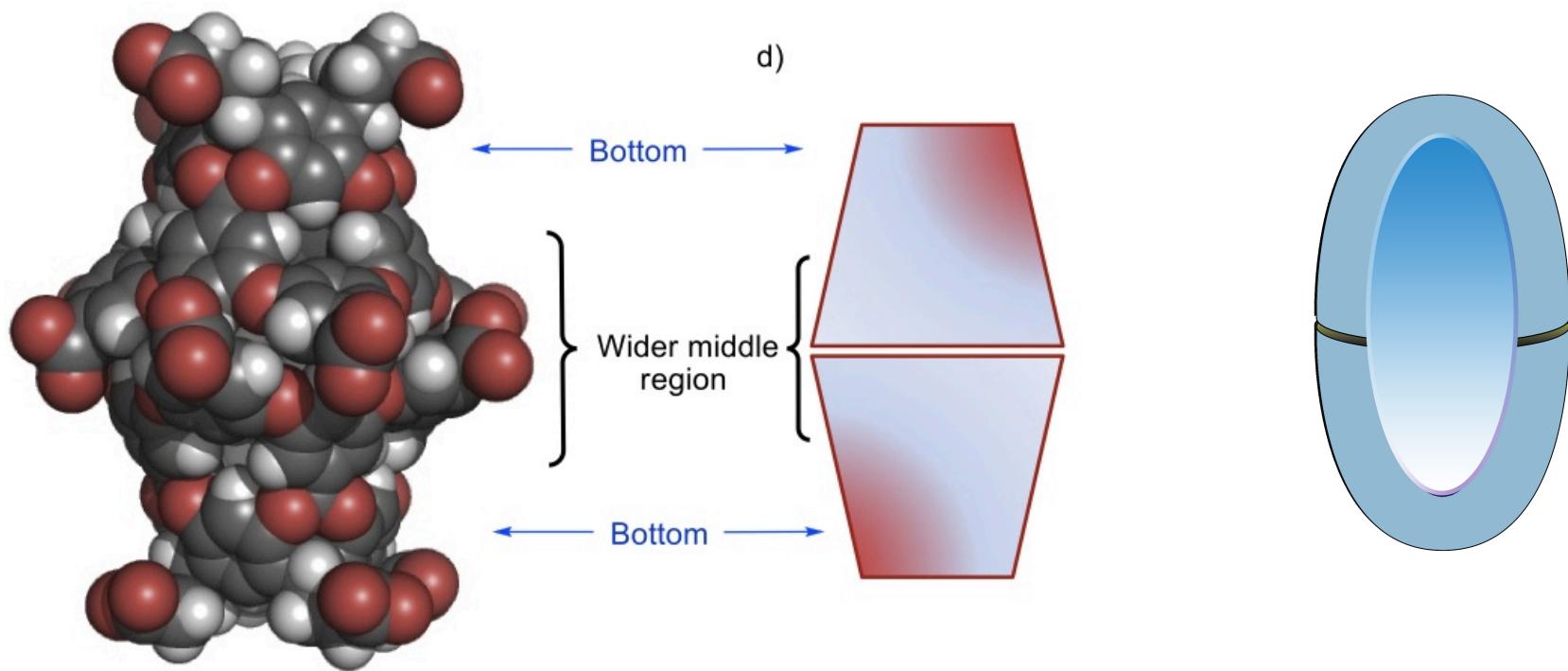
Zeolites



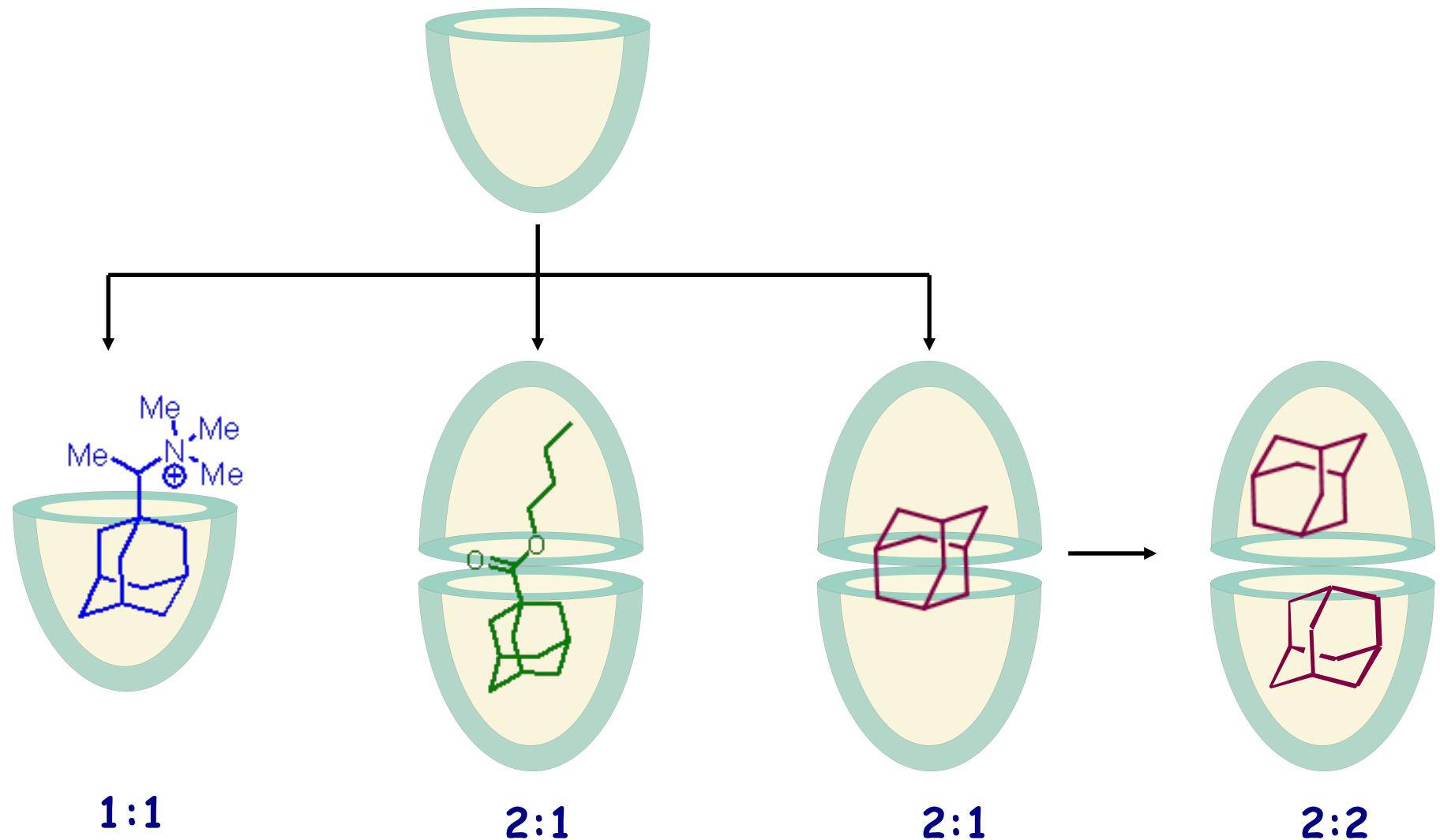
Crystals



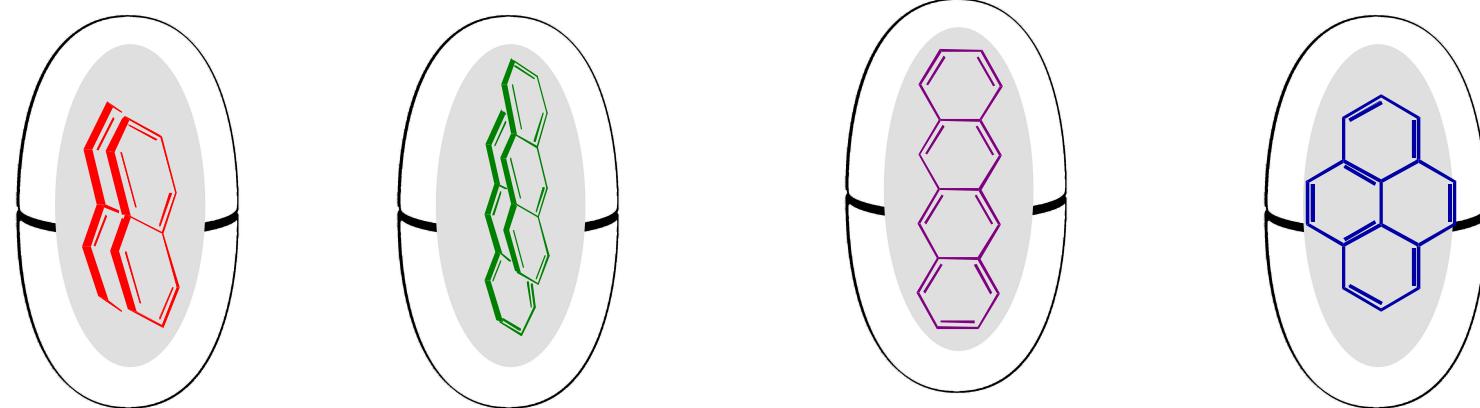
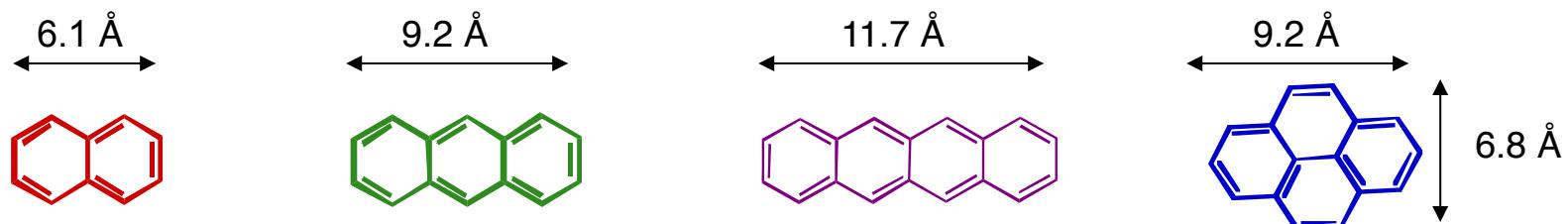
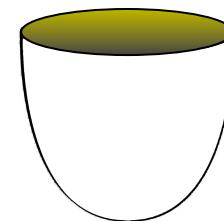
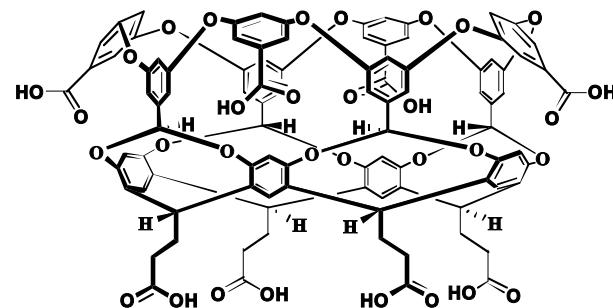
C. L. D. Gibb, and B. C. Gibb, *J. Am. Chem. Soc.*, 2004, 126, 11408.



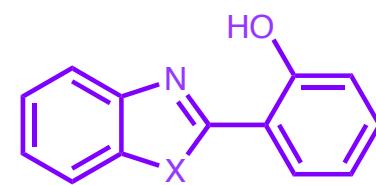
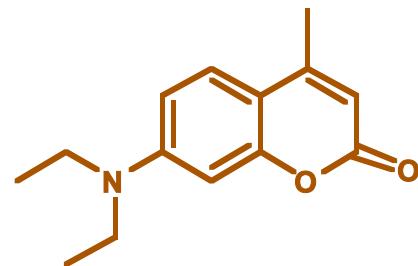
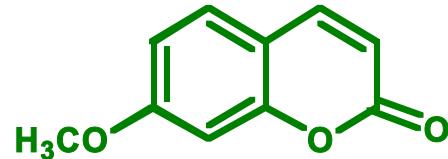
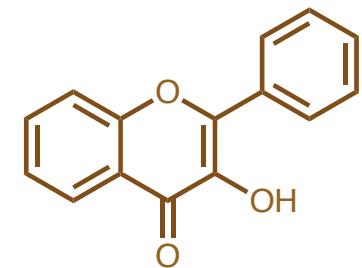
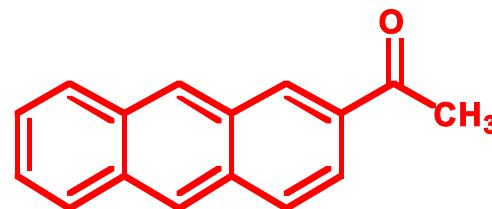
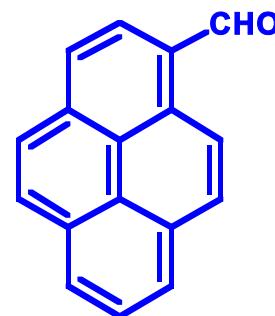
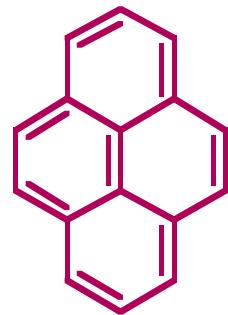
What type of and how many molecules may fit within a OA container?



Encapsulation of aromatics within octa acid



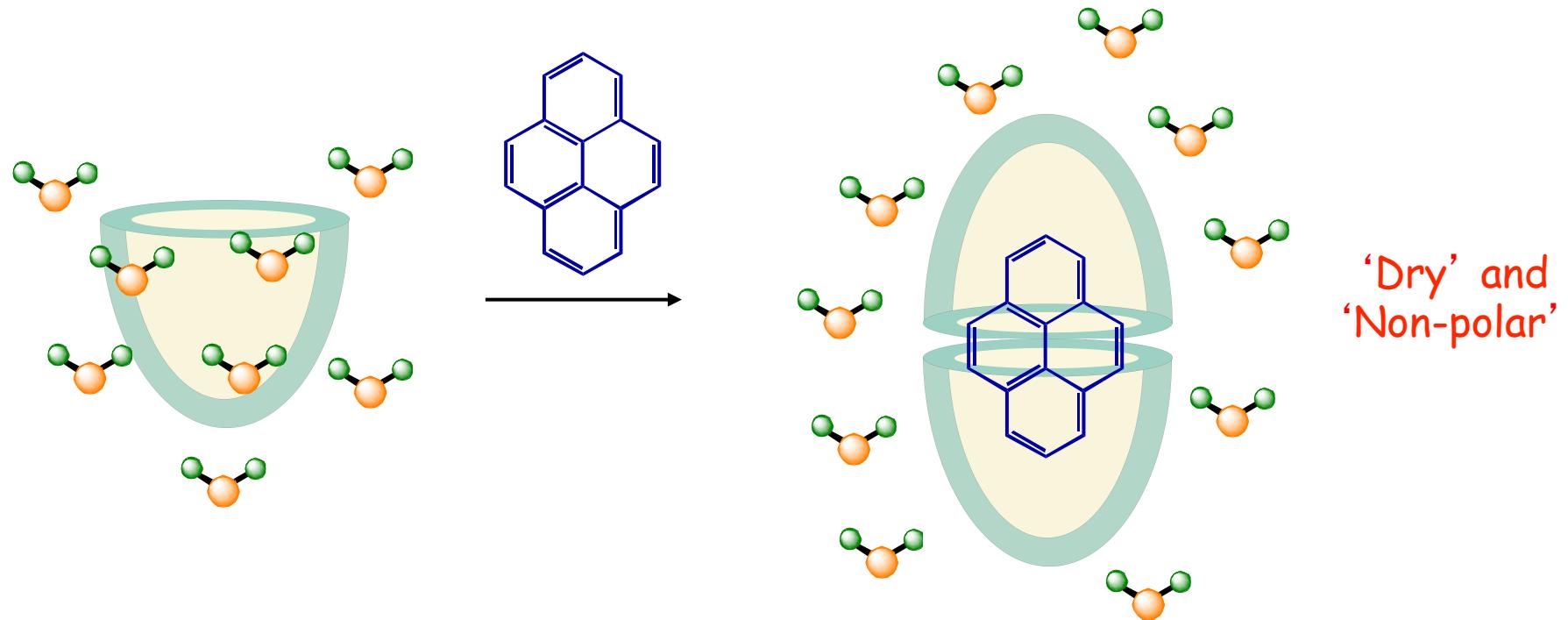
Probing the Micro-polarity of OA Capsule



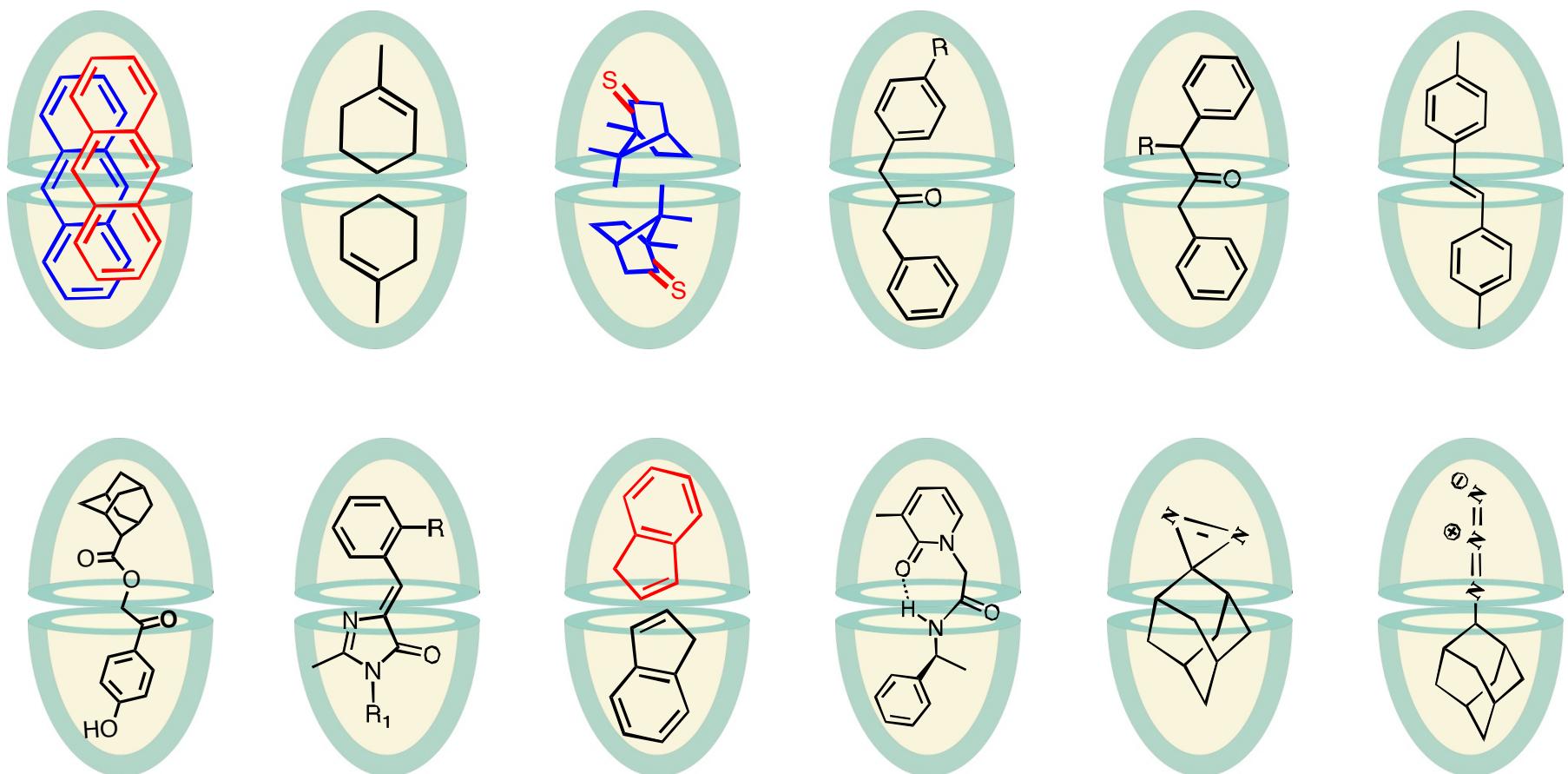
X = O, S

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

Probing the Micro-polarity of OA Capsule



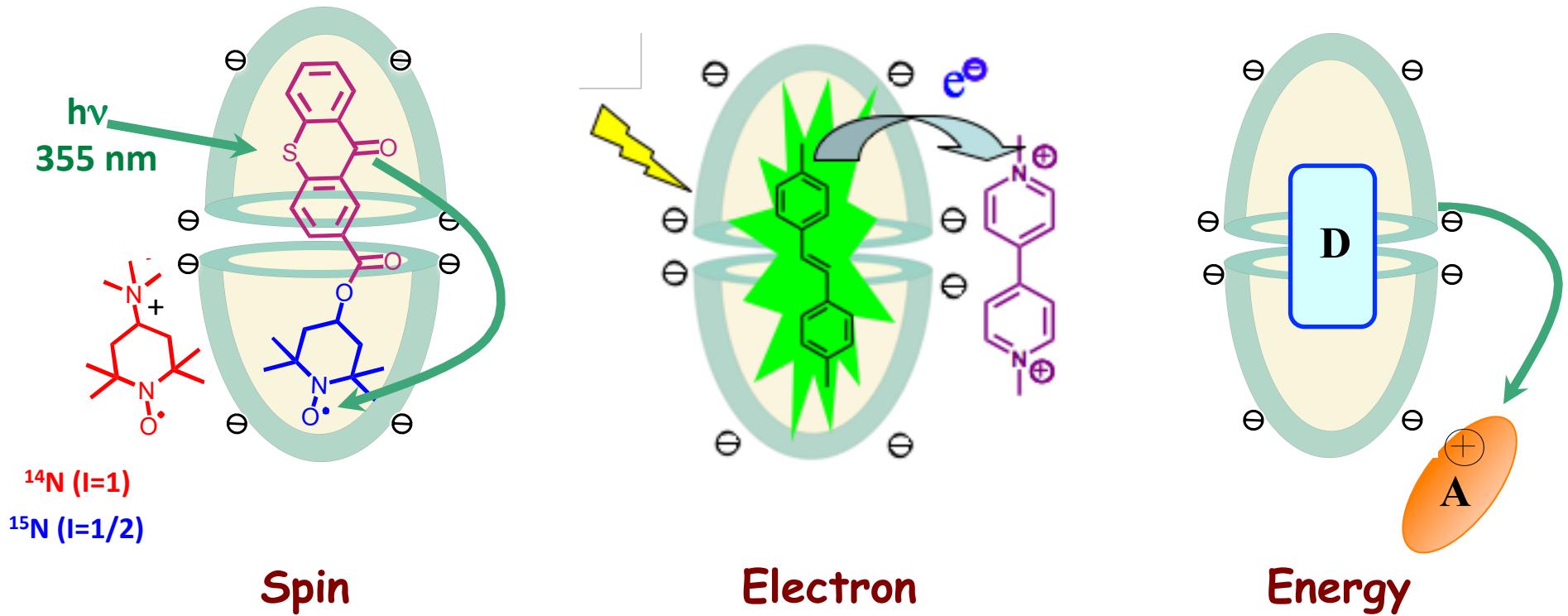
Manipulating photophysics and photochemistry through confinement



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

Communication between confined and free molecules

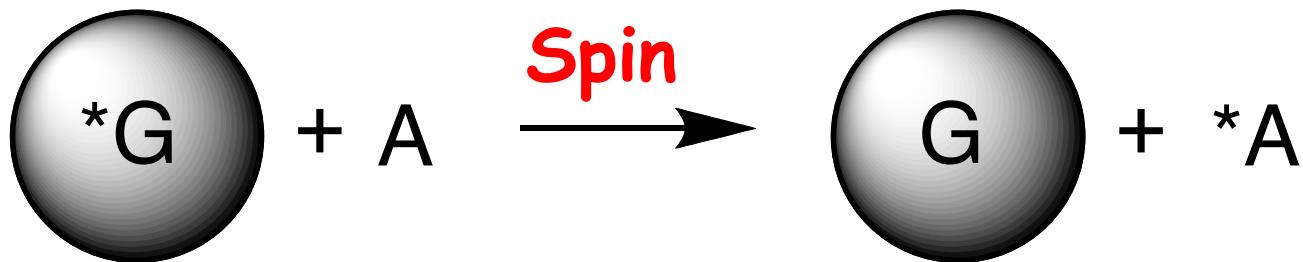
How good is the wall of a carcerand at protecting a guest?



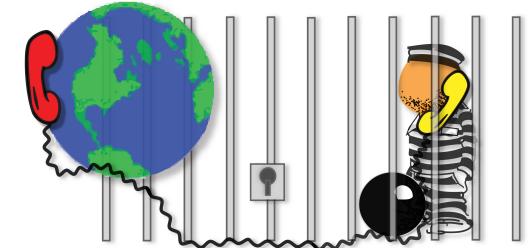
Supramolecular Photochemistry in Solution and on Surfaces: Encapsulation and Dynamics of Guest Molecules, and Communication Between Encapsulated and Free Molecules

V. Ramamurthy, S. Jockusch and M. Porel, *Langmuir*, 2015, 31, 5554-5570 (Feature review article)

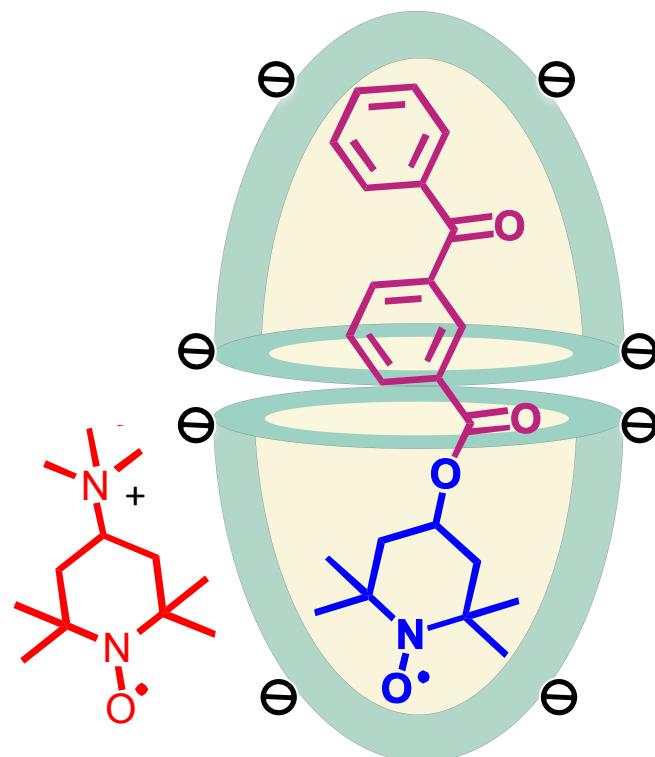
Spin transfer between confined and free molecules



Probing the spin-spin interaction between caged and free nitroxides



Spin transfer

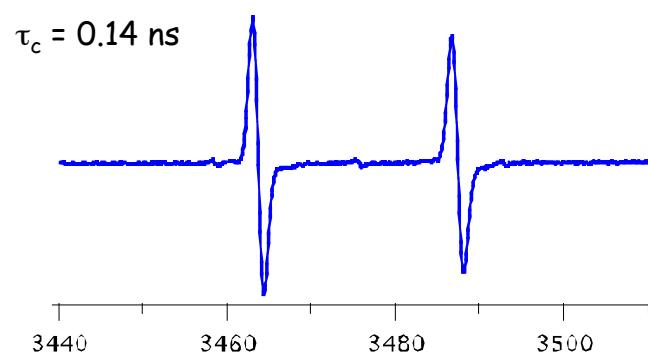
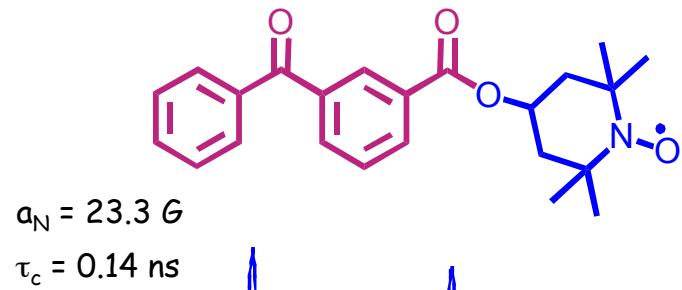


Nuclear spin labeling

^{14}N ($I=1$)

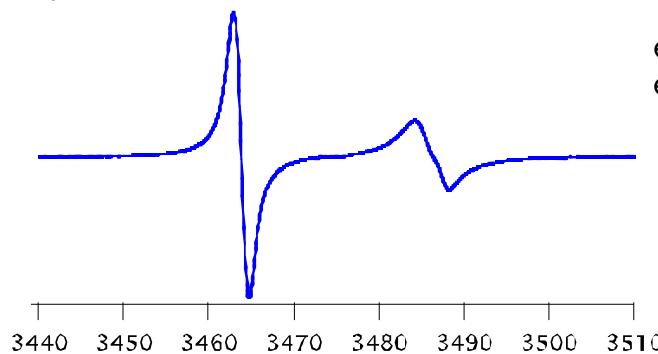
^{15}N ($I=1/2$)

Probing the location of nitroxides by EPR



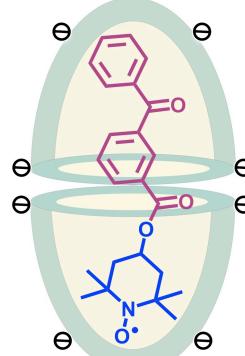
$a_N = 21.0 \text{ G}$

$\tau_c = 2.1 \text{ ns}$

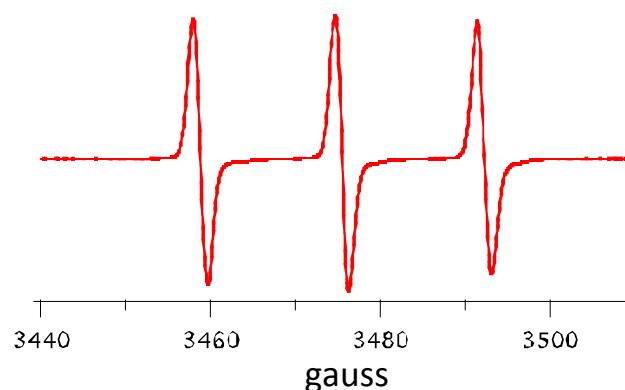


^{15}N

water

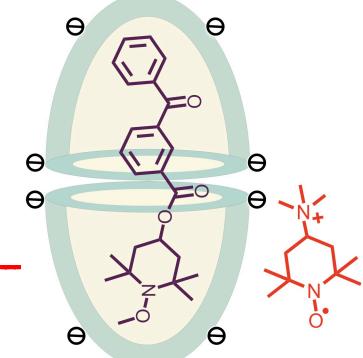
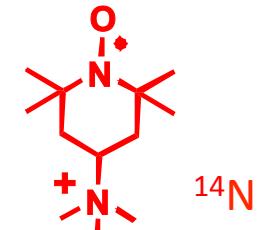
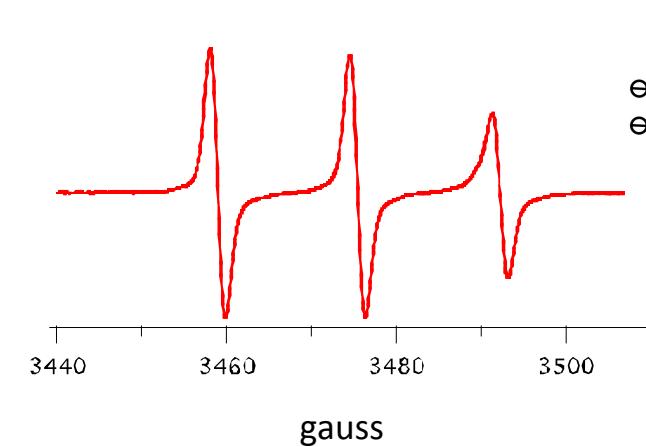


$a_N = 16.8 \text{ G}$
 $\tau_c = 0.025 \text{ ns}$

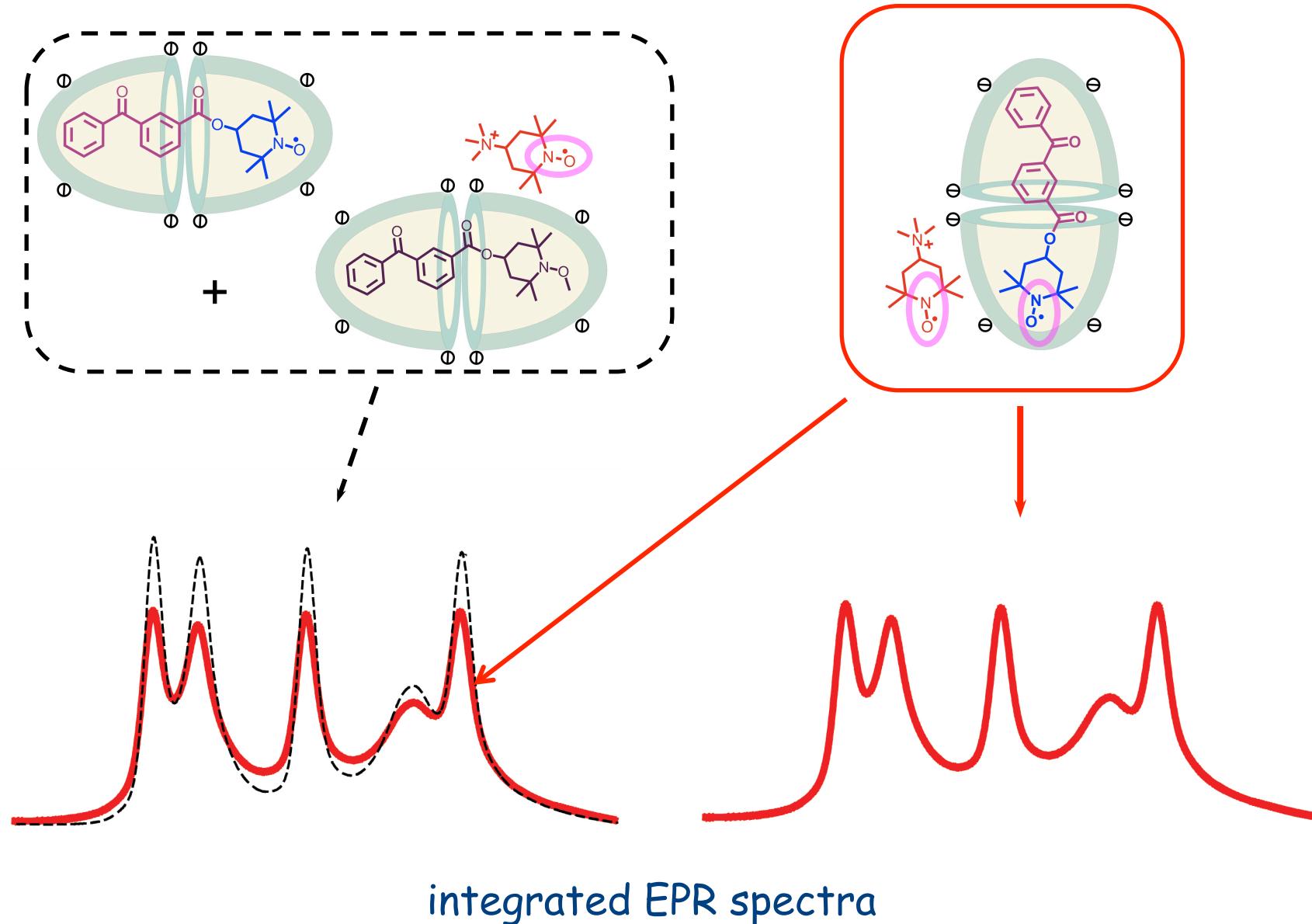


$a_N = 16.7 \text{ G}$

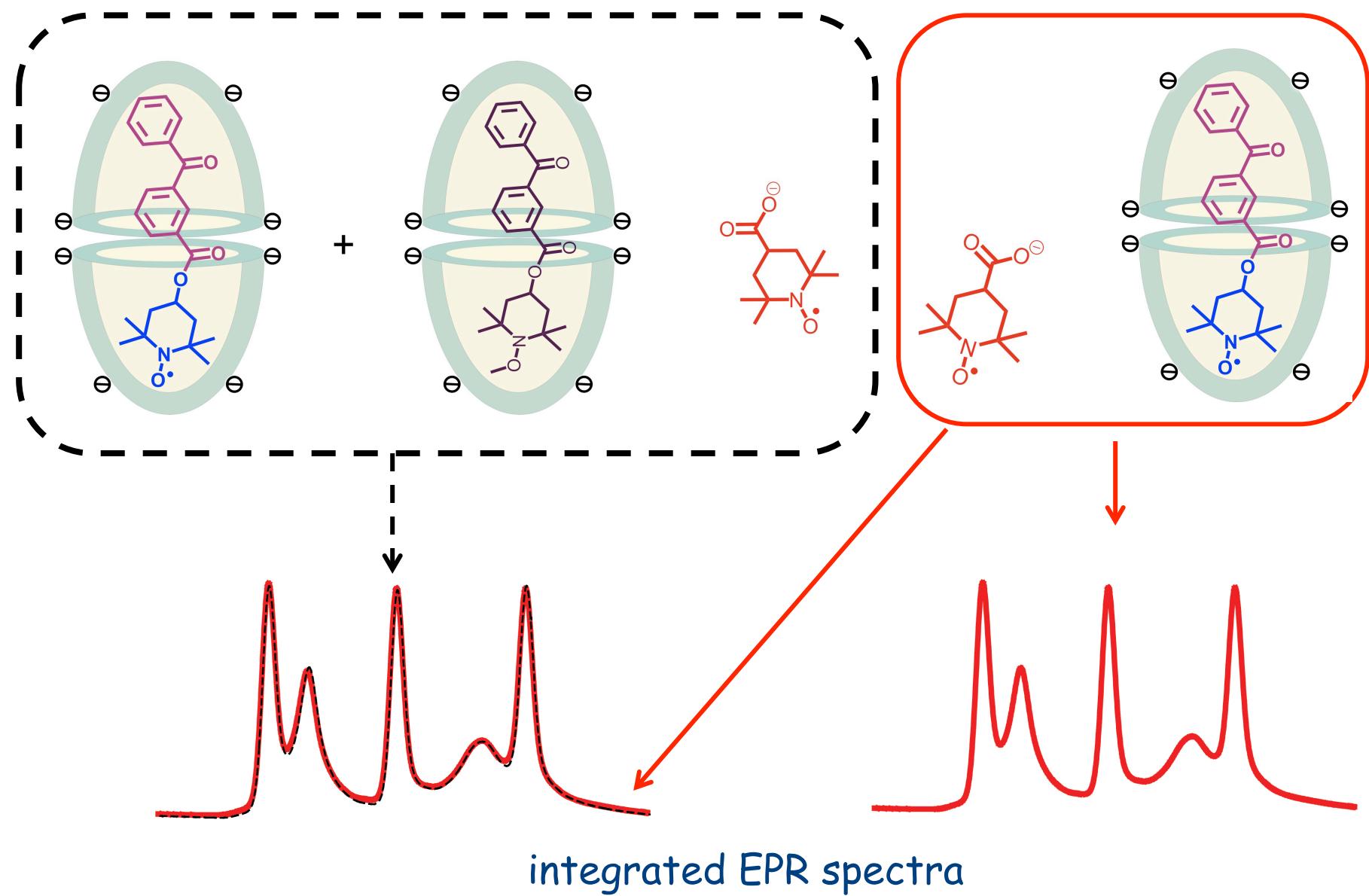
$\tau_c = 0.10 \text{ ns}$



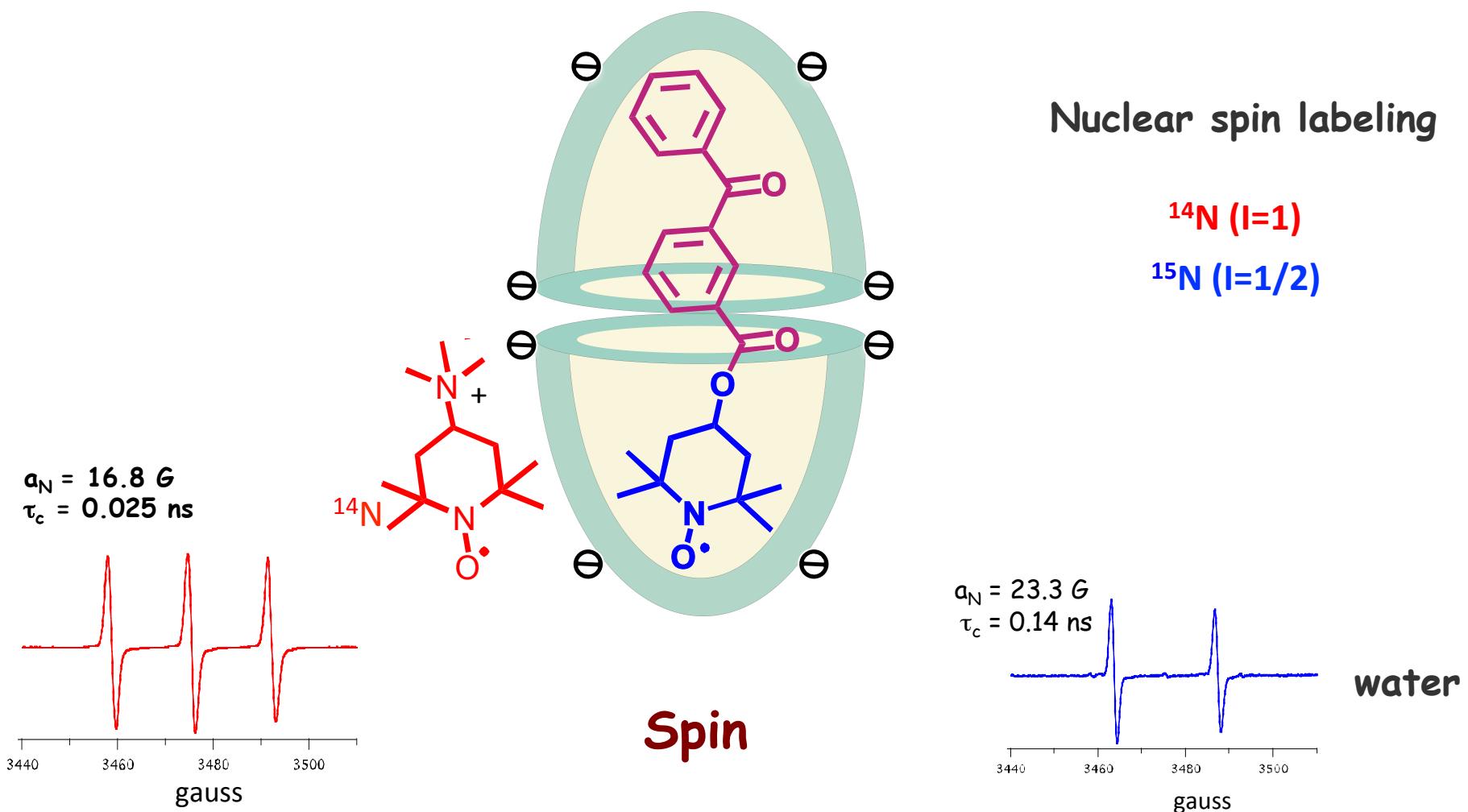
EPR spectrum of mixture of BP- ^{15}NO and ^{14}NO in OA



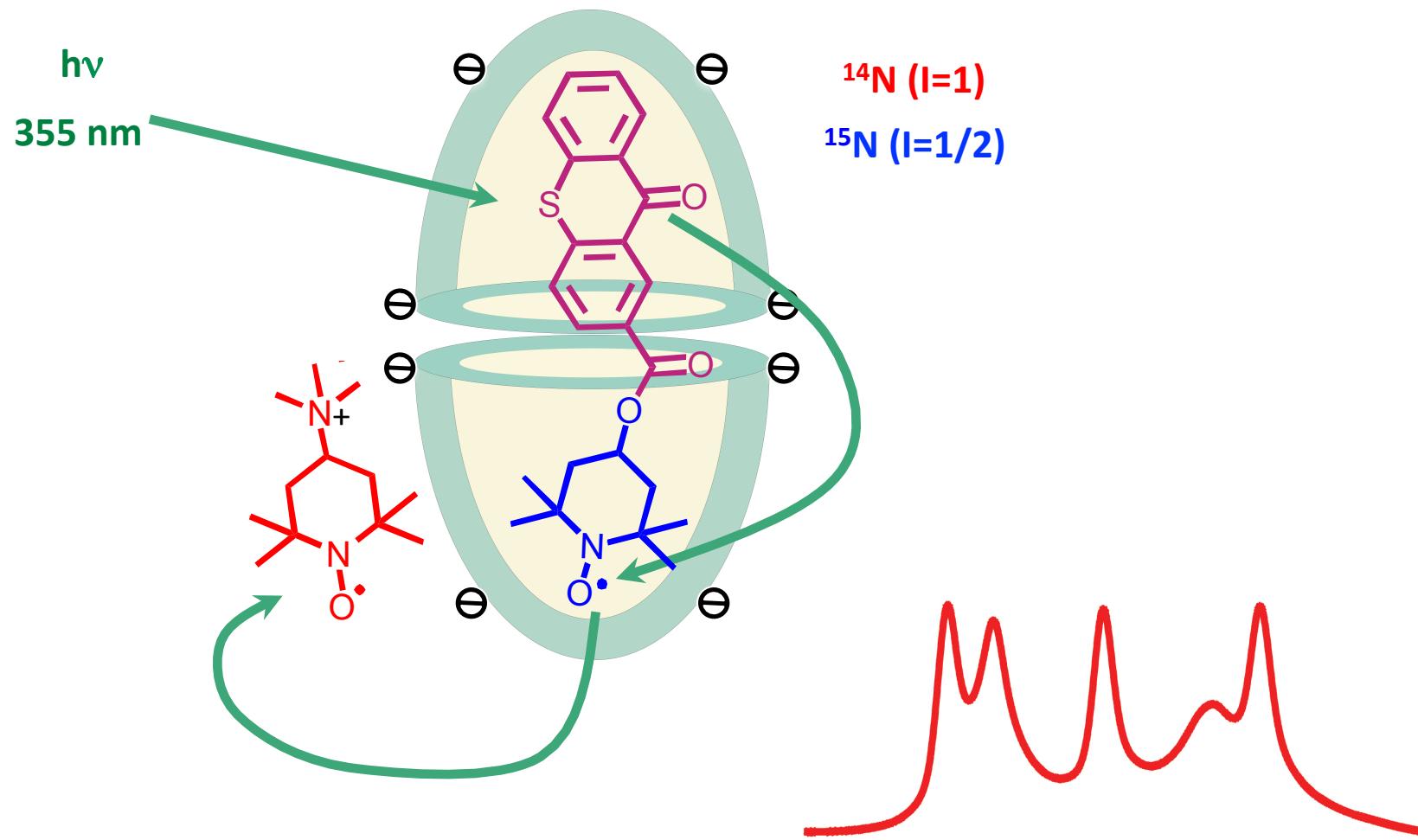
No spin-spin interactions between internal and external guests



Probing the spin-spin interaction between caged and free nitroxides

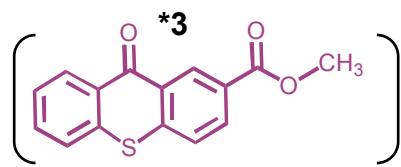
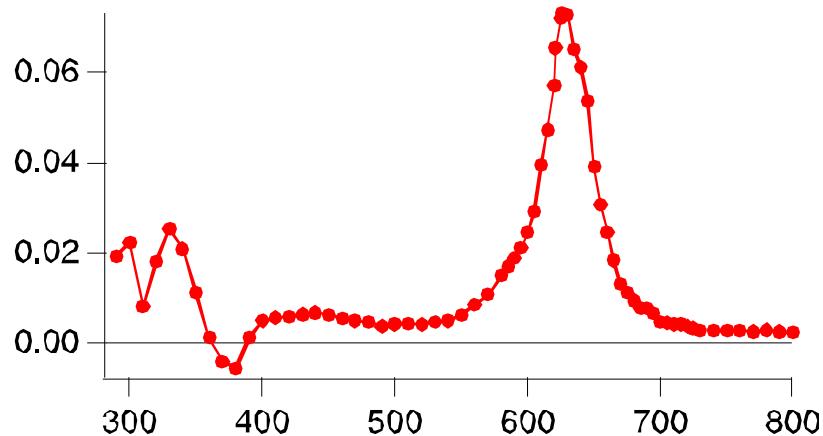


Spin polarization transfer through a molecular wall

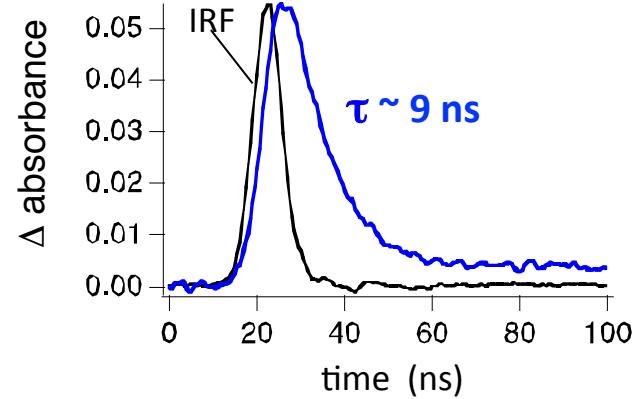
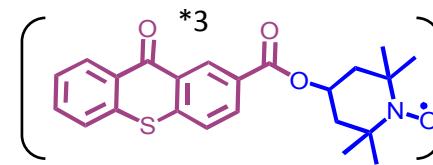
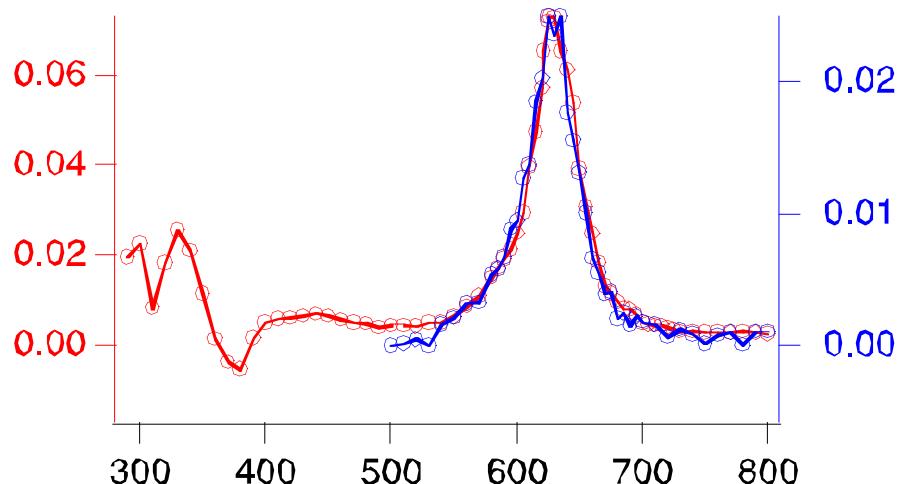
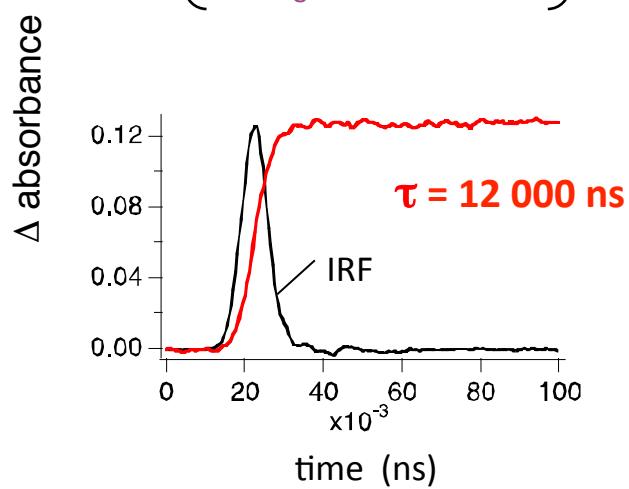


Interaction of spin polarized ketone triplets with nitroxide

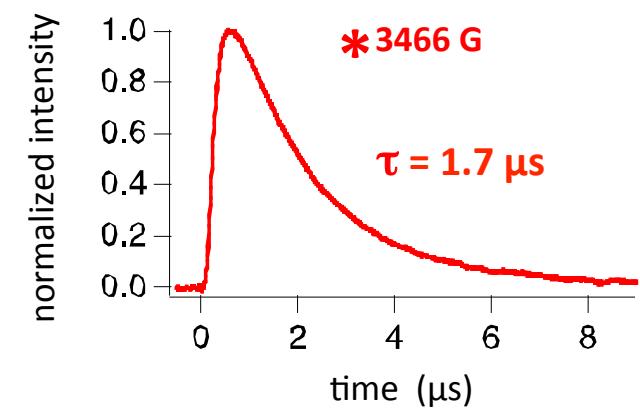
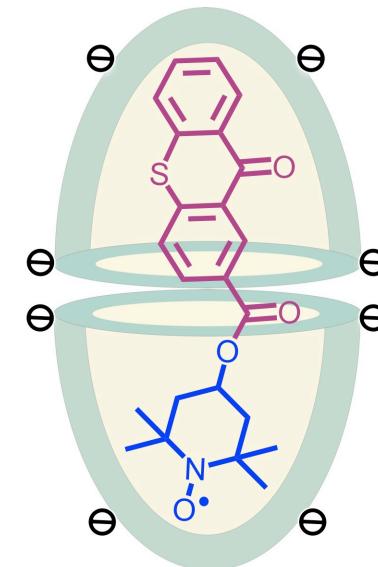
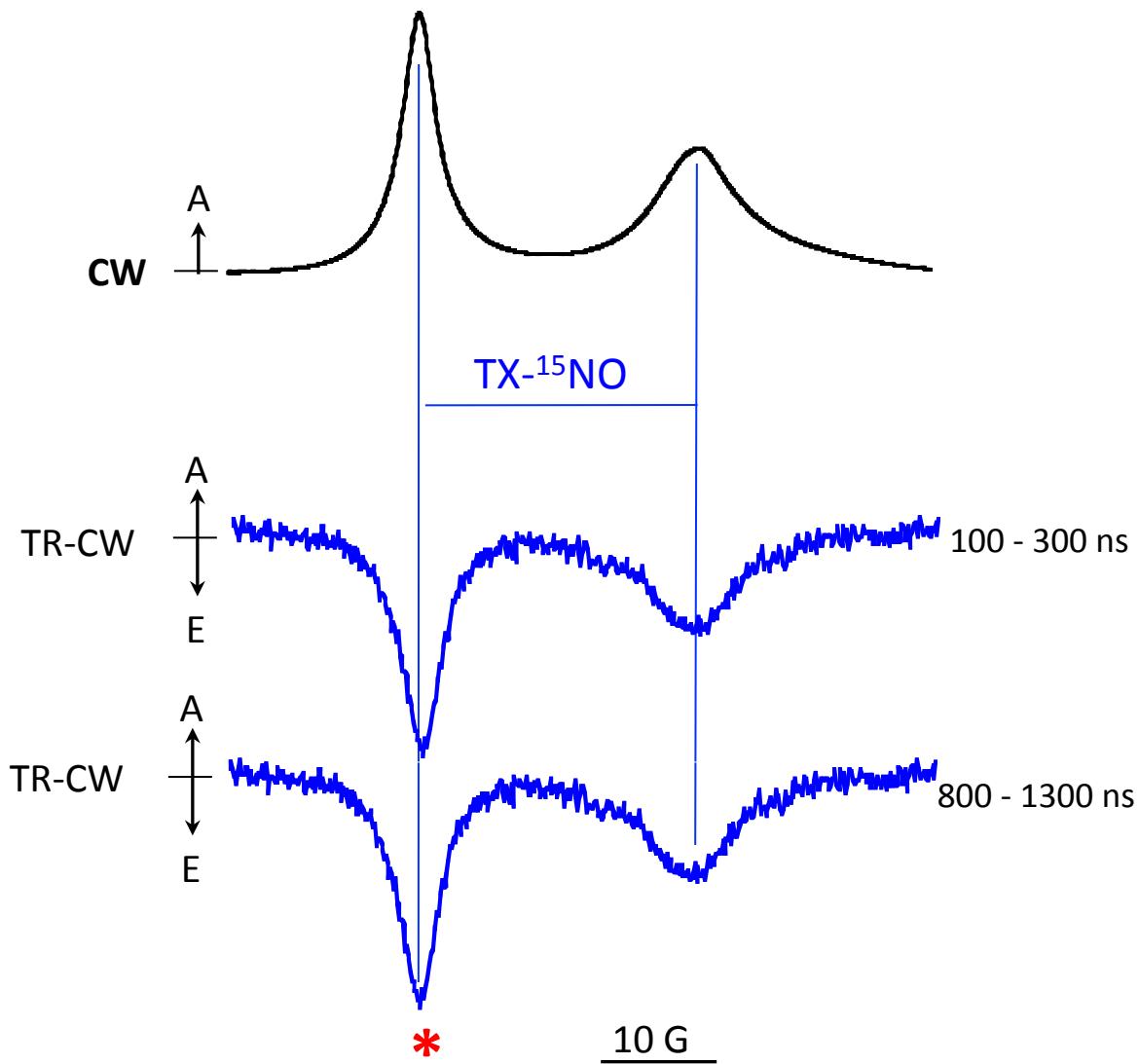
Acetonitrile solution



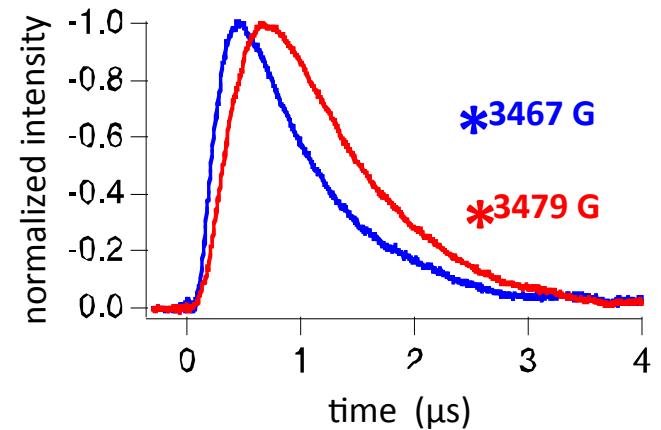
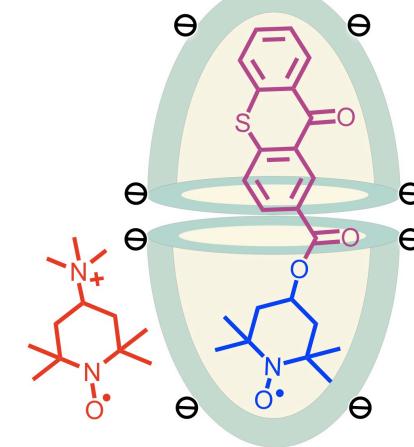
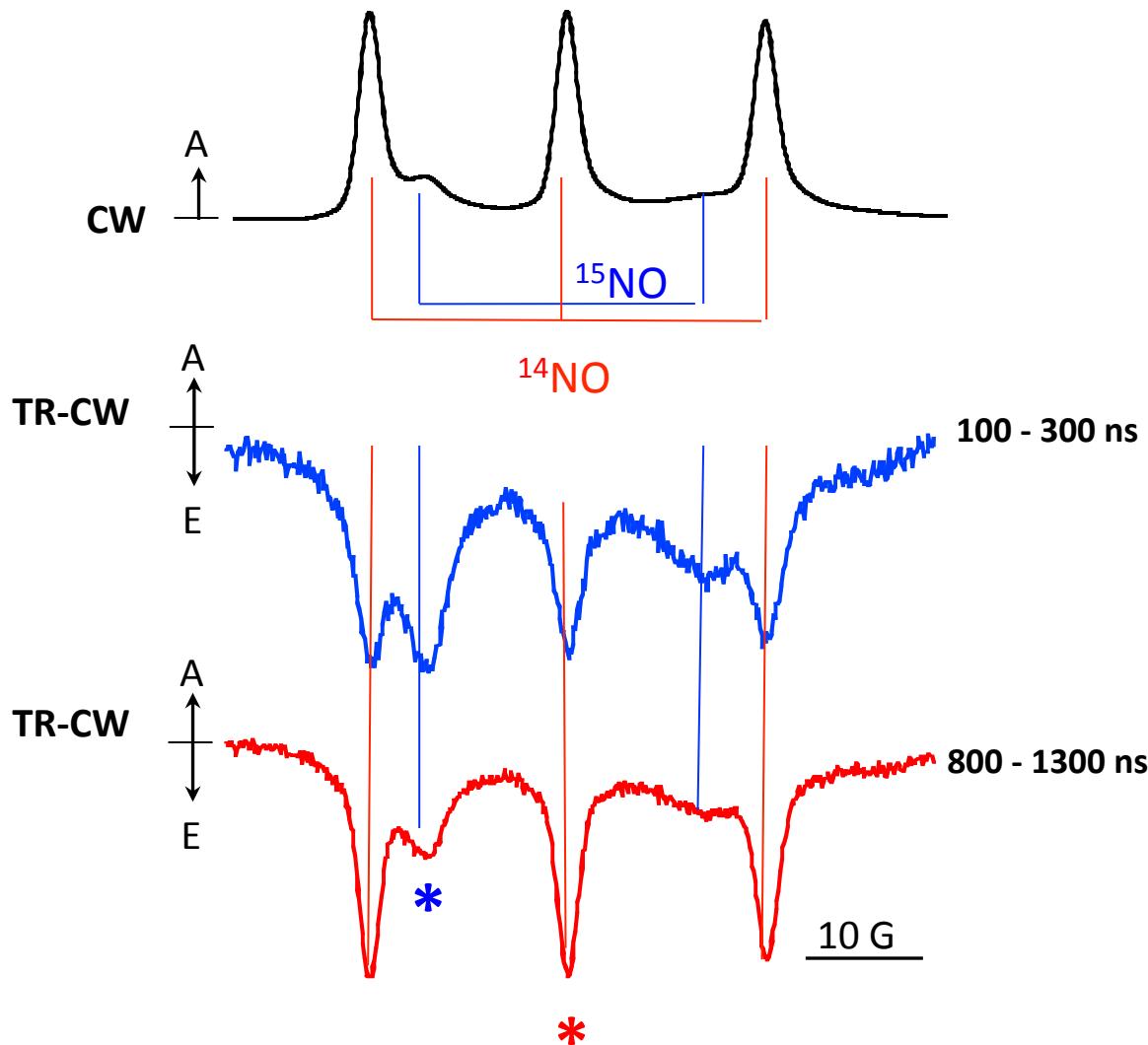
$\lambda_{\text{obs}} = 625 \text{ nm}$



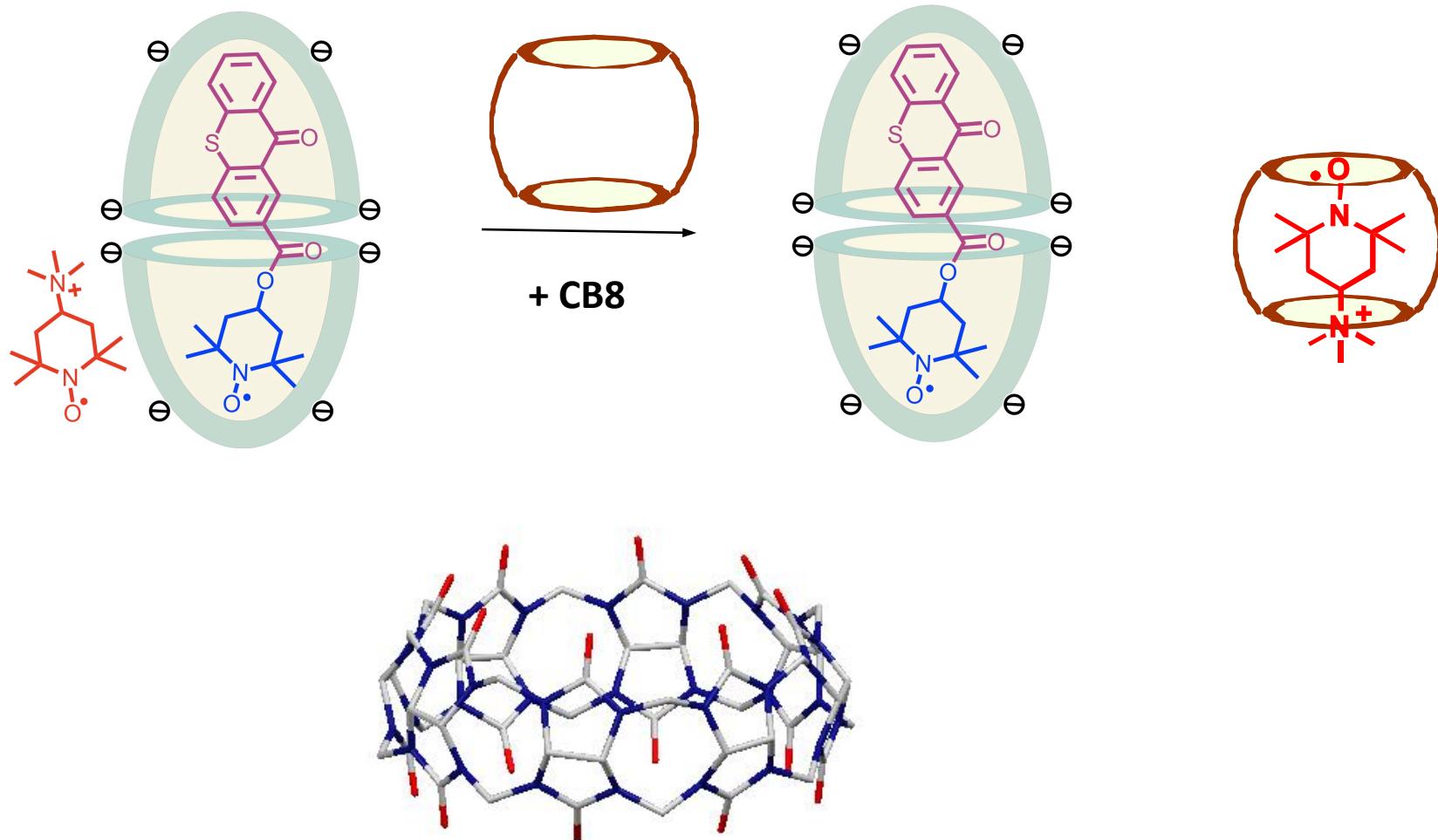
Spin polarization of TX-¹⁵NO@OA



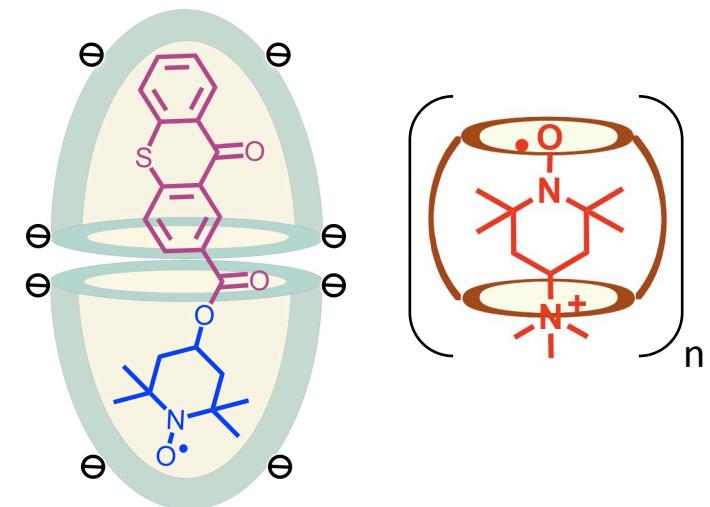
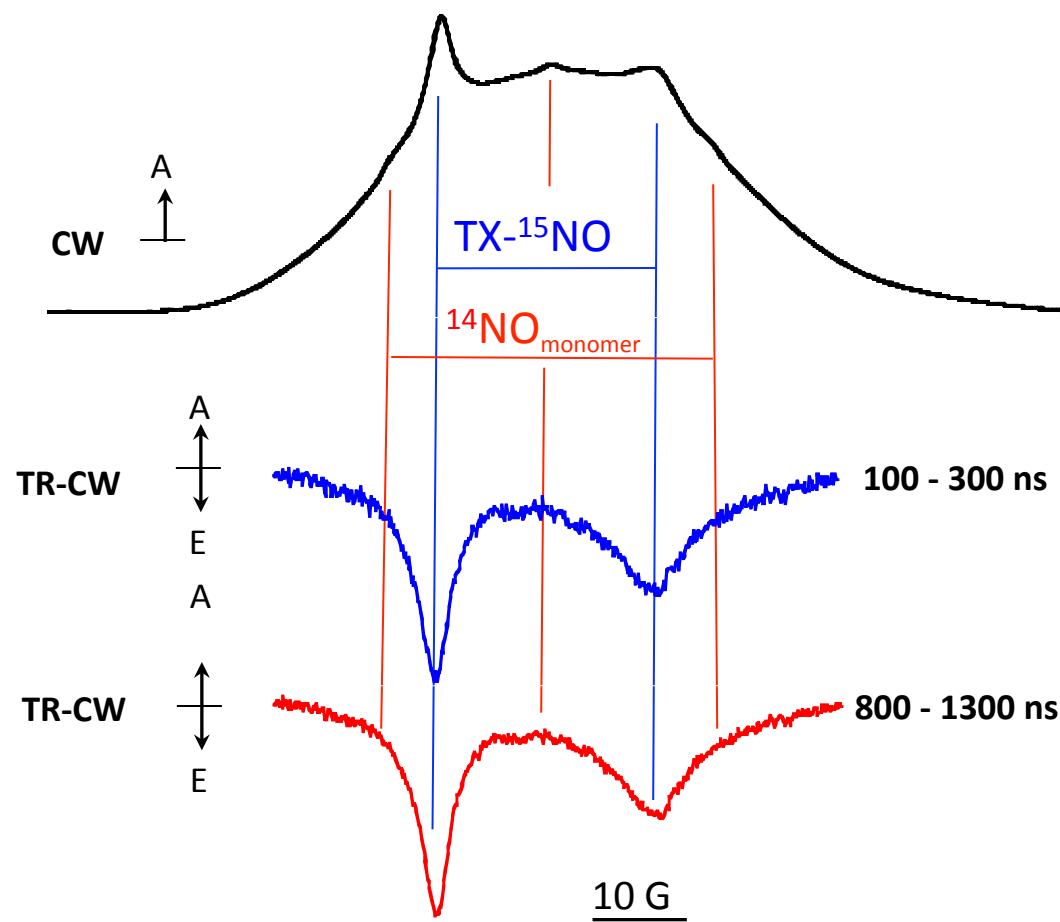
Spin polarization transfer from TX- ^{15}NO to ^{14}NO



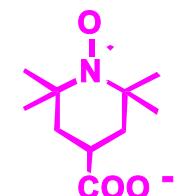
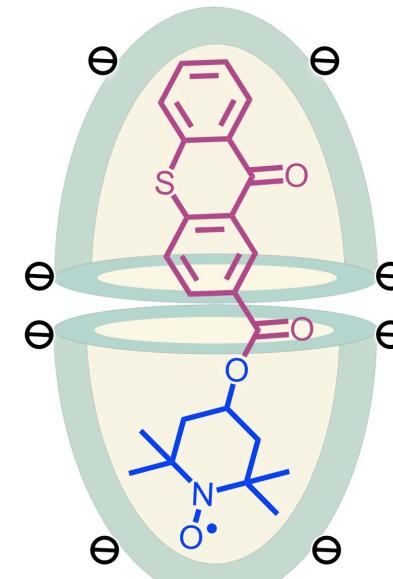
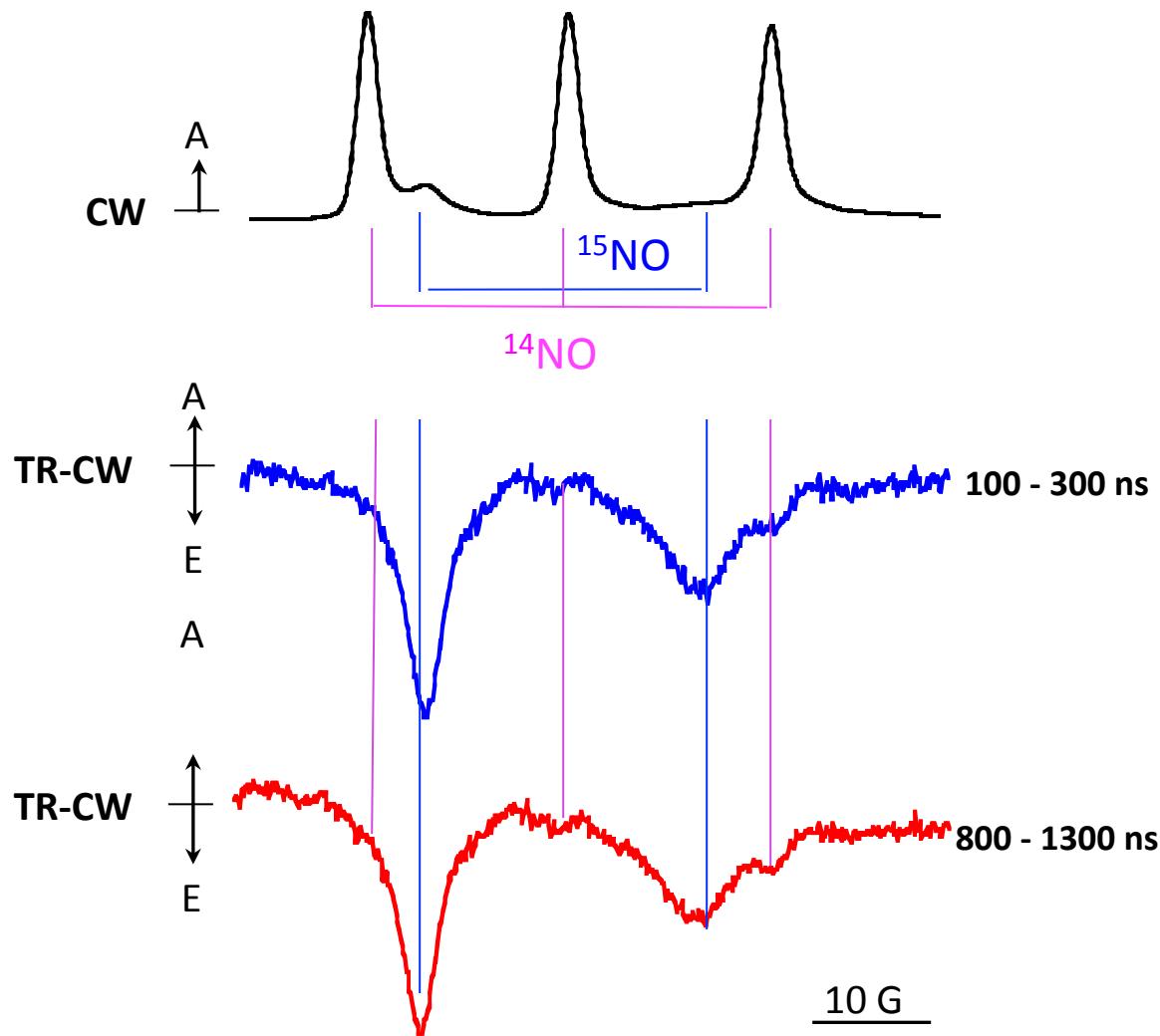
Turning spin polarization transfer off by trapping of external guest with CB[8]



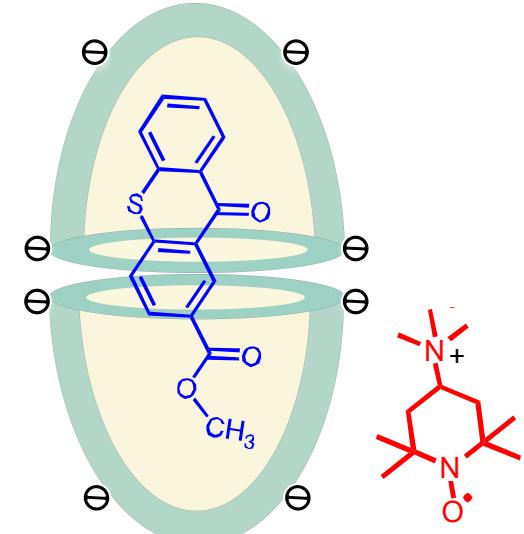
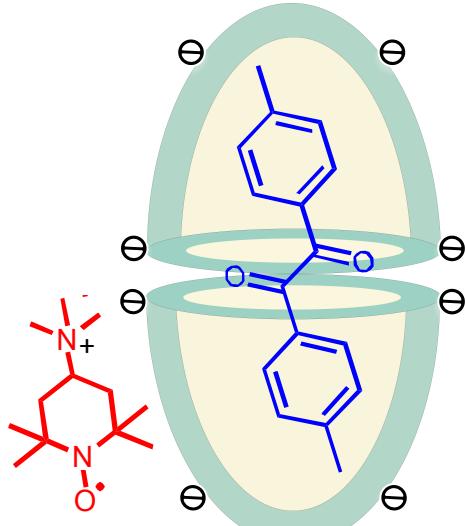
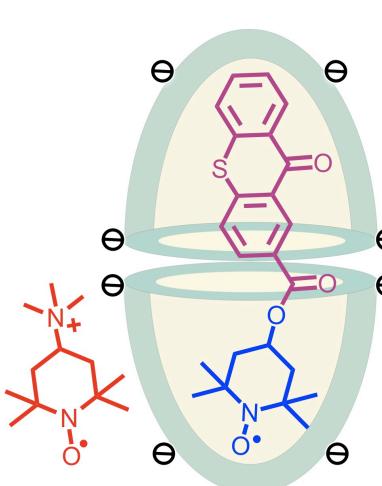
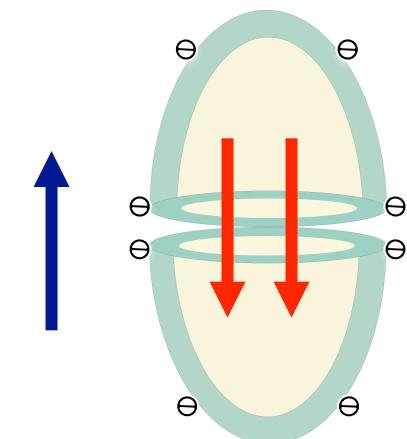
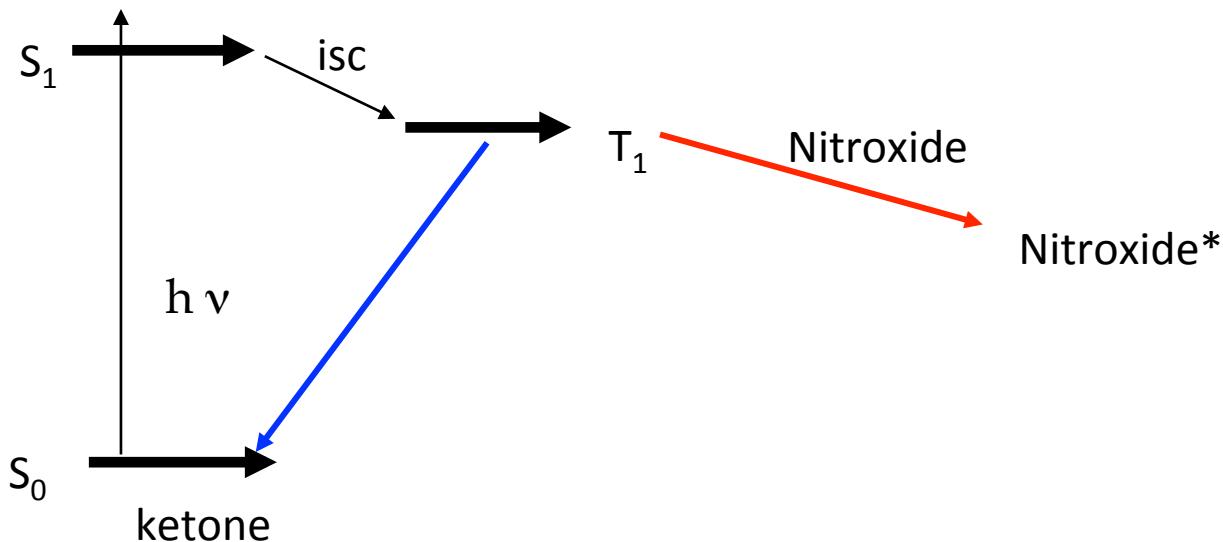
Turning spin polarization transfer off by trapping external guest with CB[8]



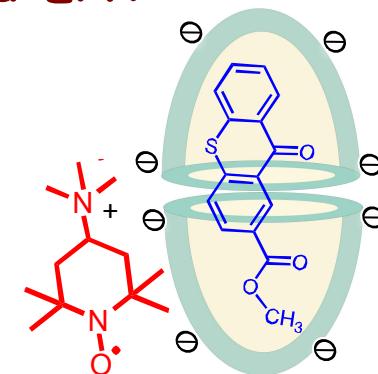
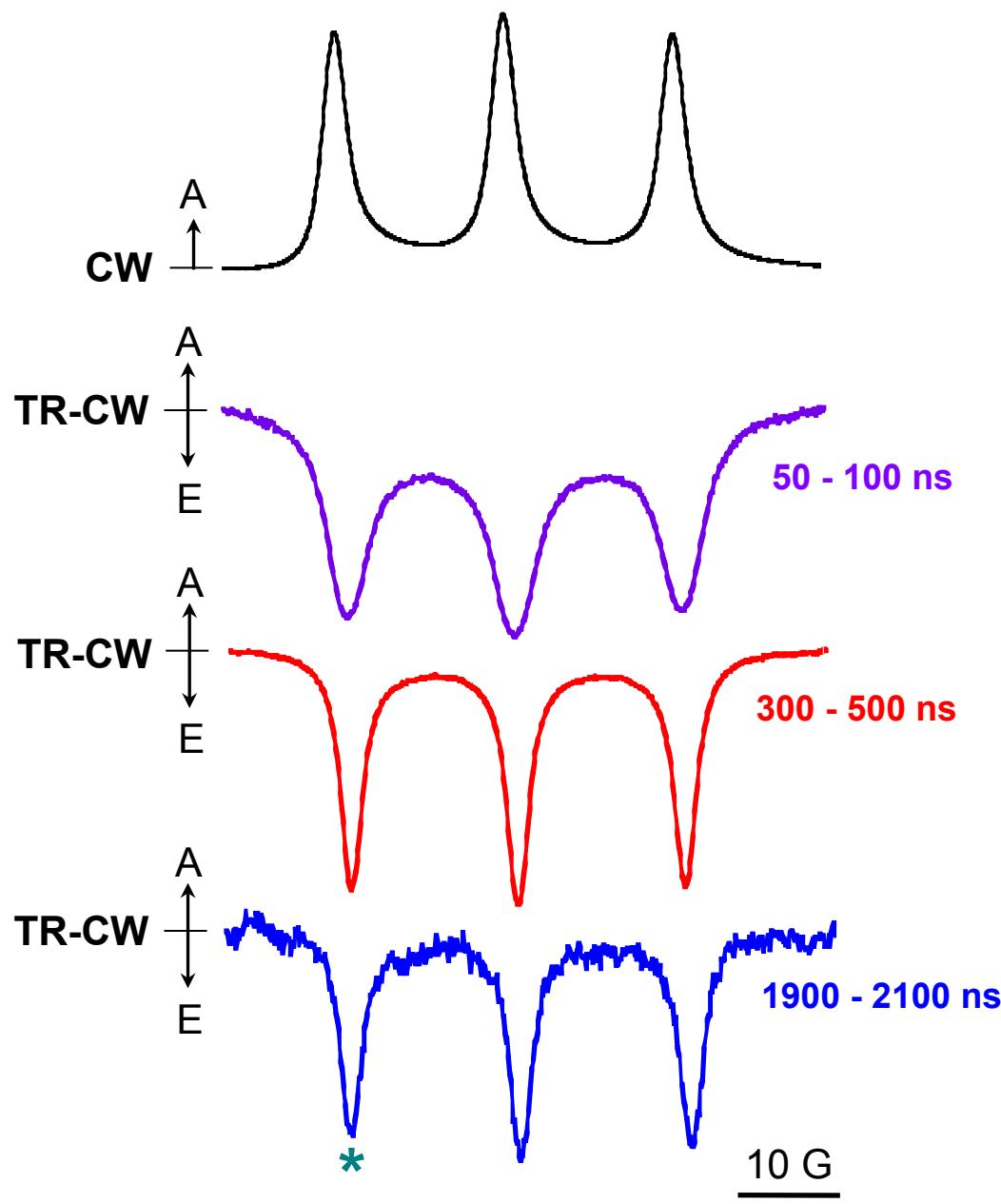
No spin polarization transfer from TX- ^{15}NO to $^{14}\text{NO}^\ominus$



Spin communication between the triplet state of the confined guest and nitroxide

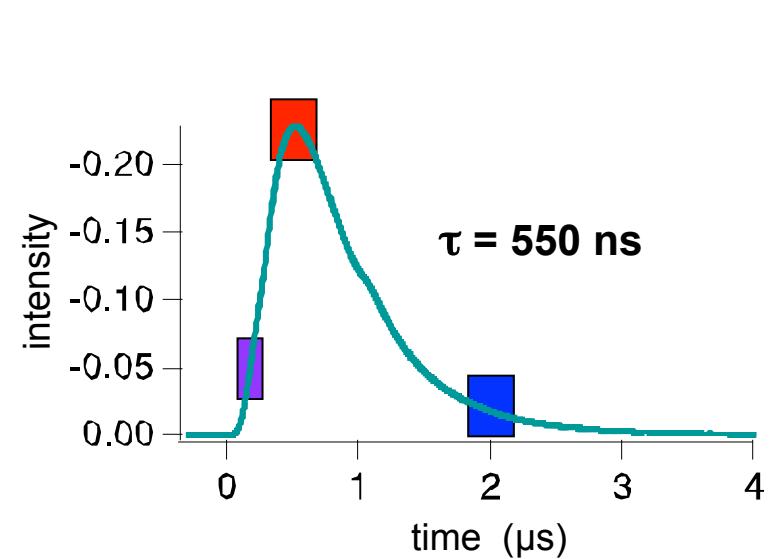


Spin polarization transfer monitored by time-resolved EPR

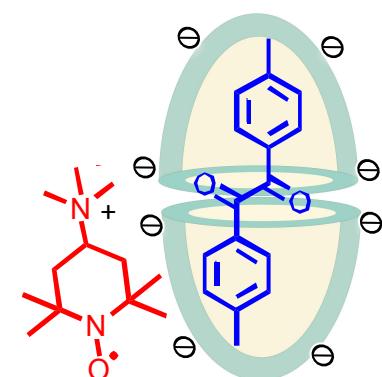
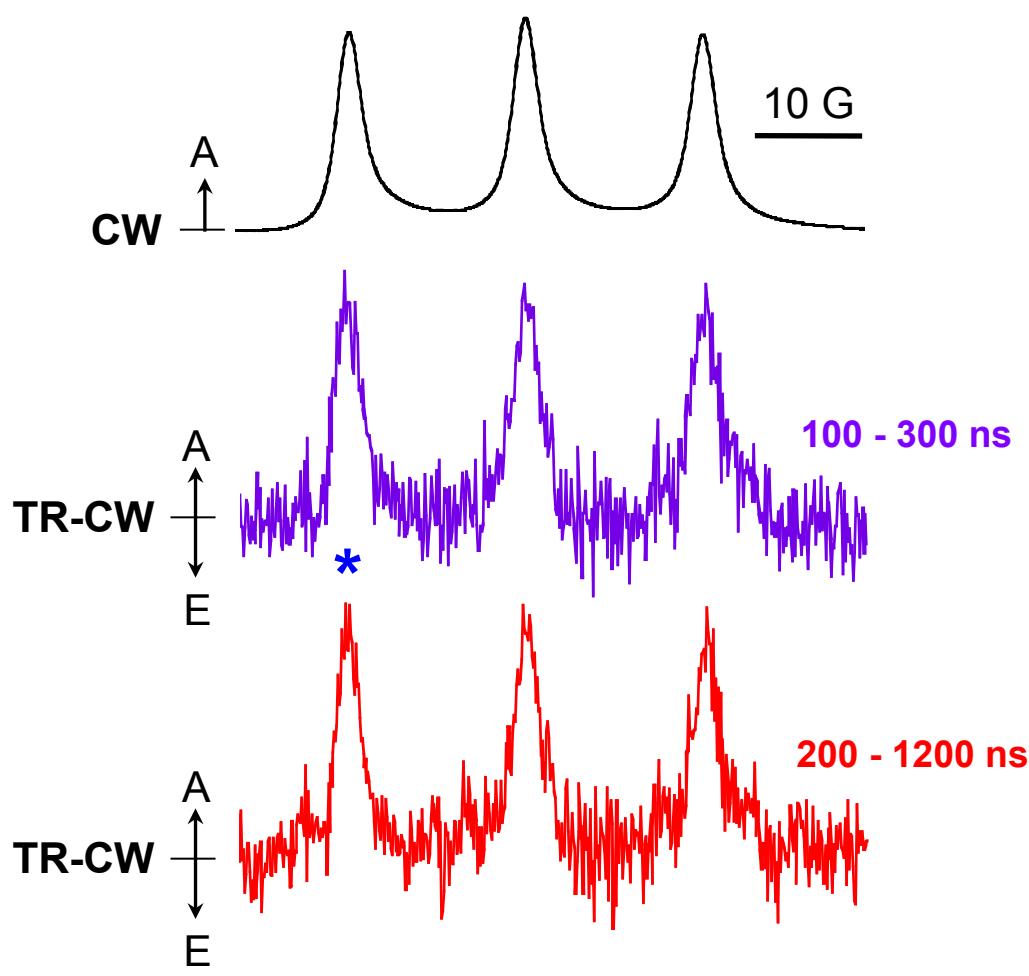


$\lambda_{\text{ex}} = 355 \text{ nm}$

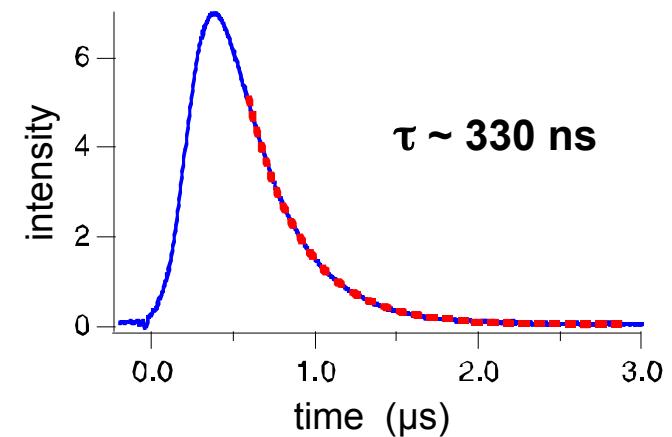
TX-COOMe = 0.5 mM
OA = 1 mM
NO⁺ = 10 mM



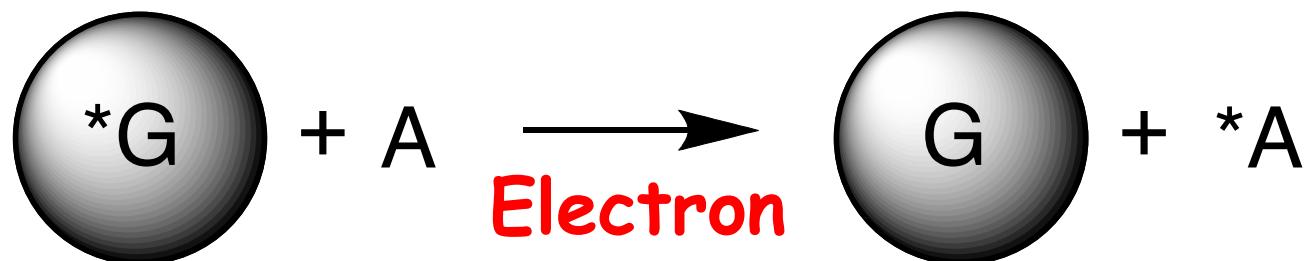
Time-resolved EPR (CIDEP)



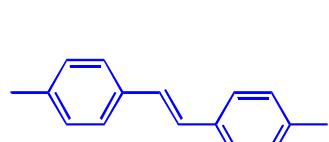
$\lambda_{ex} = 308 \text{ nm}$
DMB = 0.5 mM
OA = 1 mM
CAT1 = 10 mM



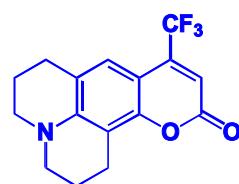
Energy transfer between confined and free molecules



Donors



4,4' -Dimethyl stilbene



Coumarin 153
(C 153)



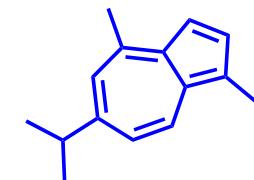
Coumarin 480
(C 480)



Coumarin 1
(C 1)

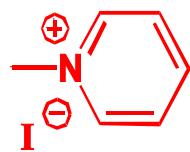


Azulene

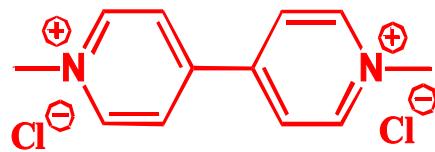


Guiazulene

Acceptors



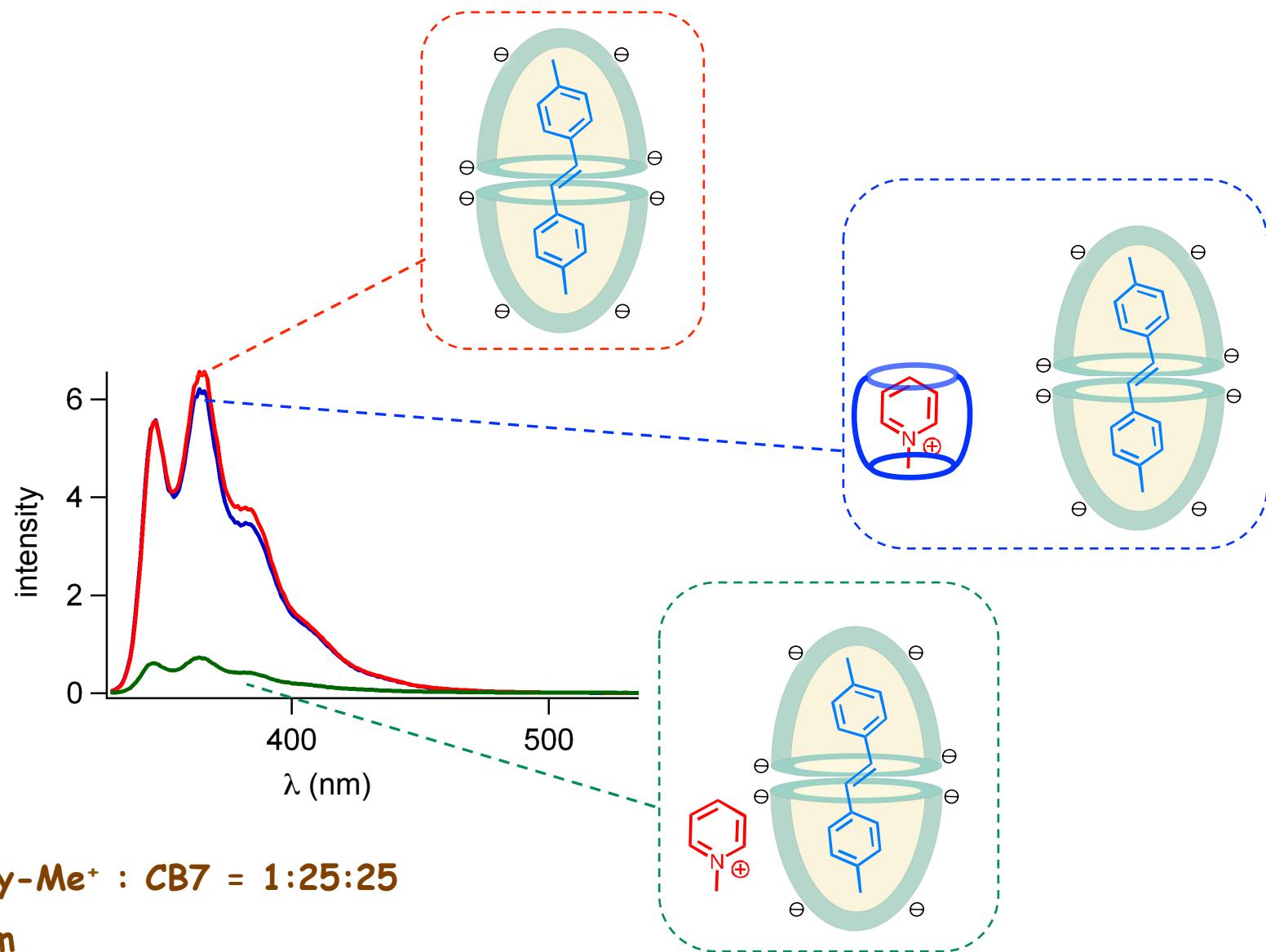
N-Methyl pyridinium
Iodide



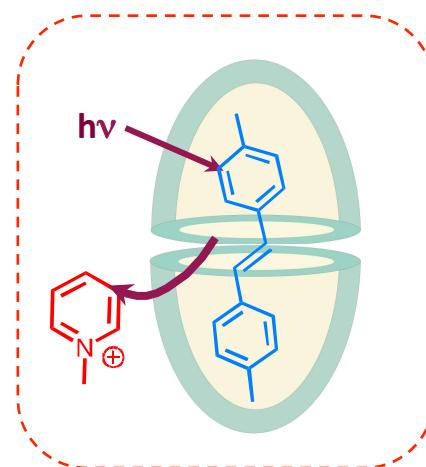
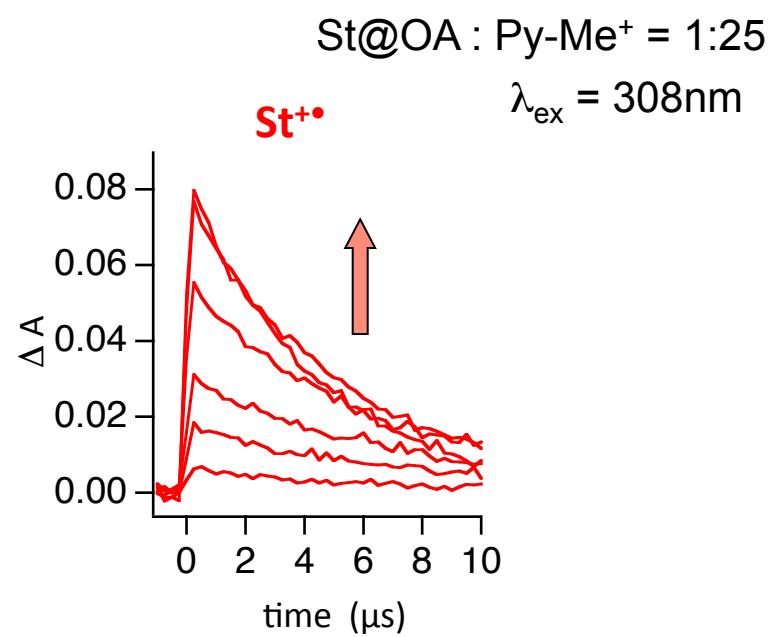
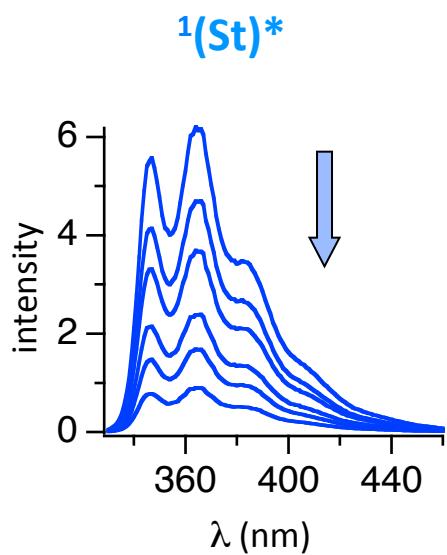
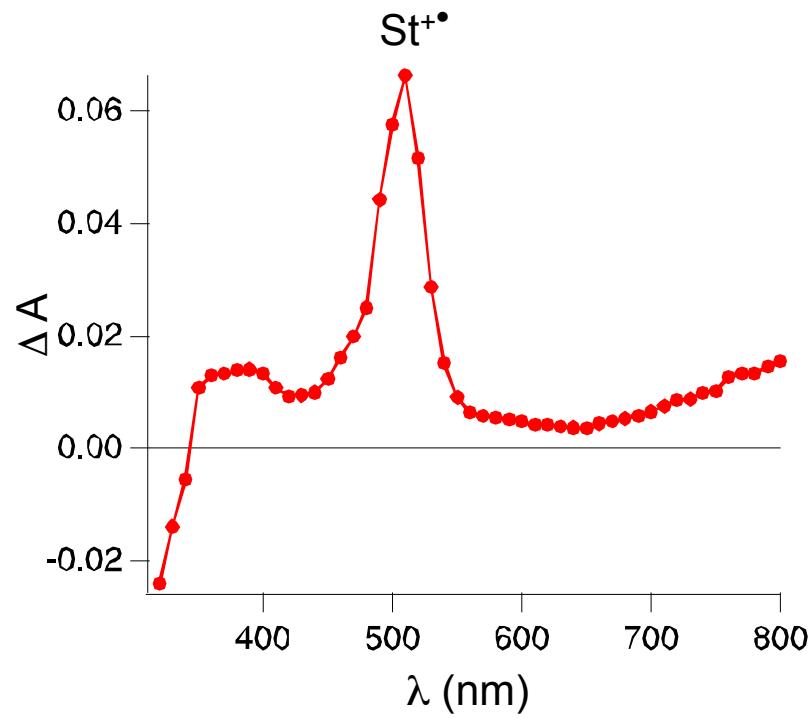
Methyl viologen
dichloride



Fluorescence (S_1) quenching: Possibility of electron transfer



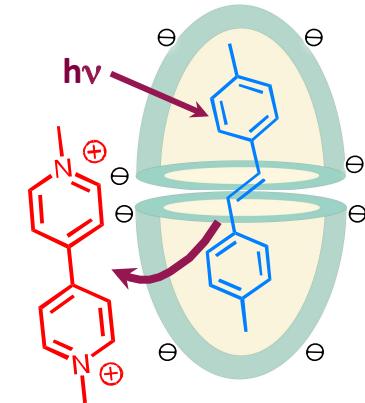
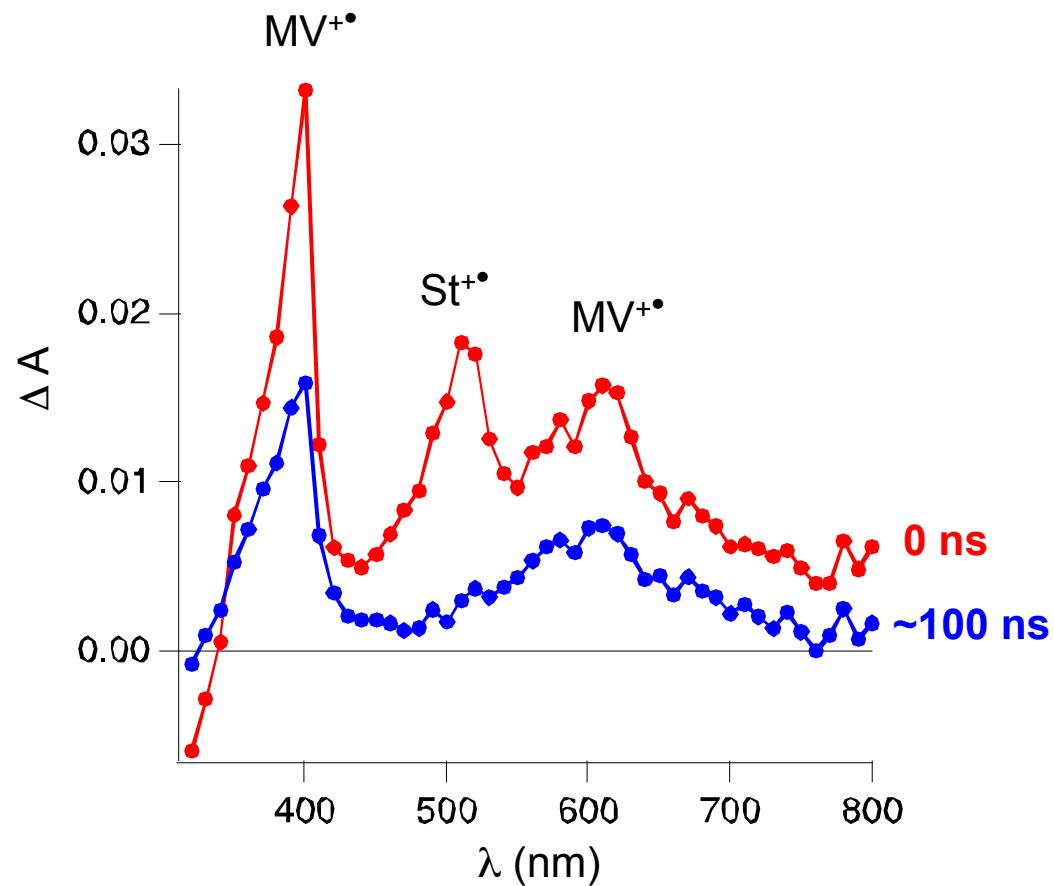
Laser Flash Photolysis of St@OA\Py-Me⁺



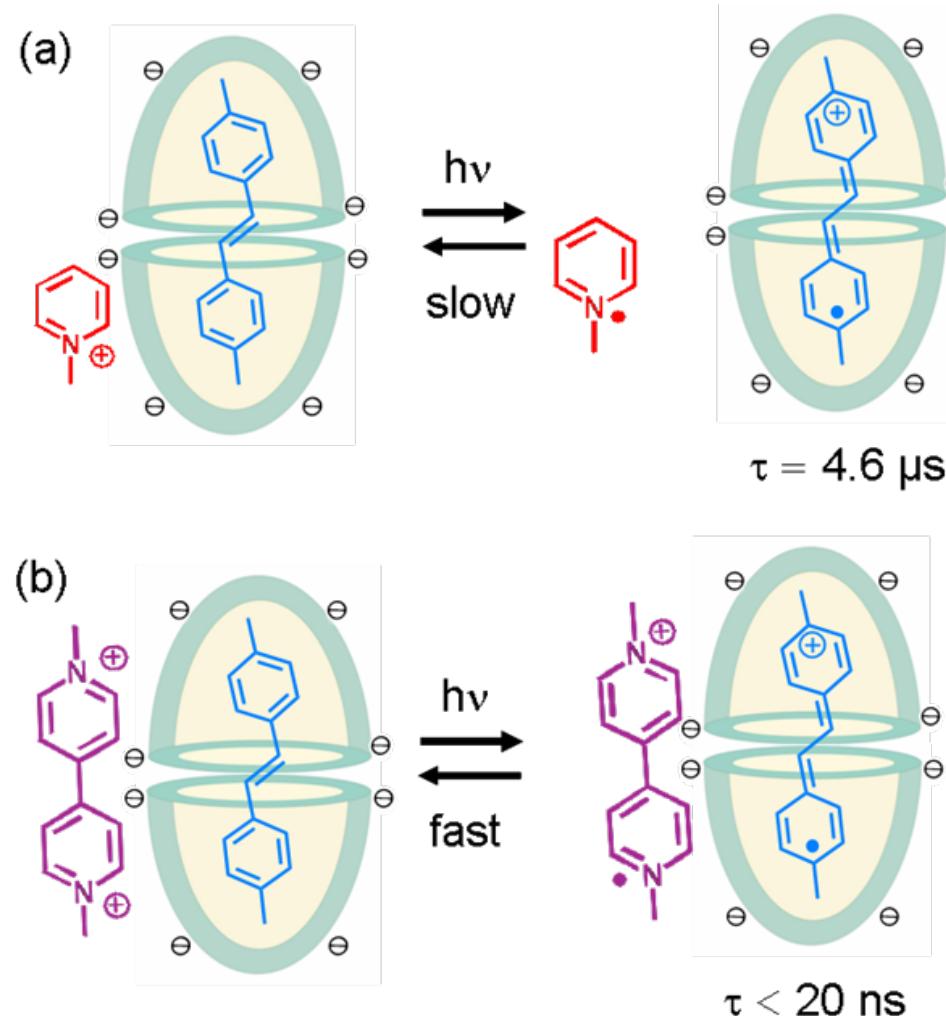
Laser Flash Photolysis of St@OA/MV²⁺

St@OA : MV²⁺ = 1:2

$\lambda_{ex} = 308 \text{ nm}$

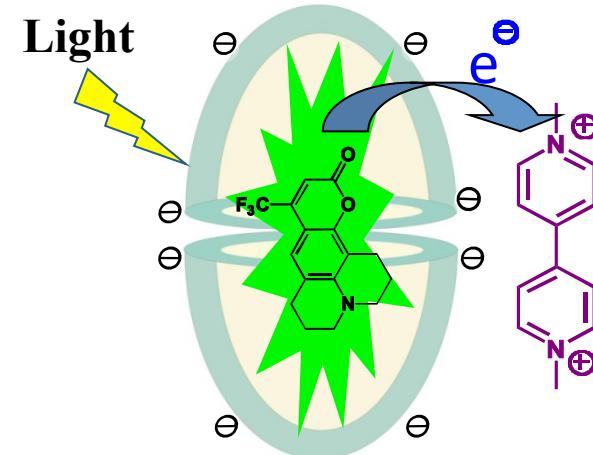
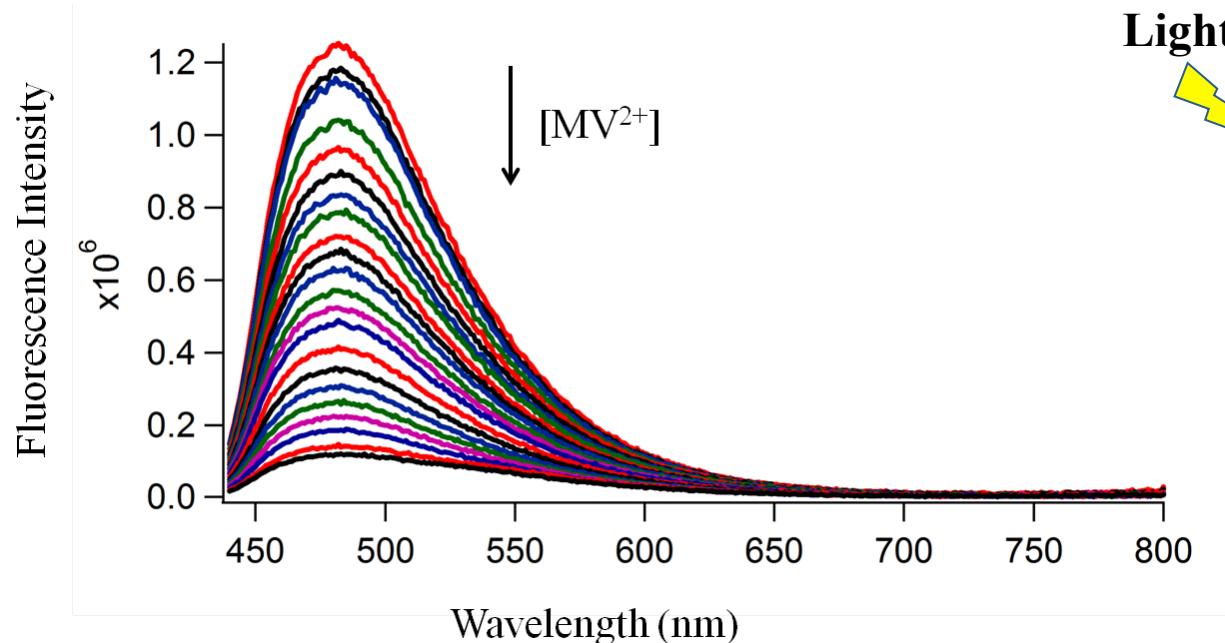


Back electron transfer increases with charge attraction

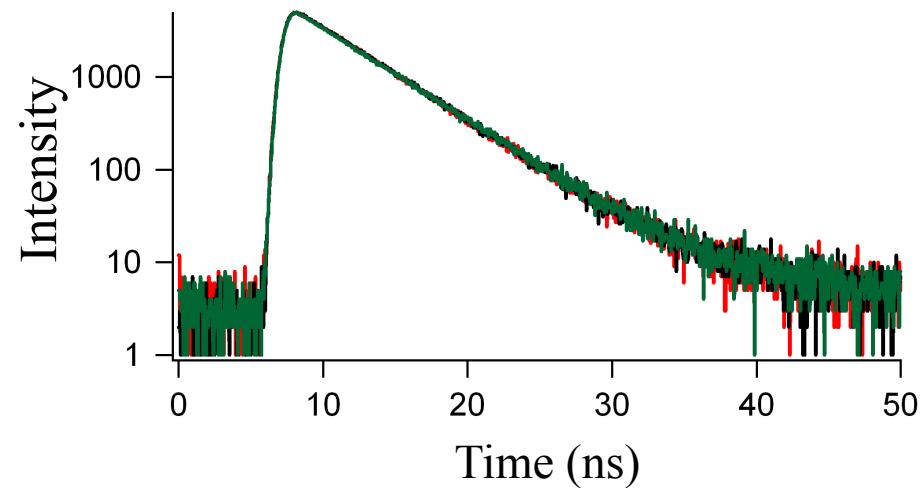


Fluorescence titration of C153@OA₂ with MV²⁺

Steady state:

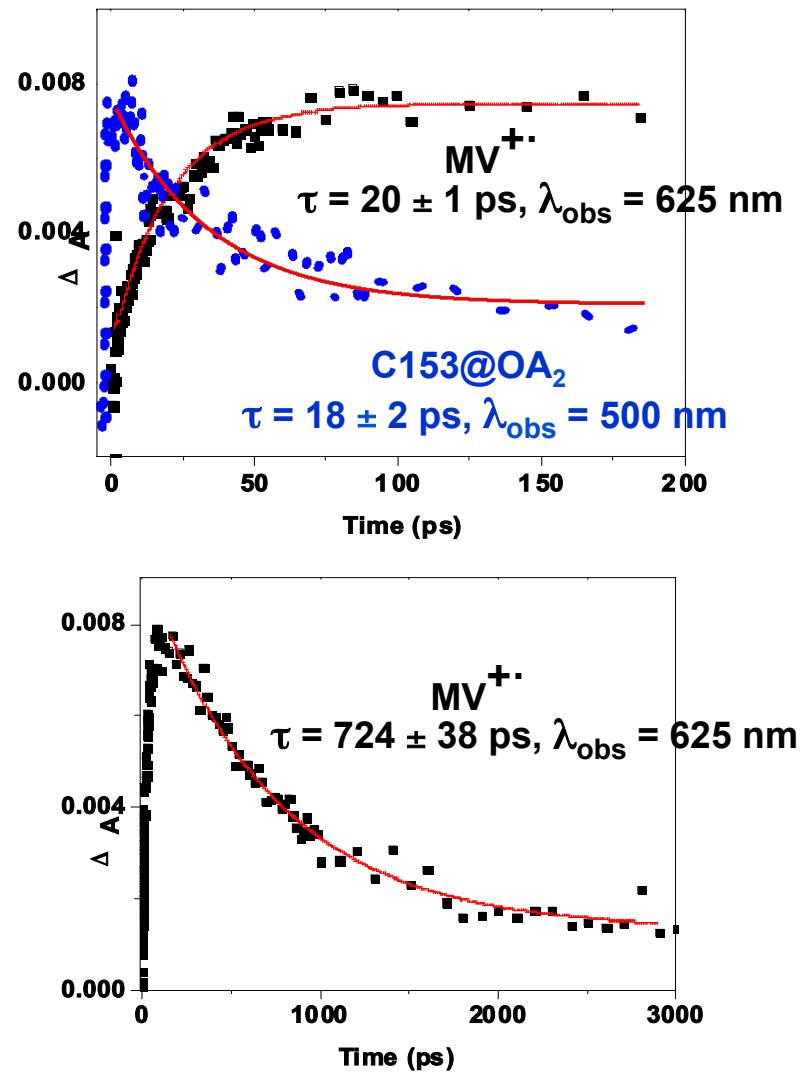
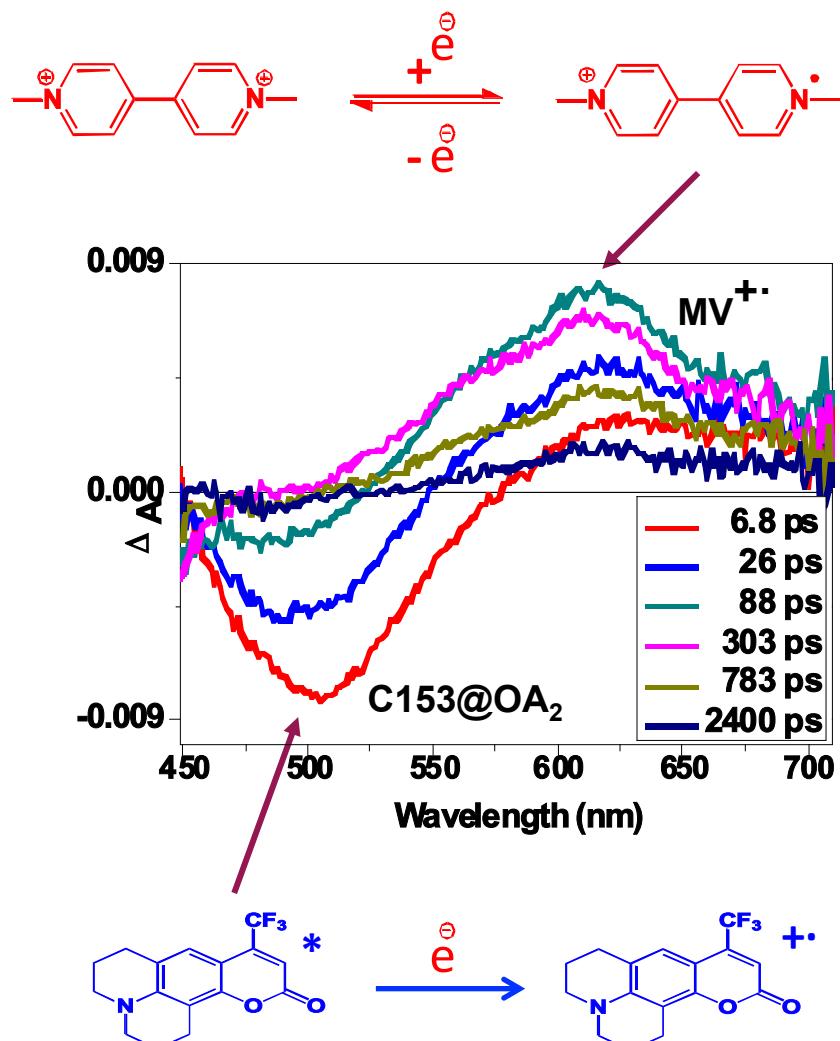


Time resolved:



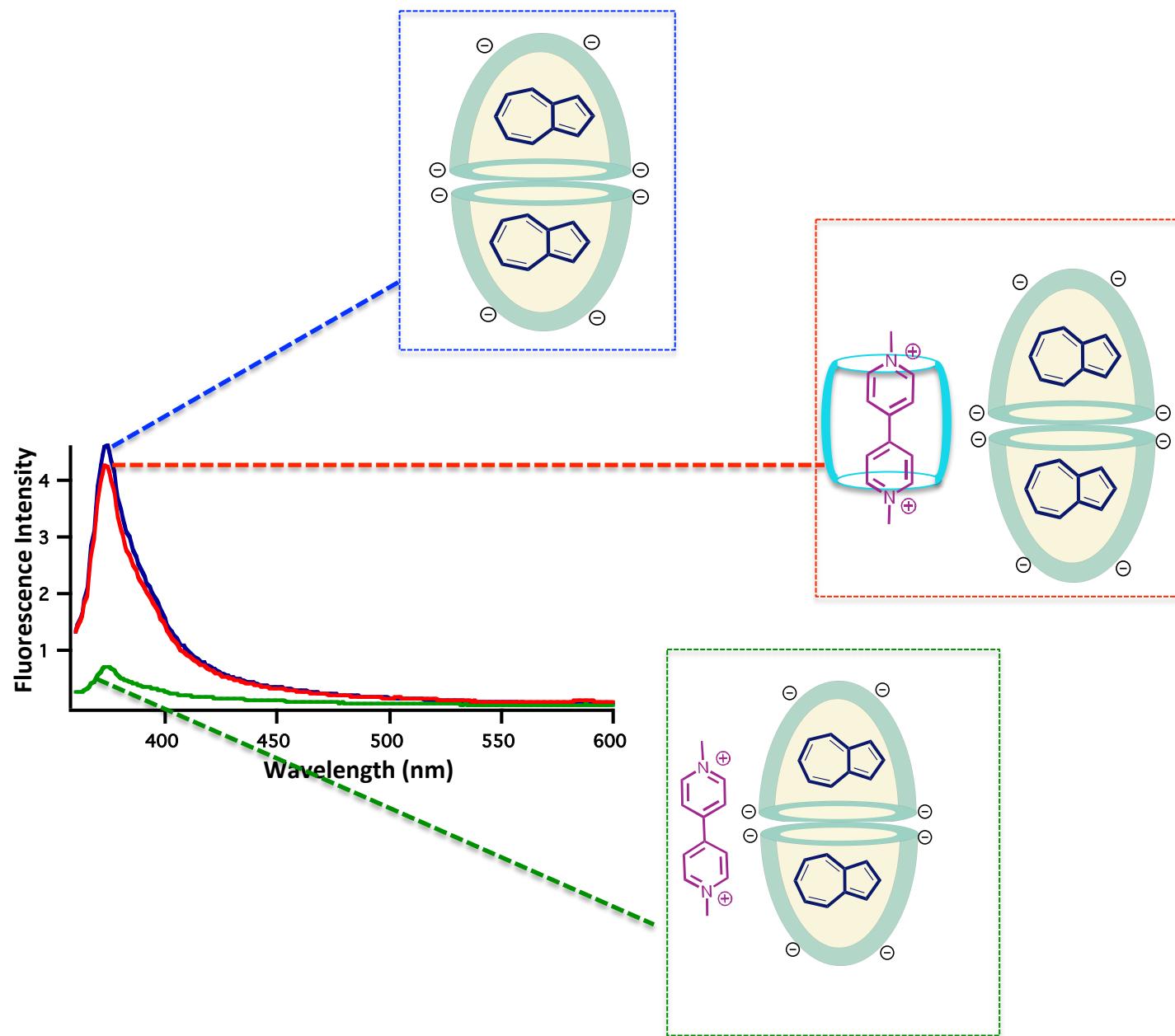
Transient absorption of C153@OA₂ with MV²⁺ Time Constant for Electron Transfer

$\lambda_{ex} = 390$ nm
pulse width = 150 fs



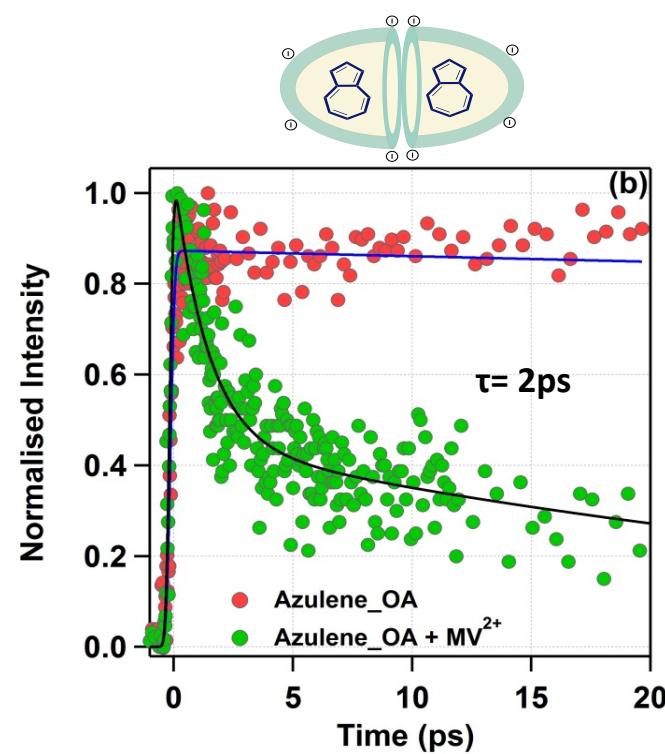
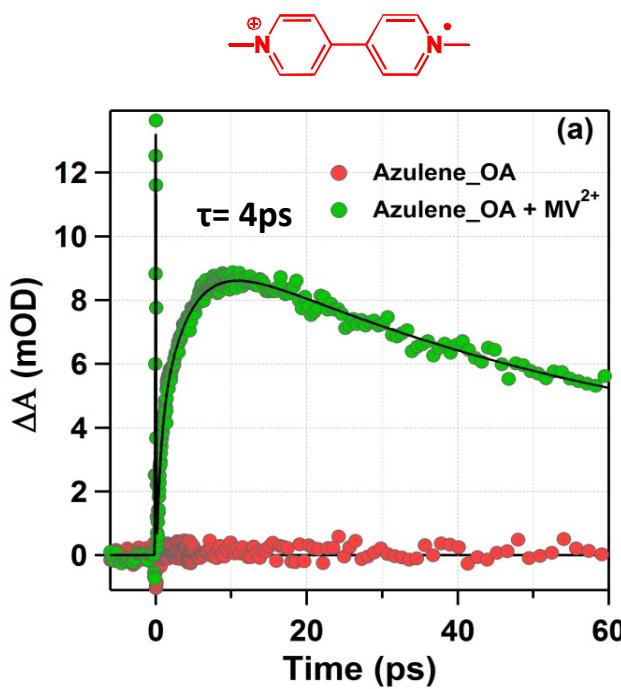
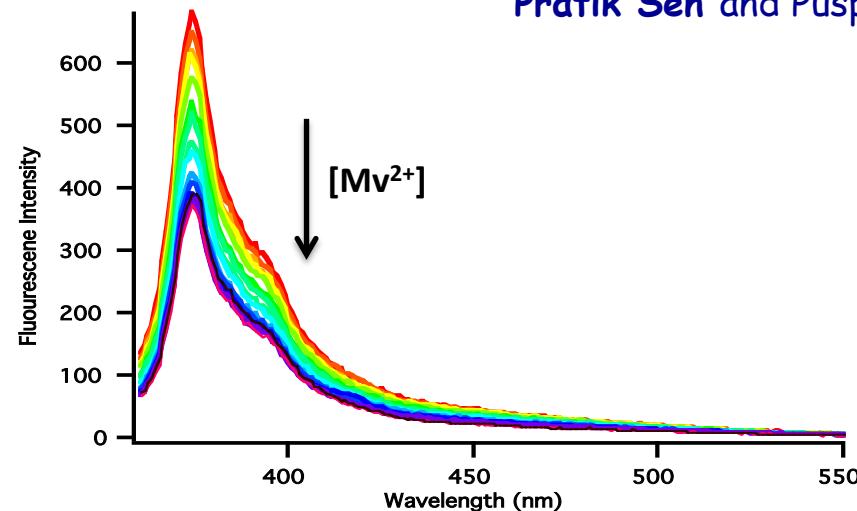
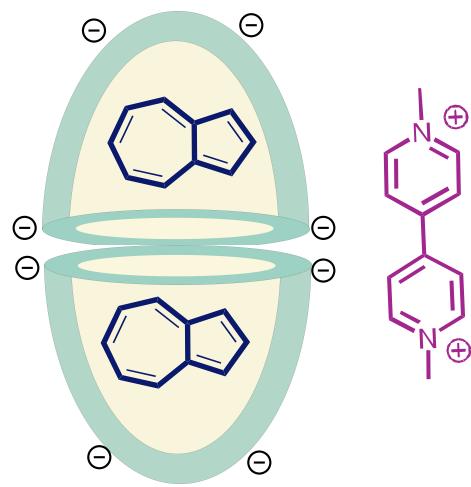
C. Burda and C. H. Chuang

Fluorescence (S_2) quenching: Possibility of electron transfer

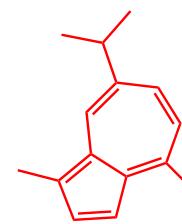
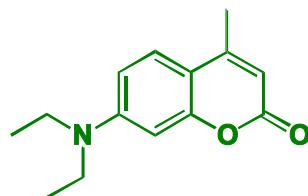
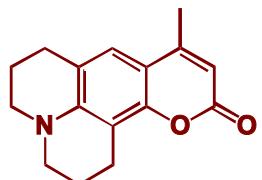
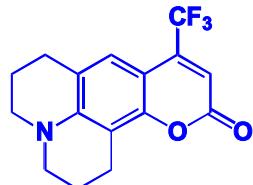


Time Constant for Electron Transfer between Azulene₂*@OA₂ and MV²⁺

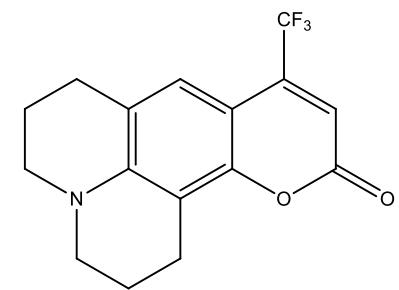
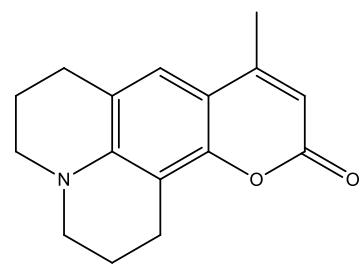
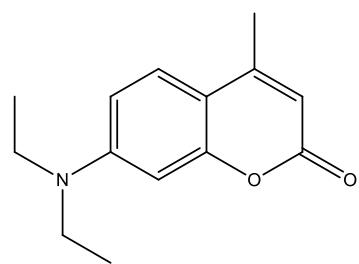
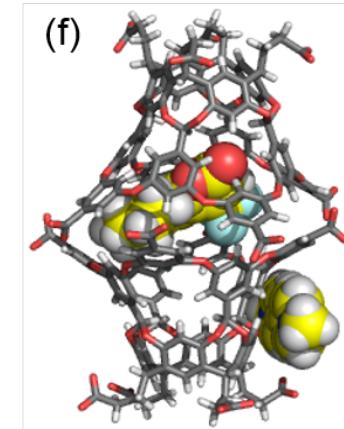
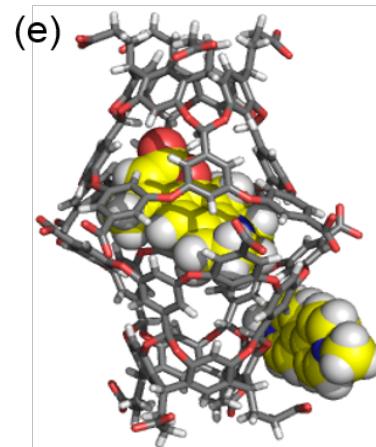
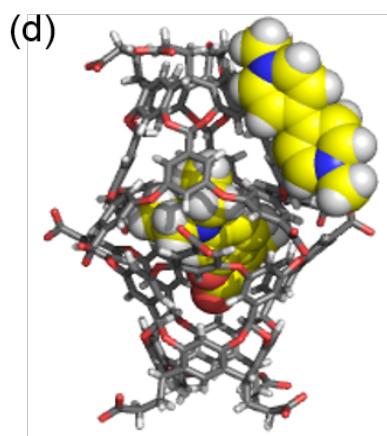
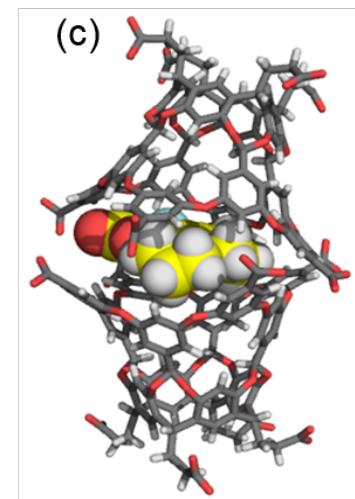
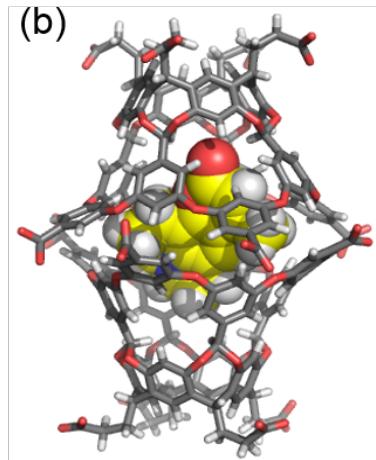
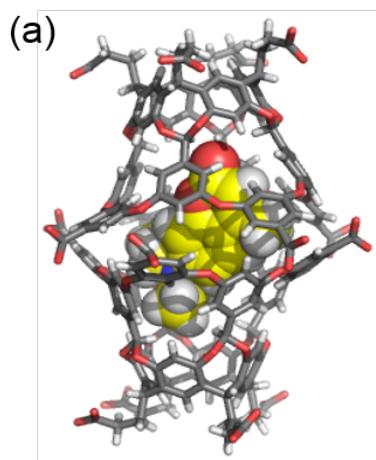
Pratik Sen and Pupal Mukherjee



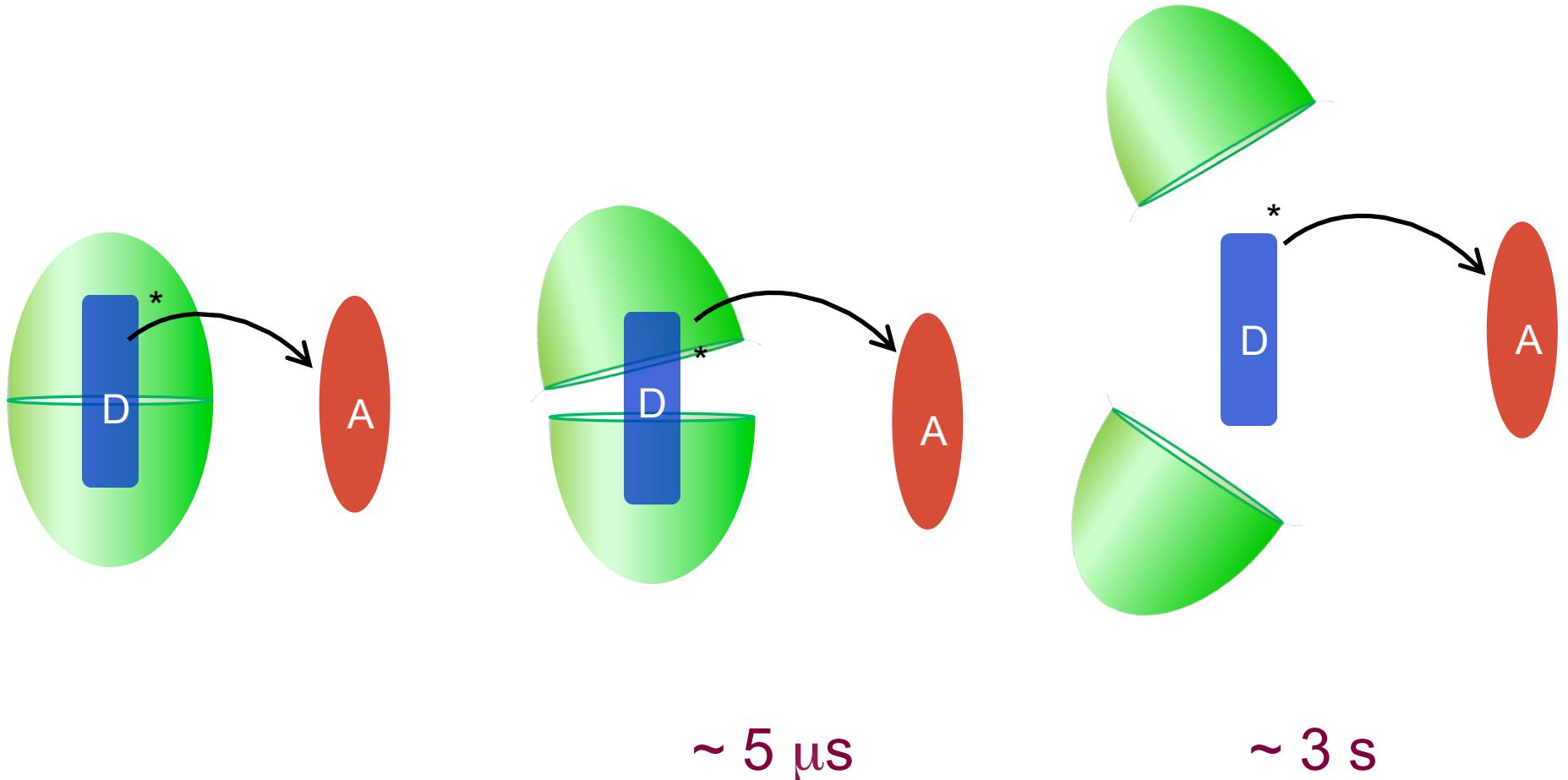
Electron transfer rates from encapsulated guests to methylviologen



Solution	$\text{MV}^{+}\cdot$ (625 nm)	Time constant (τ , ps)
$(\text{C153}@\text{OA}_2) + \text{MV}^{2+}$	Rise	20 ± 0.8
	Decay	724 ± 38
$(\text{C480}@\text{OA}_2) + \text{MV}^{2+}$	Rise	1.2 ± 0.1
	Decay	575 ± 17
$(\text{C1}@\text{OA}_2) + \text{MV}^{2+}$	Rise	2.3 ± 0.3
	Decay	1003 ± 60
$(\text{Azulene}@\text{OA}_2) + \text{MV}^{2+}$	Rise	3.9 ± 0.2
	Decay	55.7 ± 1.6
$(\text{Guiazulene}@\text{OA}_2) + \text{MV}^{2+}$	Rise	3.6 ± 0.3
	Decay	36.9 ± 1.1

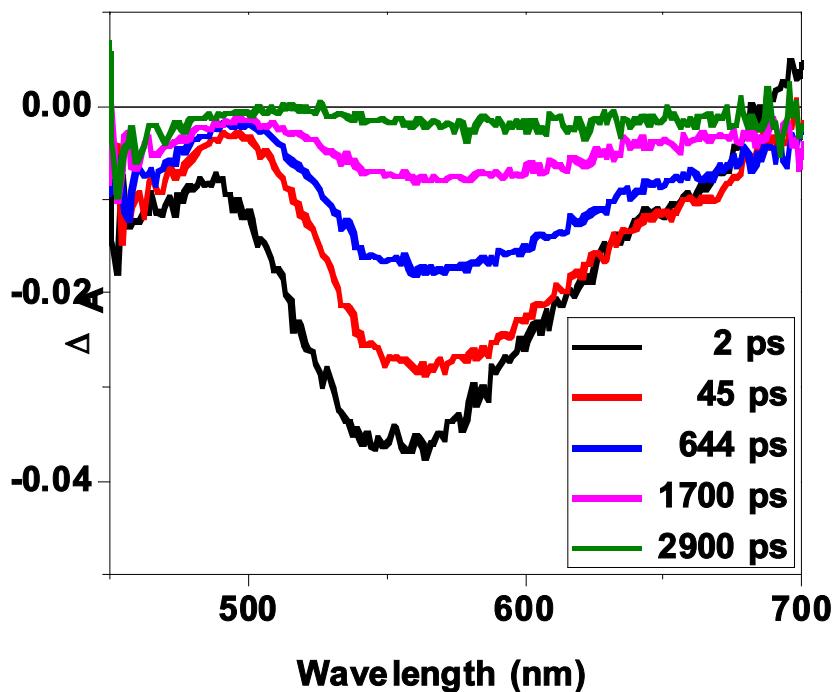


Where is the donor when et occurs?

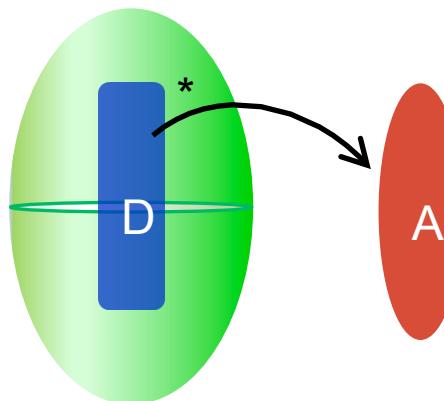
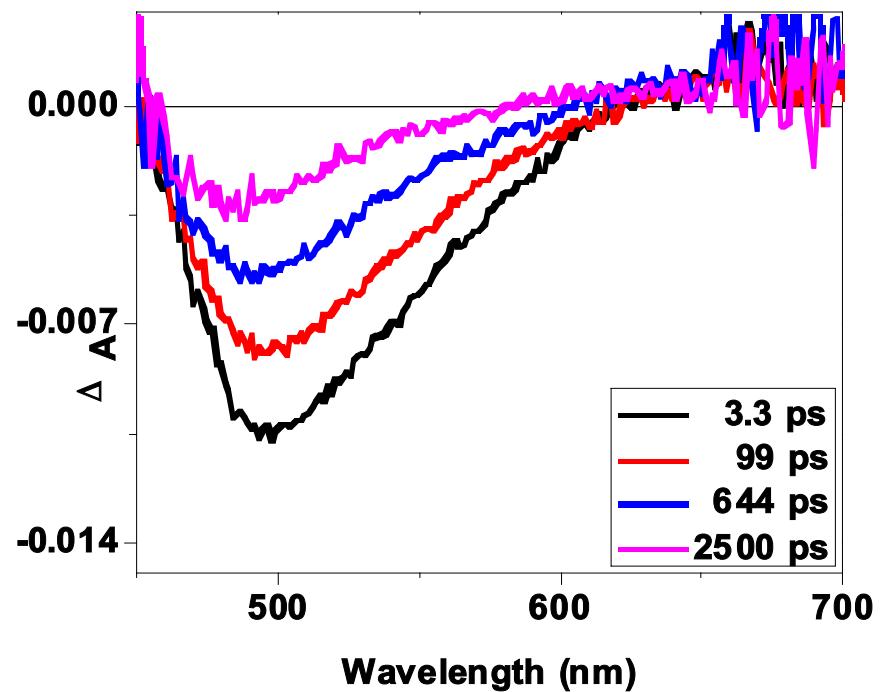


Solvation Dynamics C153 in solution and within OA_2

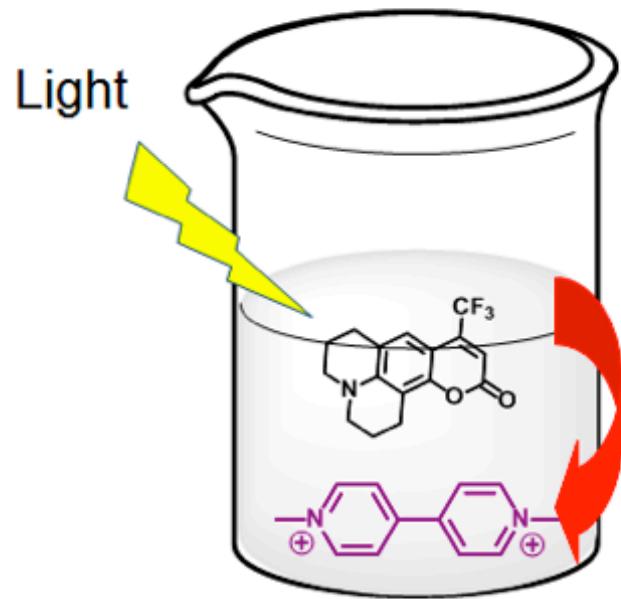
In Solution



Within OA



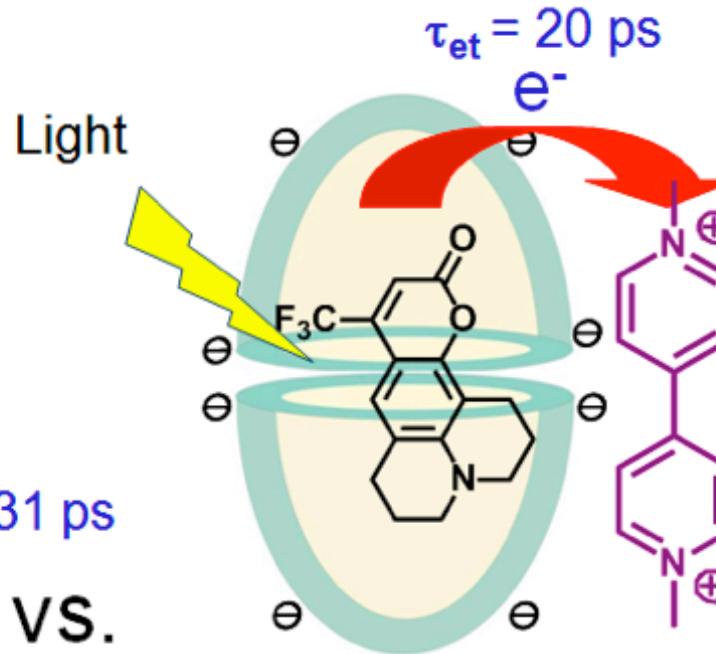
Molecular vs Supramolecular Electron Transfer



Solution

$$\tau_{\text{et}} = 631 \text{ ps}$$

$$\tau_{\text{back et}} ????$$



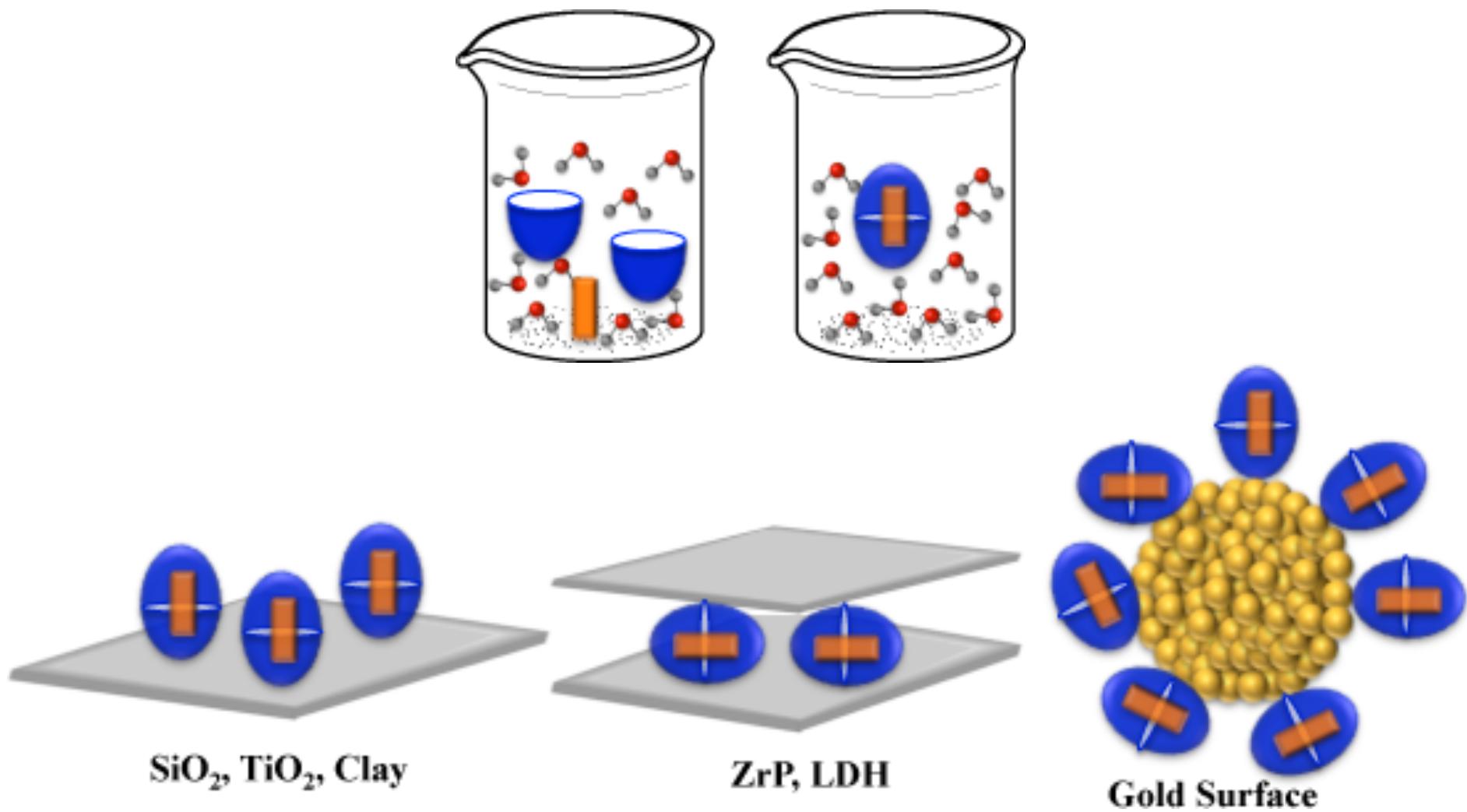
VS.

Supramolecular assembly

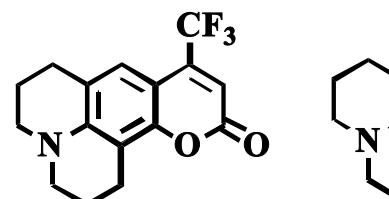
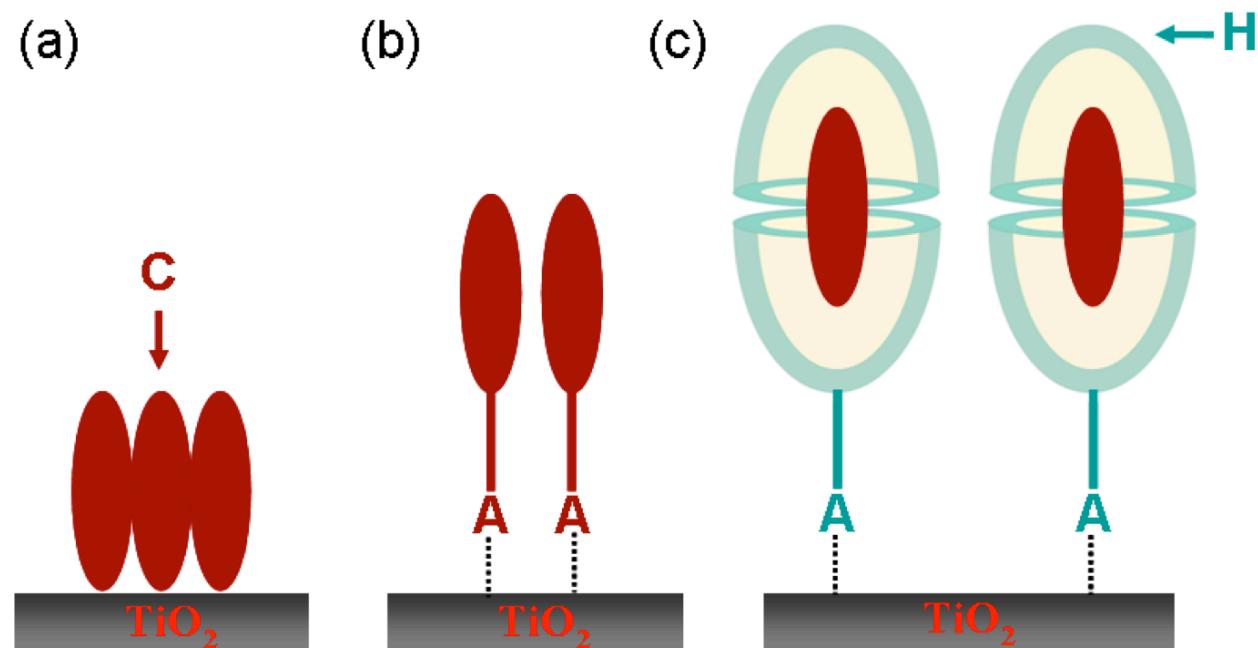
$$\tau_{\text{et}} = 1 - 20 \text{ ps}$$

$$\tau_{\text{back et}} = 35 - 1000 \text{ ps}$$

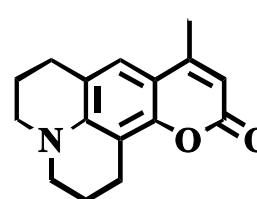
Supramolecular-Surface Photochemistry



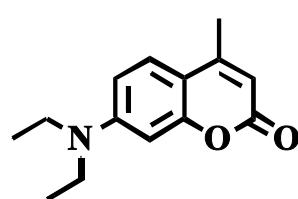
Electron transfer to TiO_2 surface



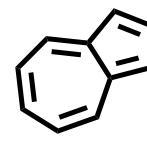
C-153



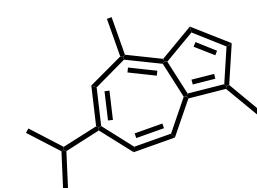
C-480



C-1

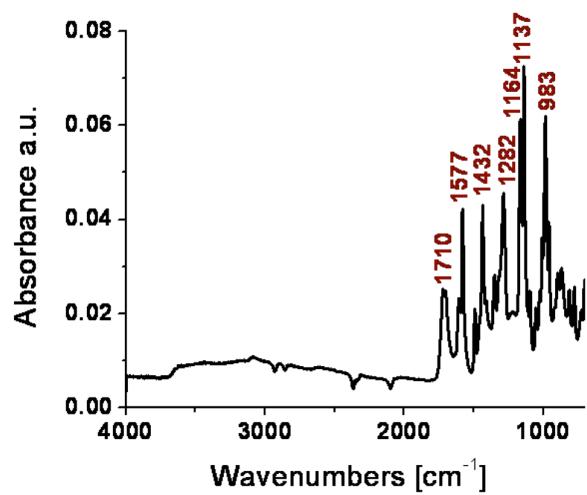


Azulene

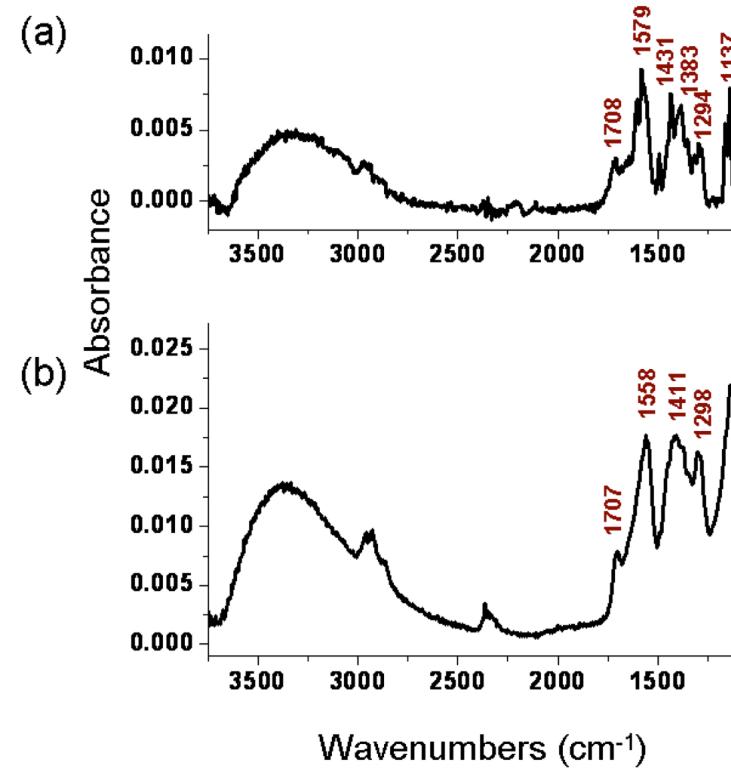


Guiazulene

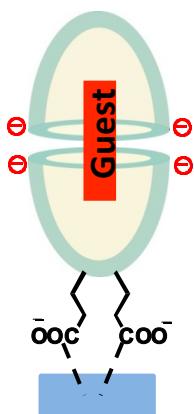
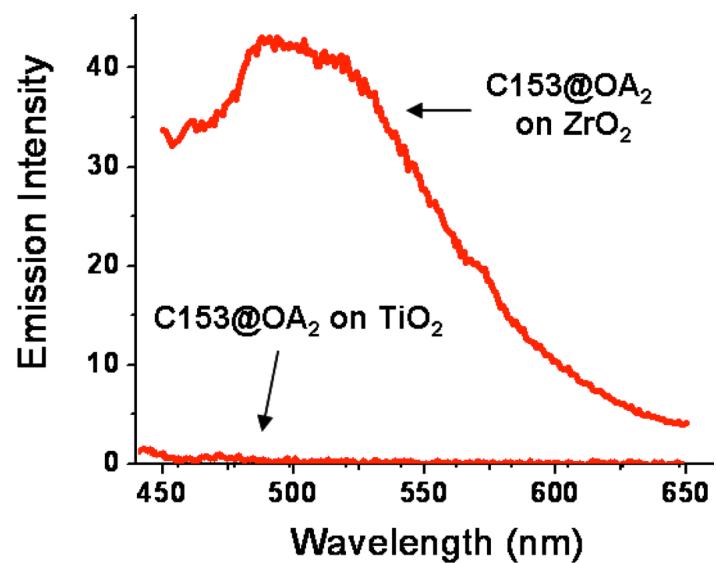
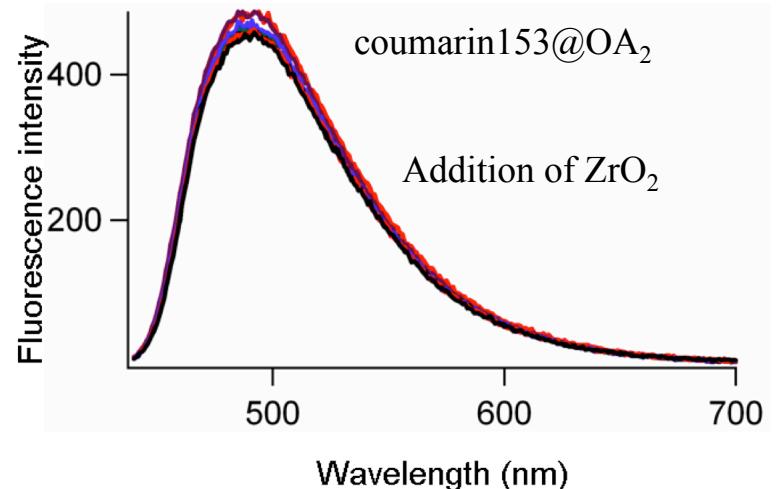
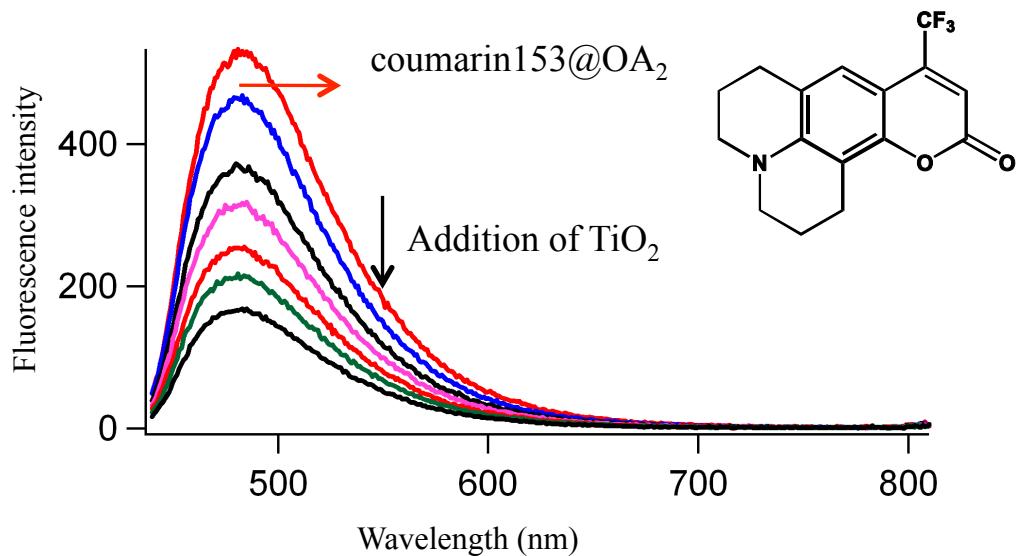
Octa acid capsule adsorbs onto TiO_2 surface



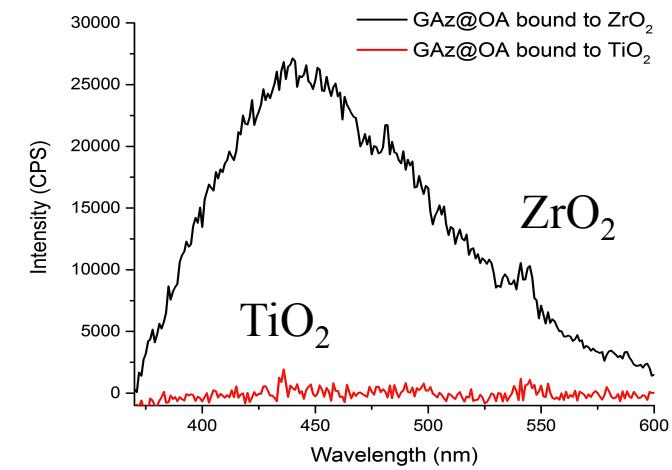
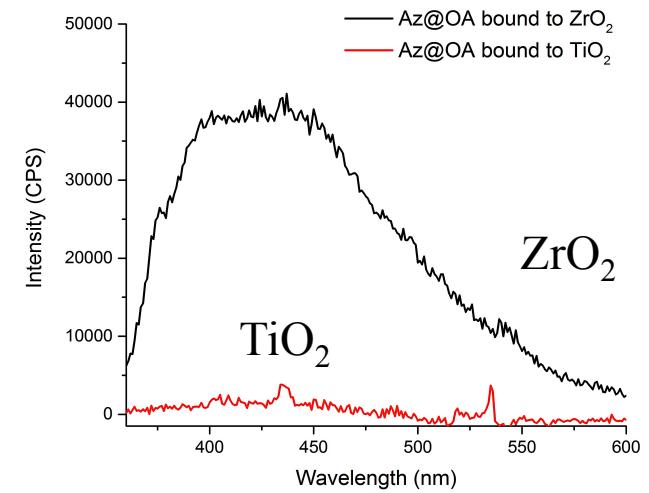
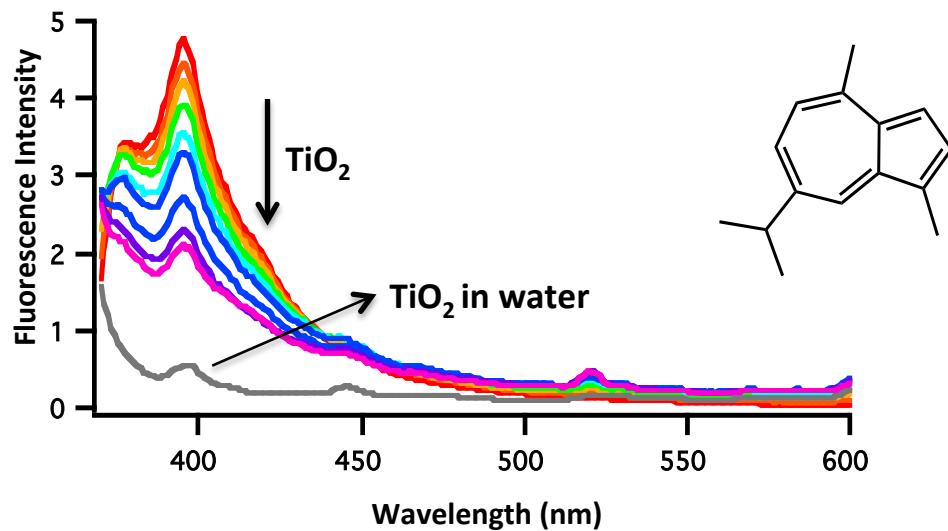
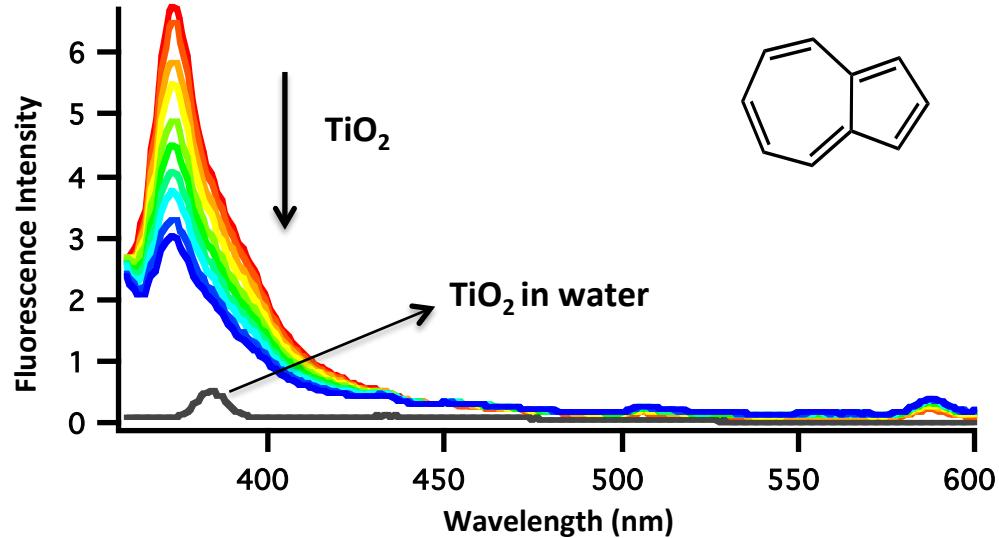
OA solid

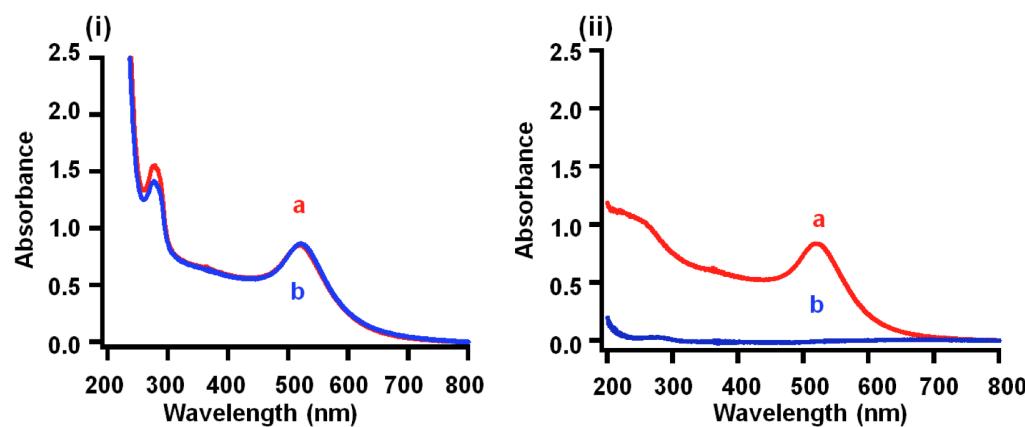
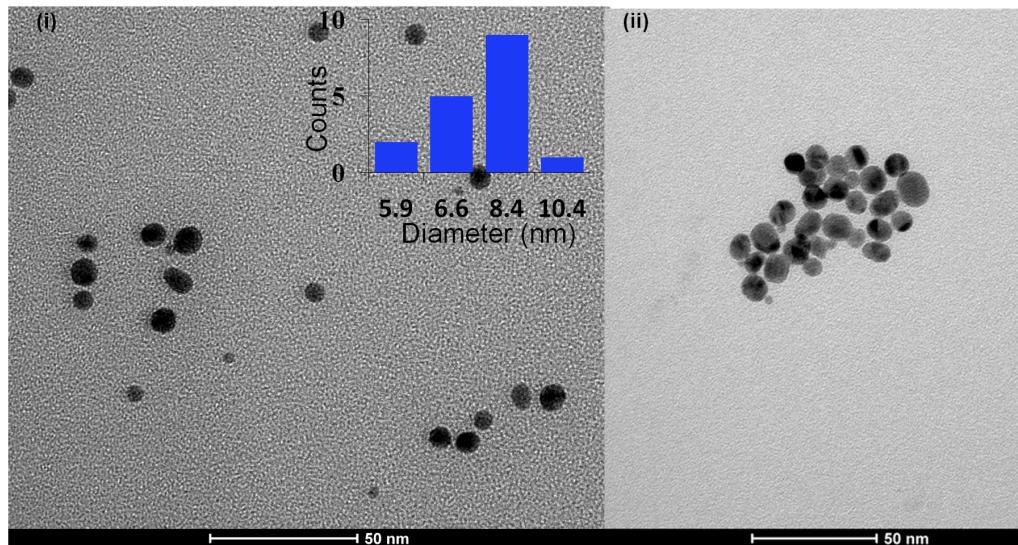


Electron transfer from coumarin153@OA₂ to TiO₂

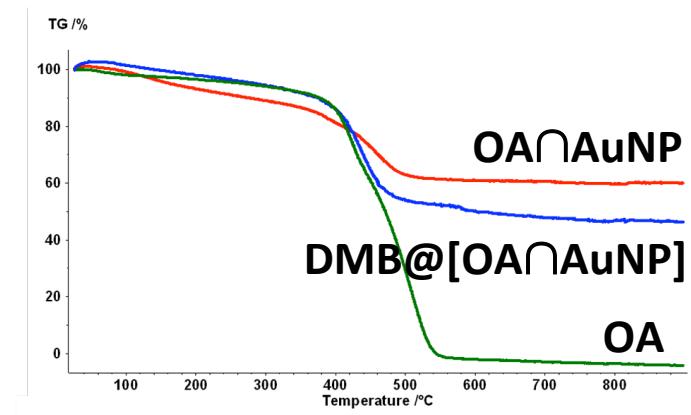
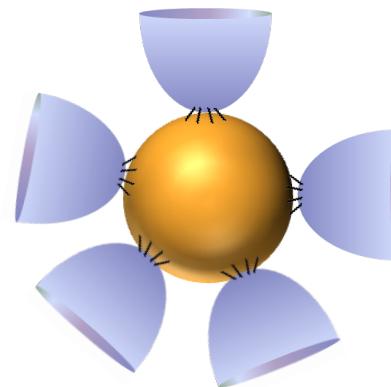
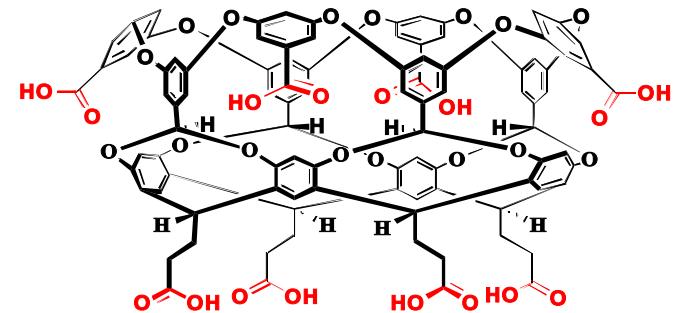


Electron transfer from azulene₂@OA₂ and guiazulene@OA₂ to TiO₂

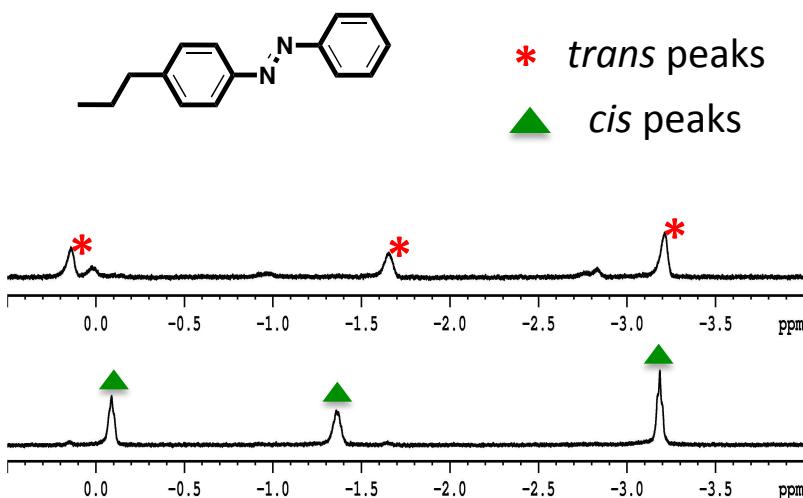




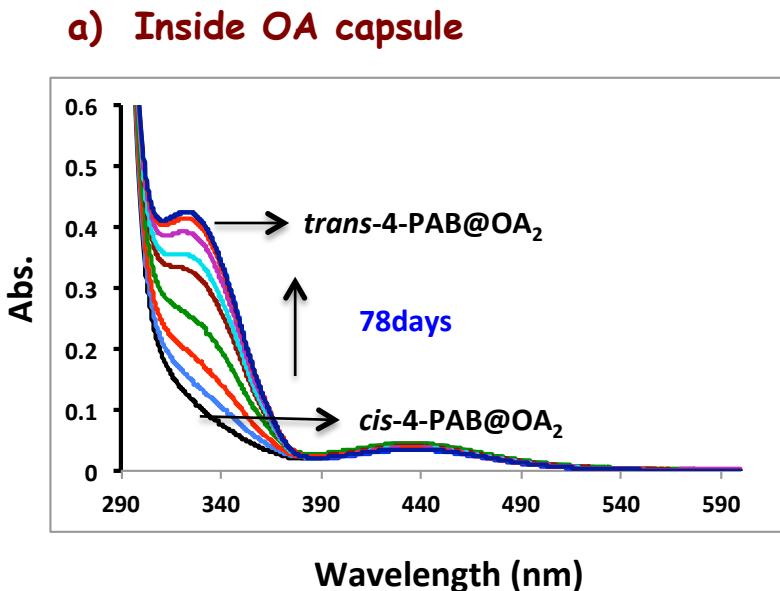
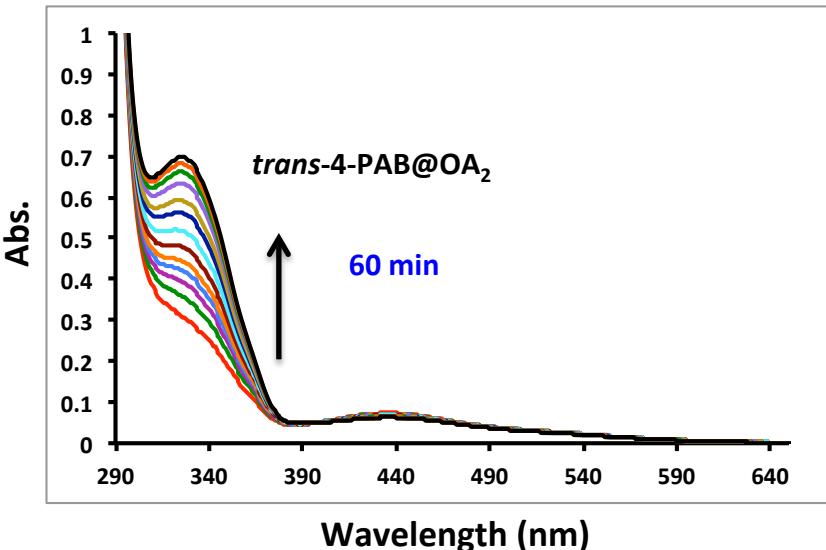
(Top) TEM photographs of (i) OA \cap AuNP (8.4 ± 1.6 nm); (ii) bare AuNP (see text for definition) and (bottom) Absorption spectra of (i) OA \cap AuNP (a) immediately after preparation (b) after distillation of H₂O and redispersing the precipitate in H₂O; Note the two spectra overlap; (ii) bare AuNP (a) immediately after preparation (b) after distillation of H₂O and redispersing the precipitate in H₂O.



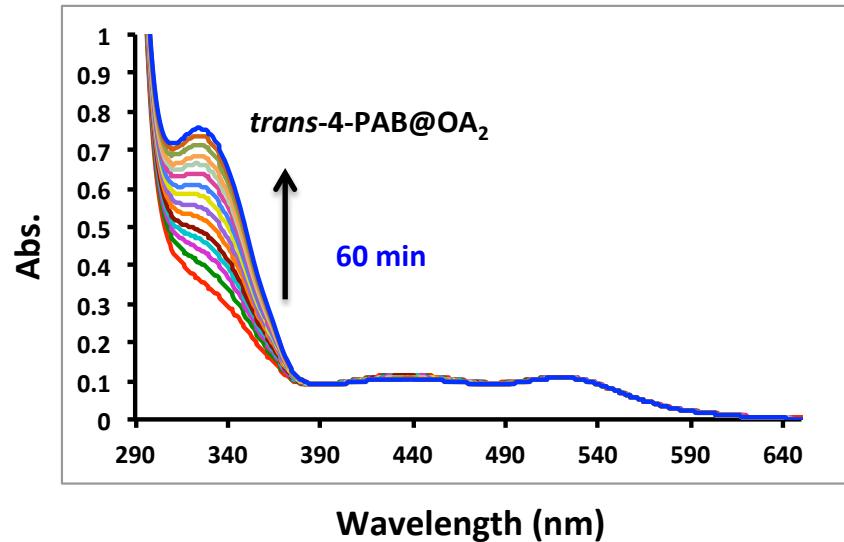
Thermal isomerization of 4-propylazobenzene@OA₂ at room temperature



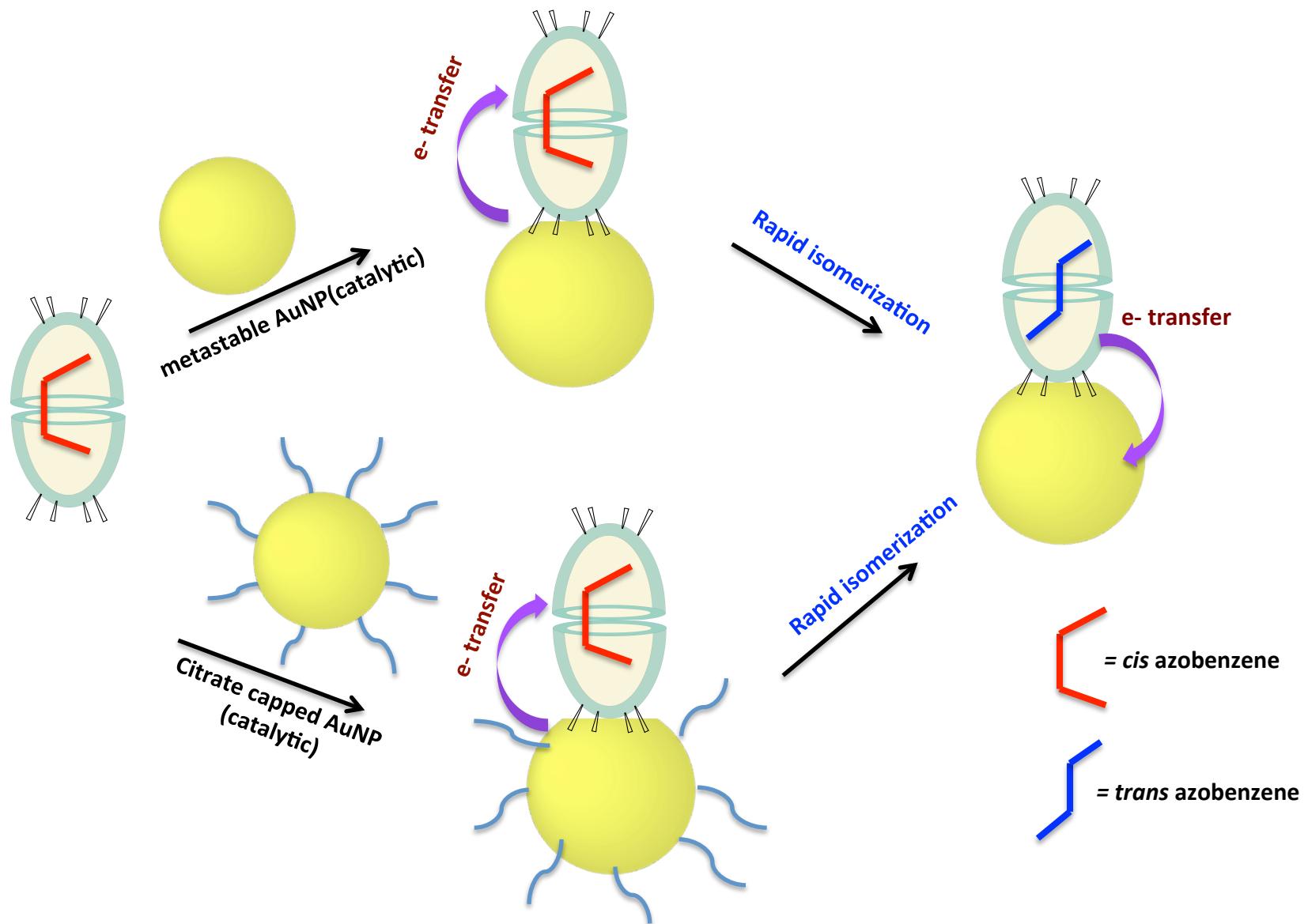
b) Inside OA capsule on metastable AuNP



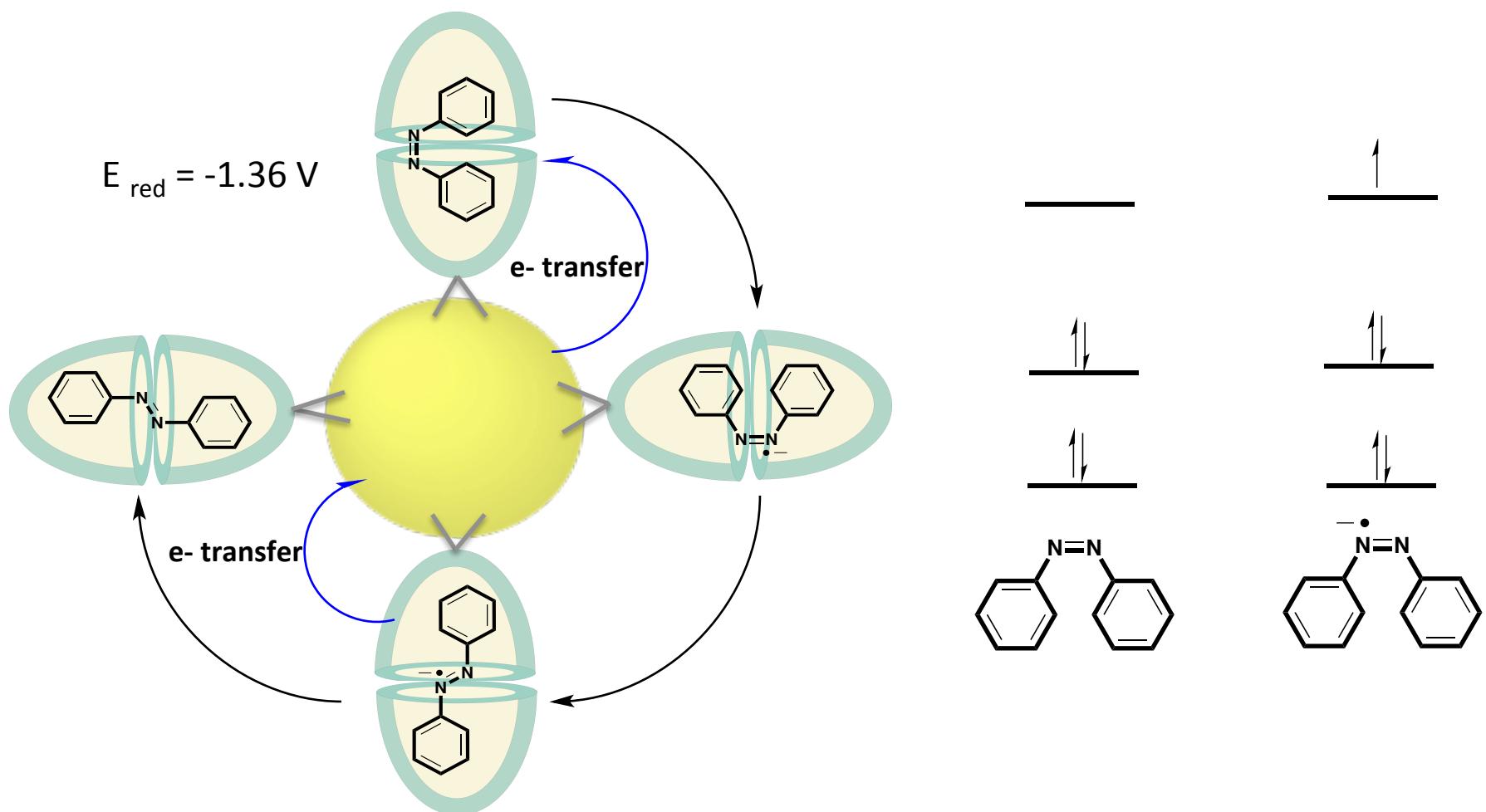
c) Inside OA capsule on citrate capped AuNP



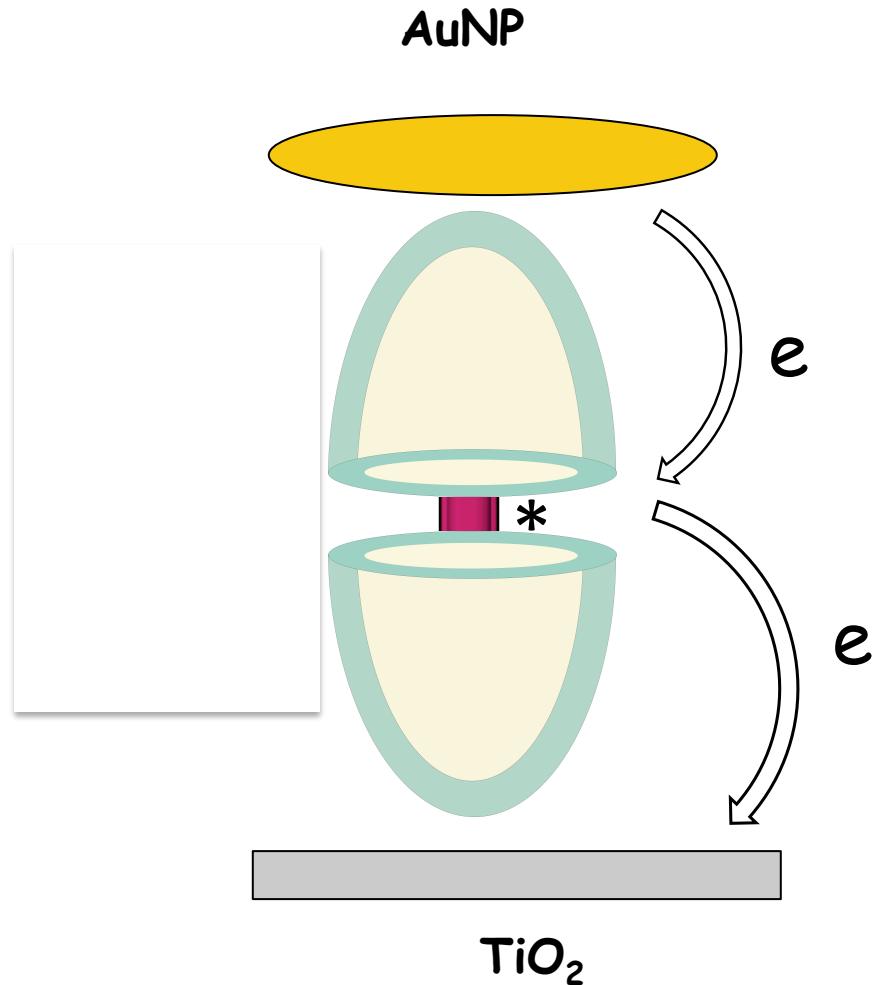
Electron transfer induced *cis* to *trans* isomerization of azobenzene@OA₂ on gold surface



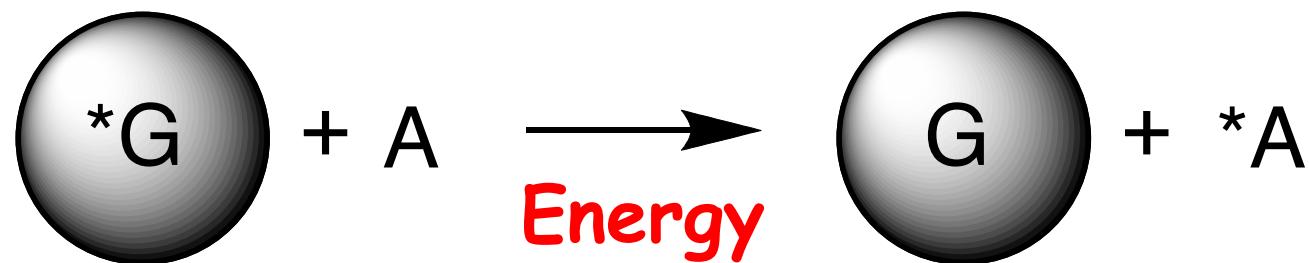
Electron transfer induced cis to trans isomerization of azobenzene@OA₂ on gold surface

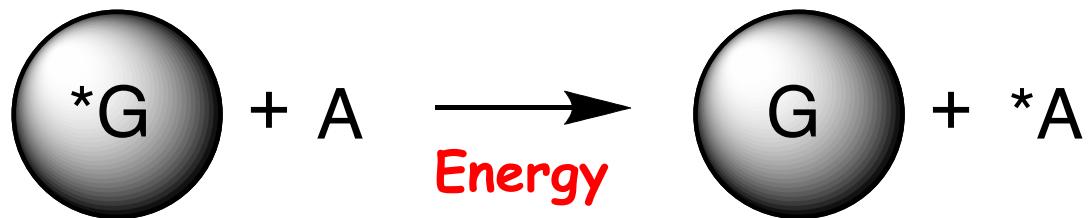


Incarceration does not stop communication

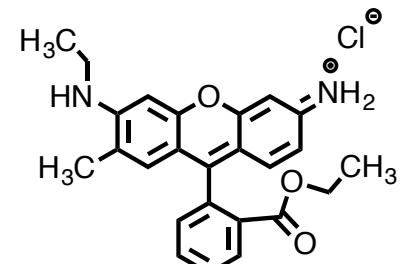


Energy transfer between confined and free molecules

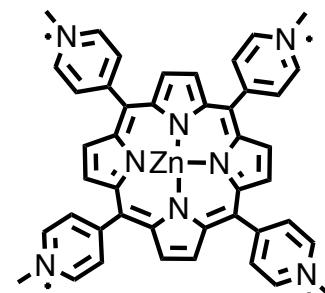
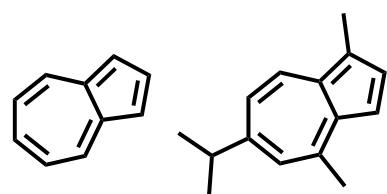
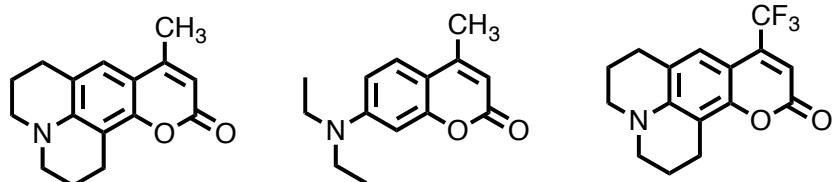




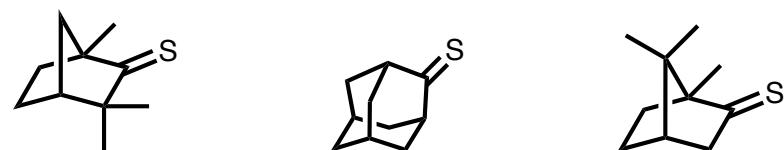
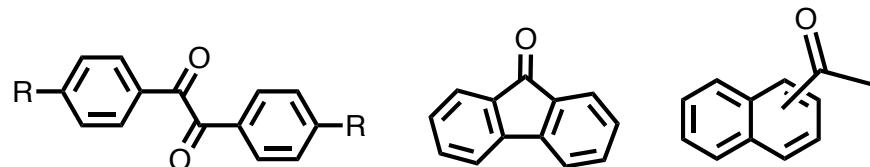
Singlet Energy Acceptor



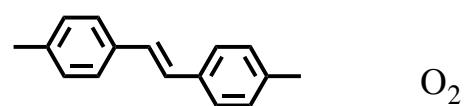
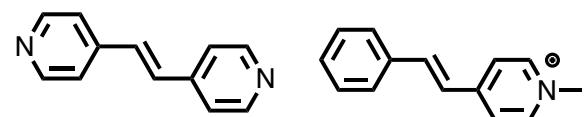
Singlet Energy Donor



Triplet Energy Donor

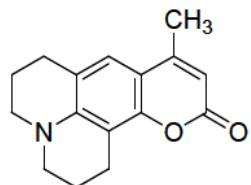


Triplet Energy Acceptor

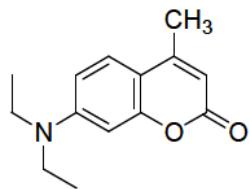


Singlet-Singlet Energy Transfer in Solution

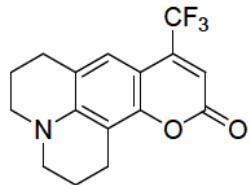
Donors



Coumarin 480 (C480)



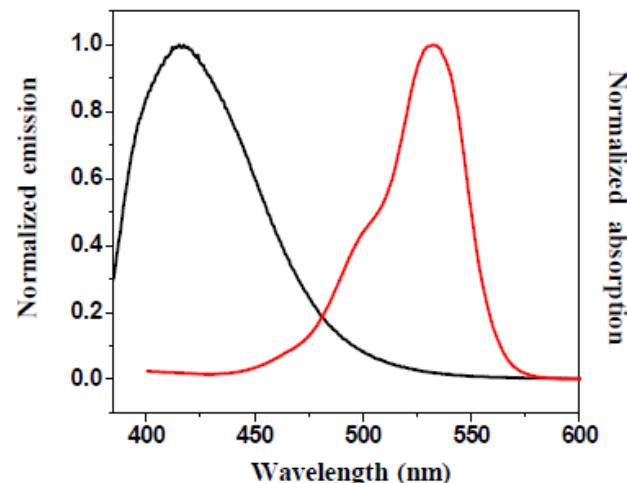
Coumarin 1 (C1)



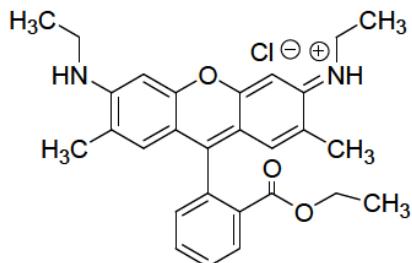
Coumarin 153 (C153)

C1-emission

R6G-absorption



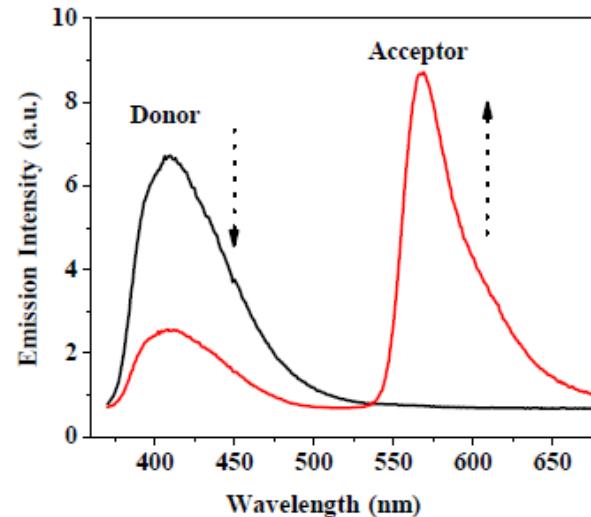
Acceptor



Rhodamine 6G (R6G)

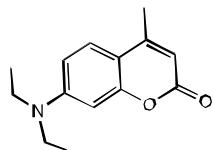
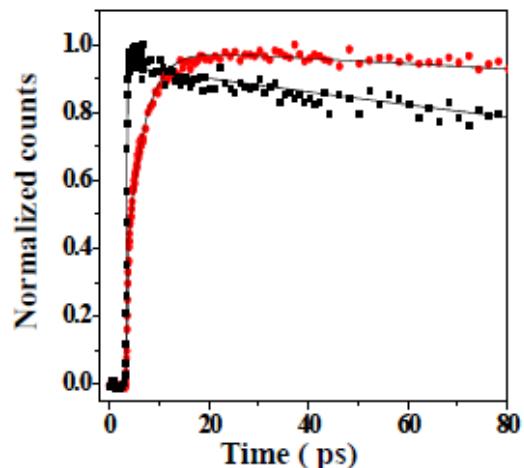
C1-emission

R6G-emission

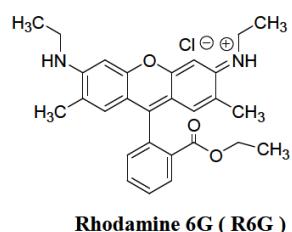
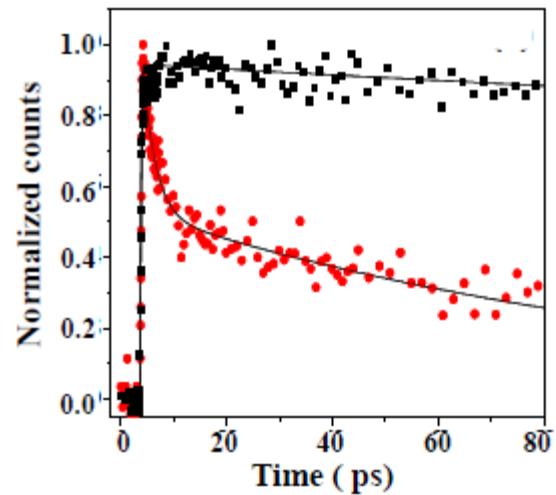


Singlet-Singlet Energy Transfer

Rise of acceptor (R6G)



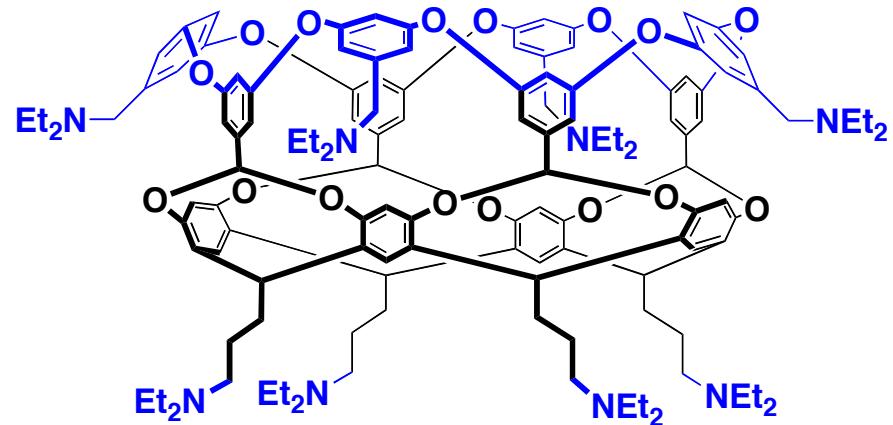
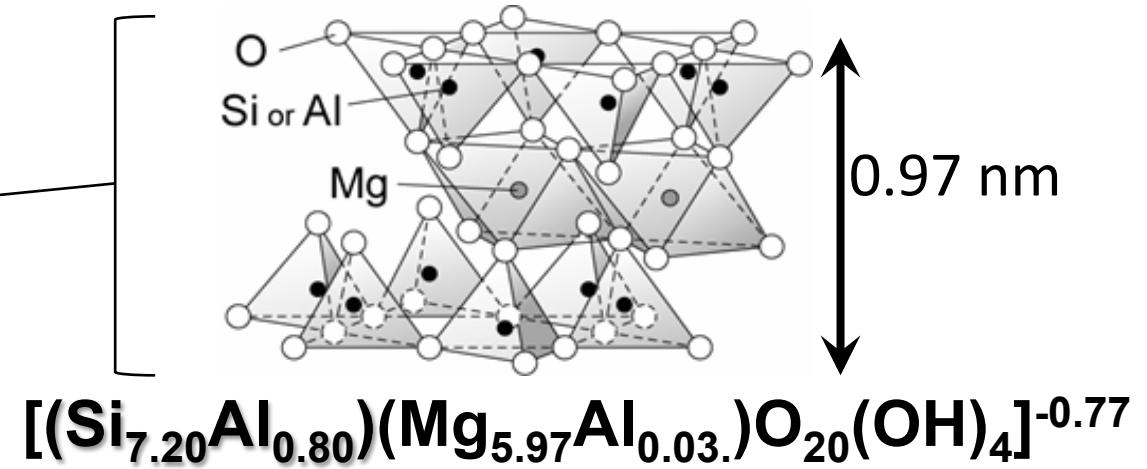
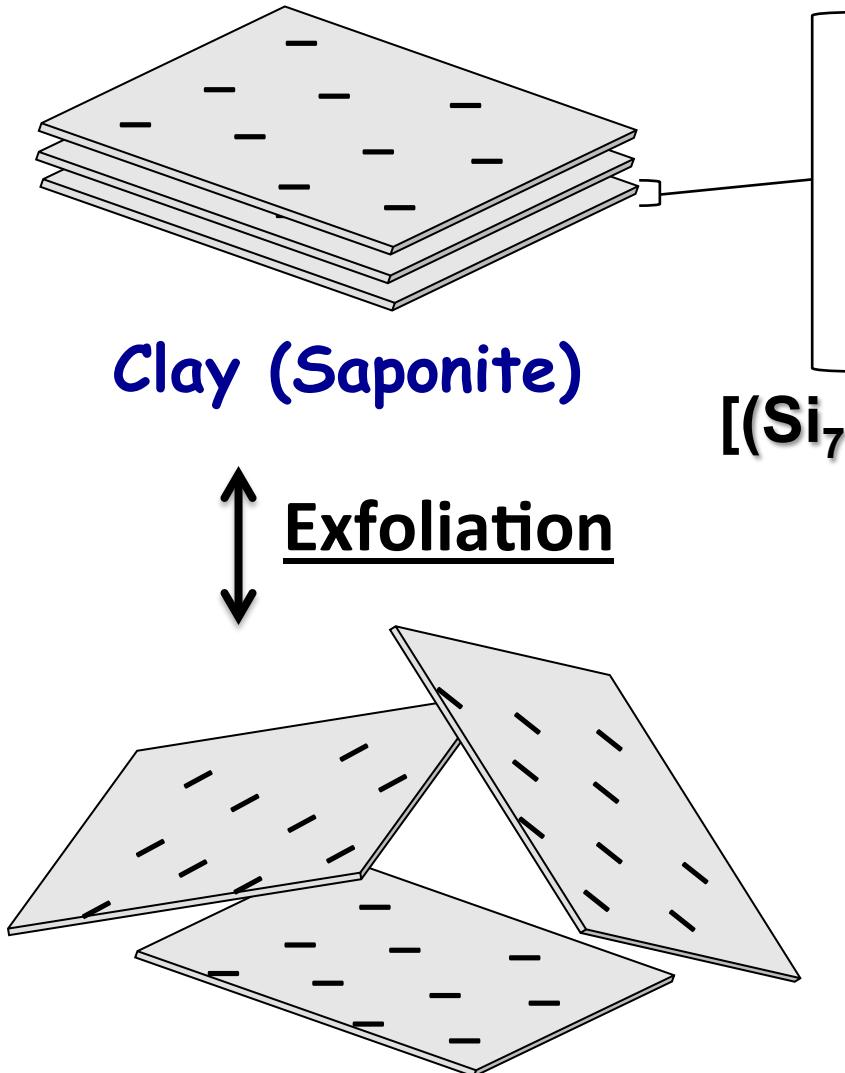
Decay of donor (C1)



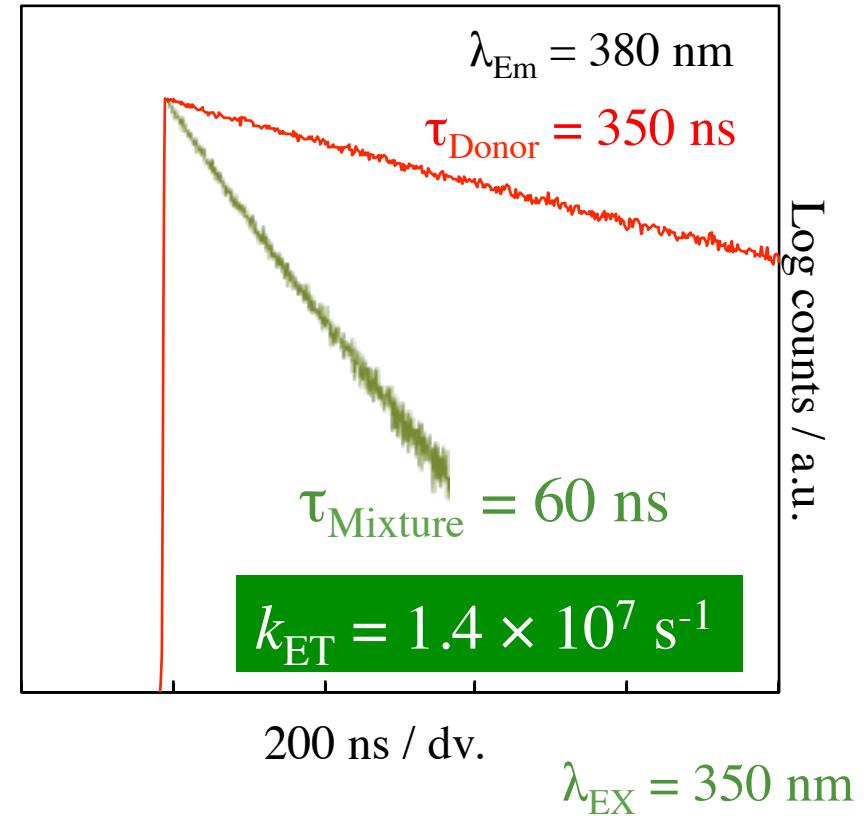
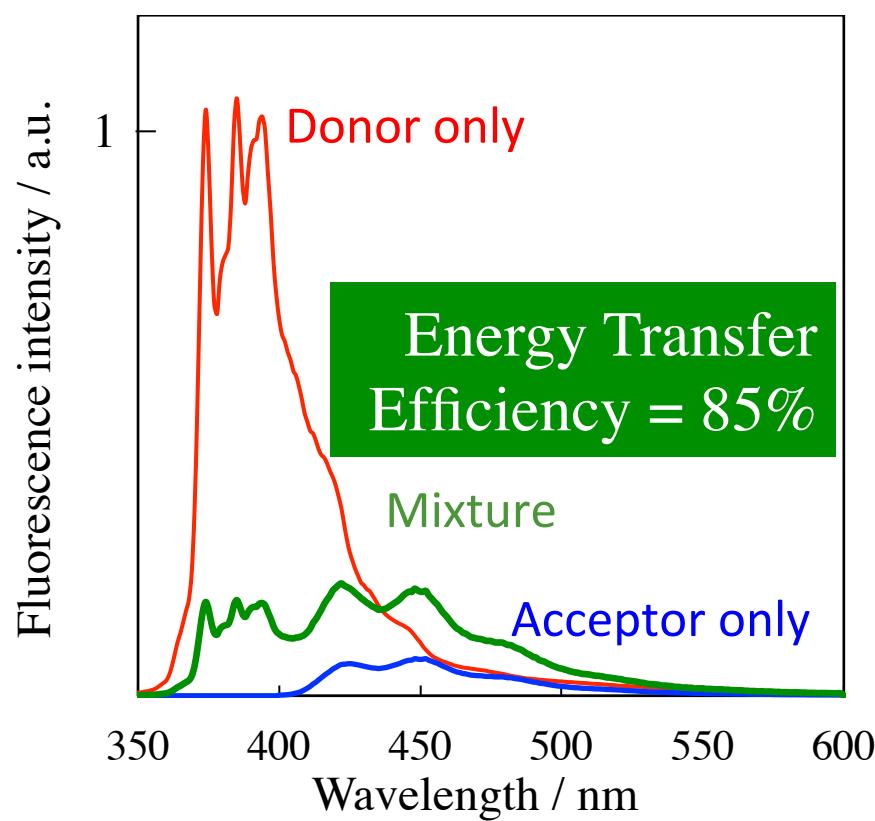
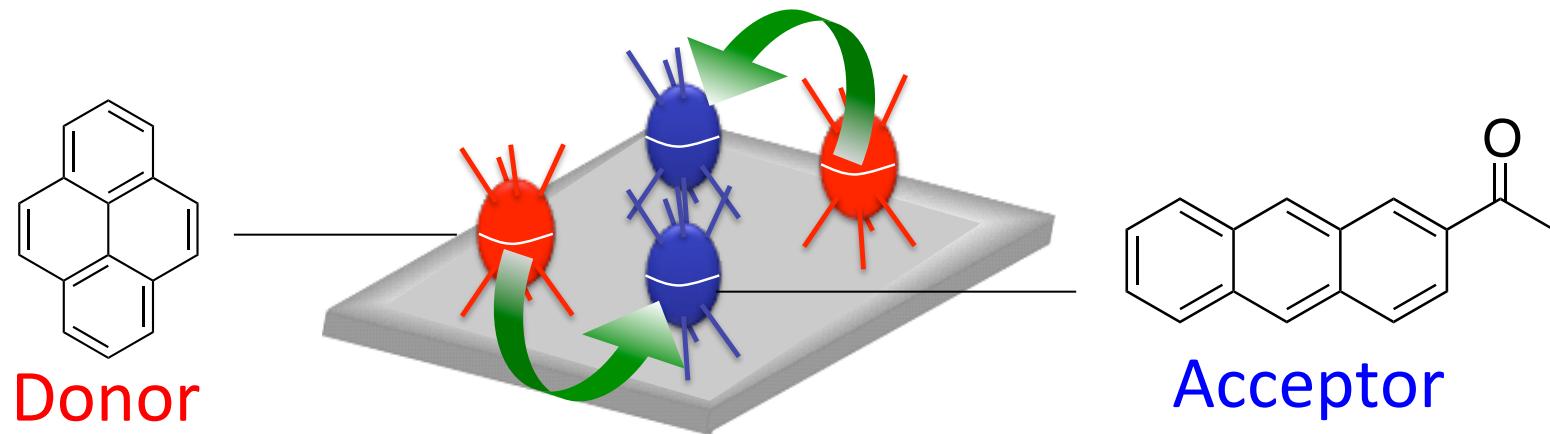
$$k_{FRET} = \frac{1}{\tau_{rise}^A} = \frac{1}{\tau_D^0} \left(\frac{R_0}{R_{DA}} \right)^6$$

System	τ_A^{rise}	τ_D^0	R_0	R_{DA}
C480@OA ₂ +R6G	1.5 ps	4900 ps	48.8 Å	13±1 Å
C153@OA ₂ +R6G	1.0 ps	7400 ps	55.7 Å	13±1 Å
C1@OA ₂ +R6G	3.5 ps	4300 ps	42.5 Å	13±1 Å

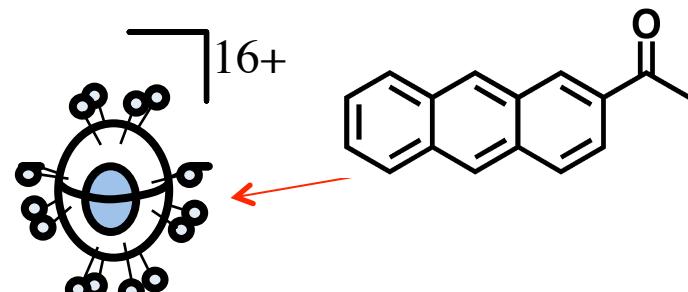
Exfoliated Saponite Clay Surface



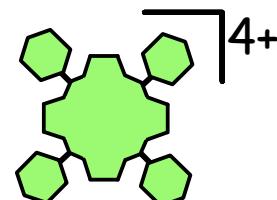
Singlet-Singlet Energy Transfer on Saponite Clay Surface



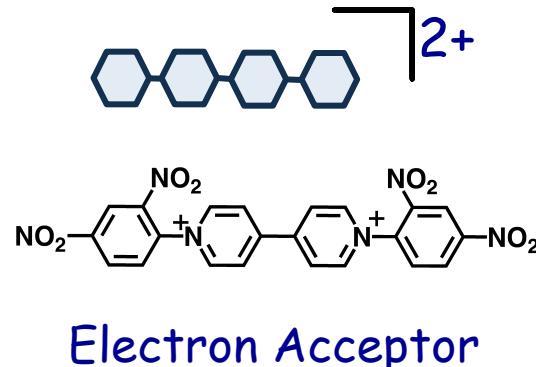
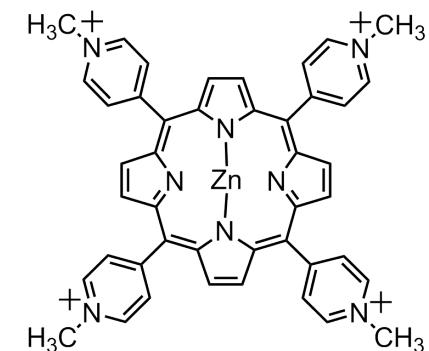
Energy Transfer and Subsequent Electron Transfer on the Clay Surface



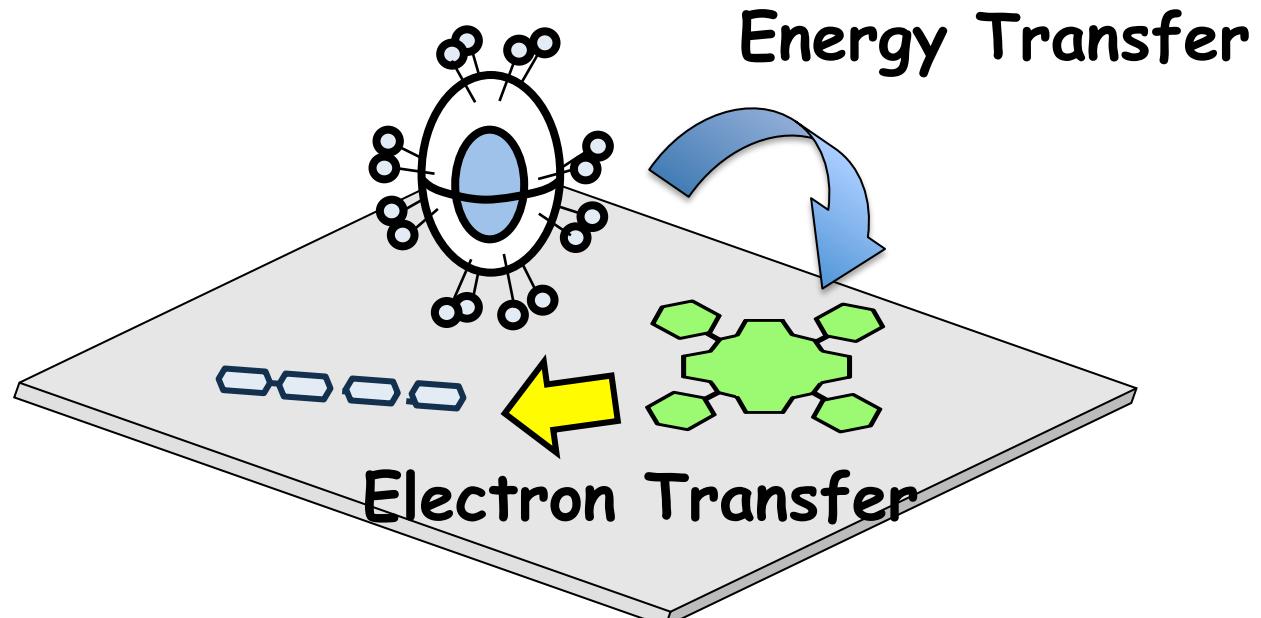
Energy Donor



Energy Acceptor
(Electron Donor)

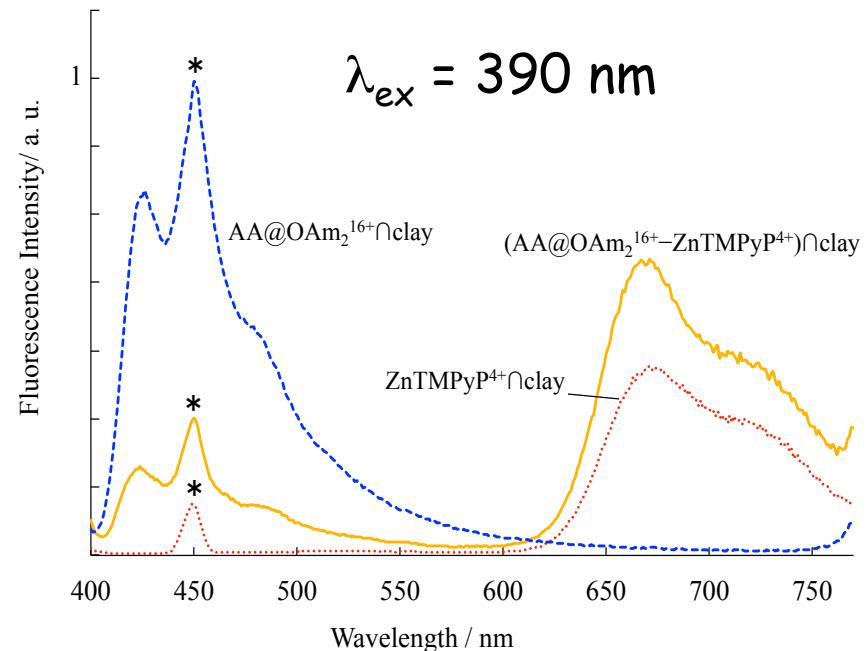
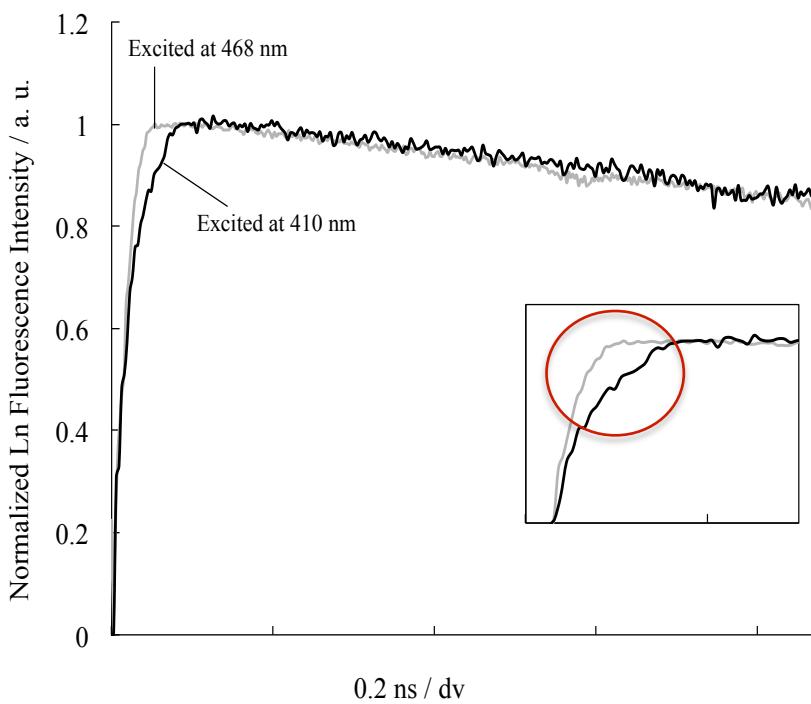
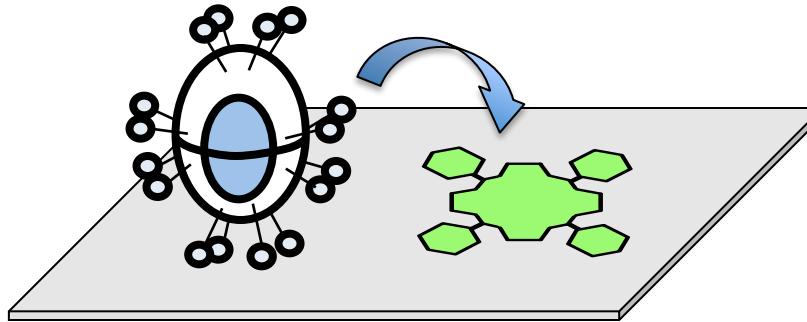


Electron Acceptor



Energy Transfer-Control Expts

Emission spectra



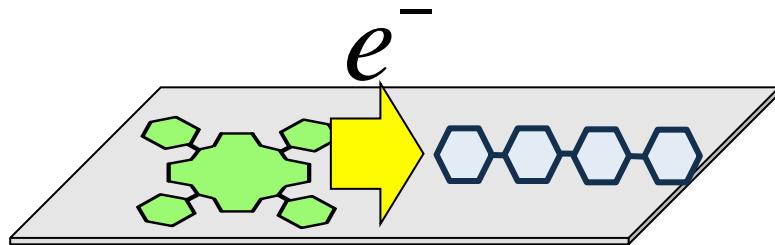
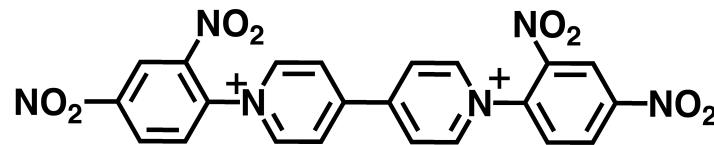
Light at 468 nm directly excites ZnTlPyP⁴⁺

Light at 410 nm excites ZnTlPyP⁴⁺ through ET

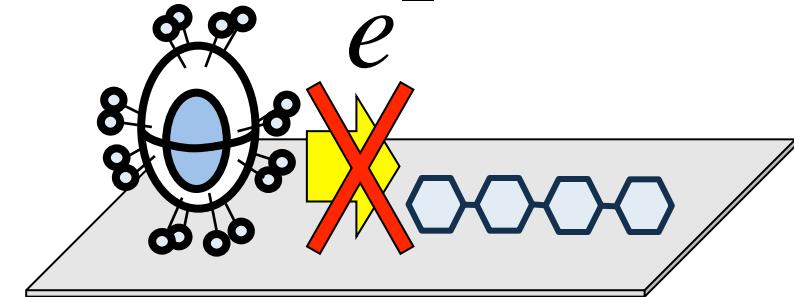
Note the rise time, two components <0.10 ns and 0.79 ns

Electron Transfer-Control Expts

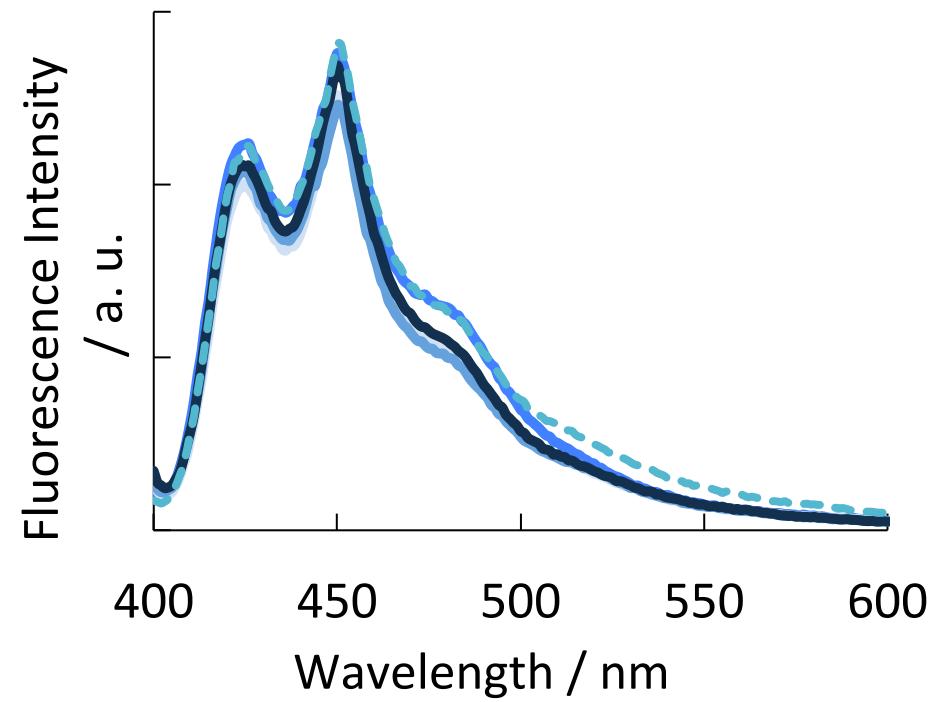
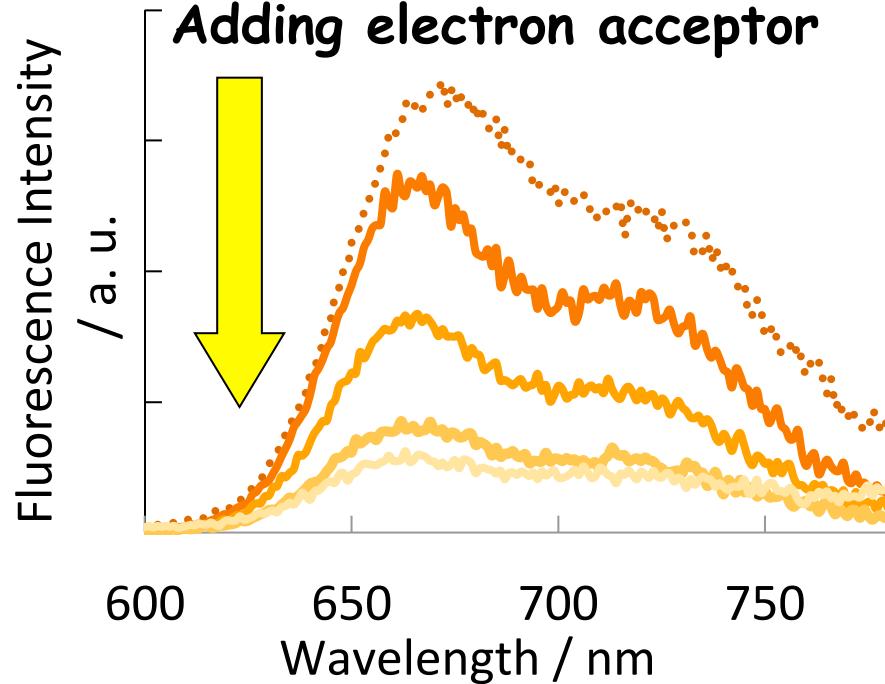
electron acceptor



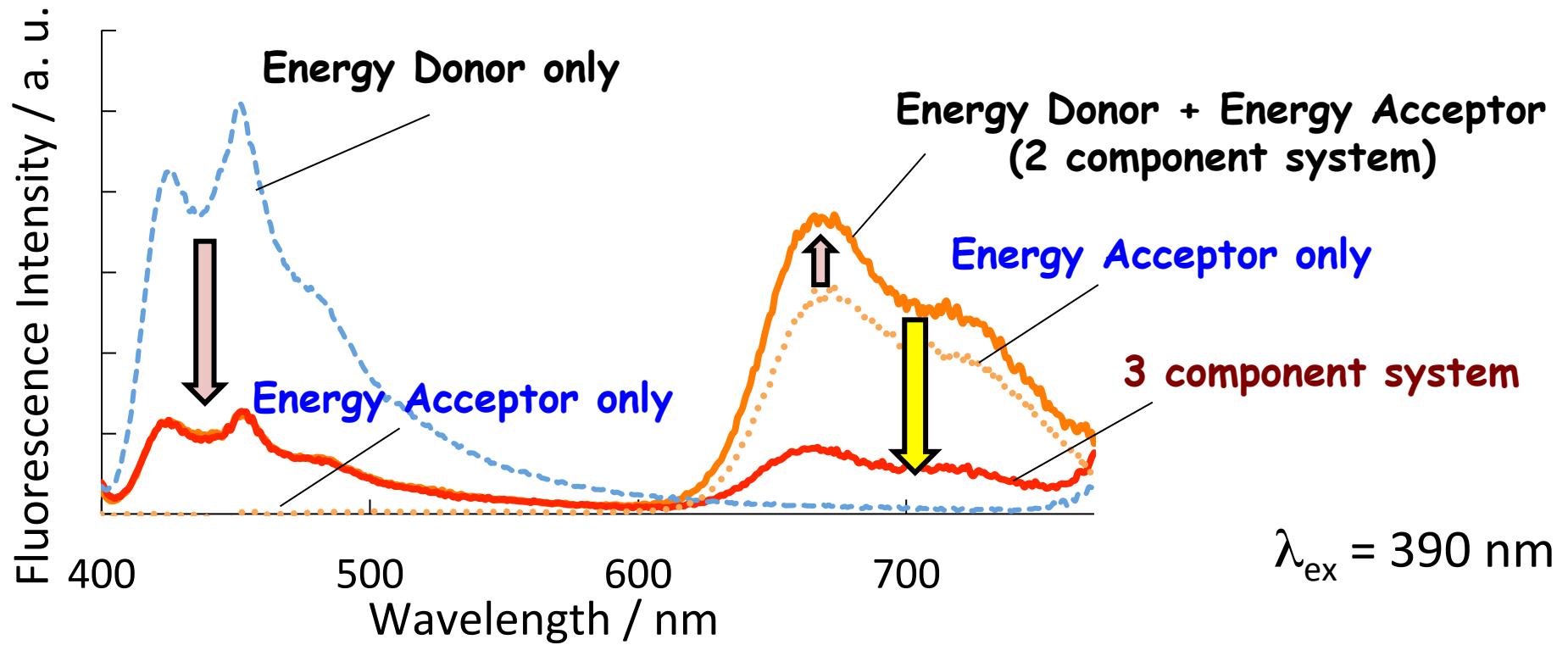
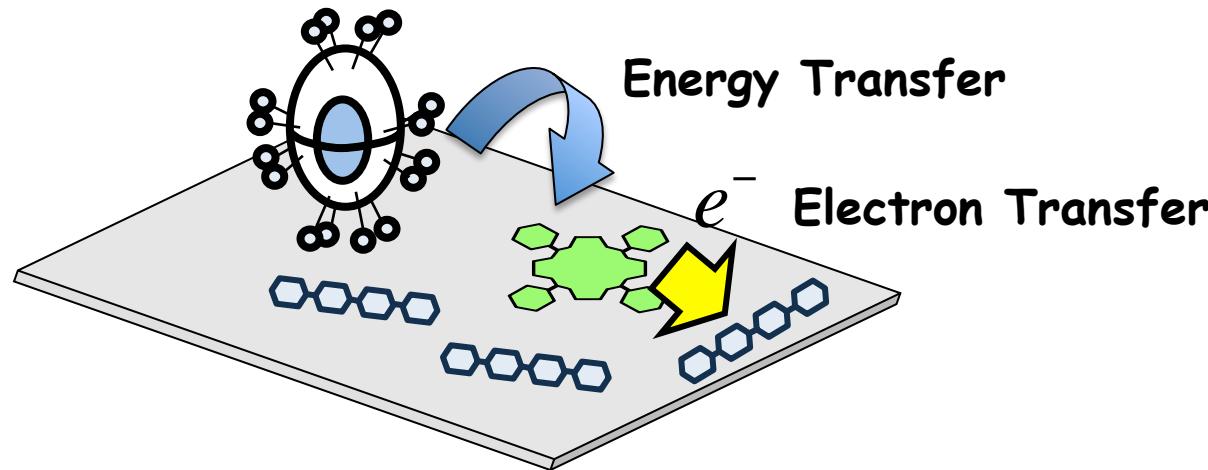
Energy Acceptor vs. Electron Acceptor
(Electron Donor)



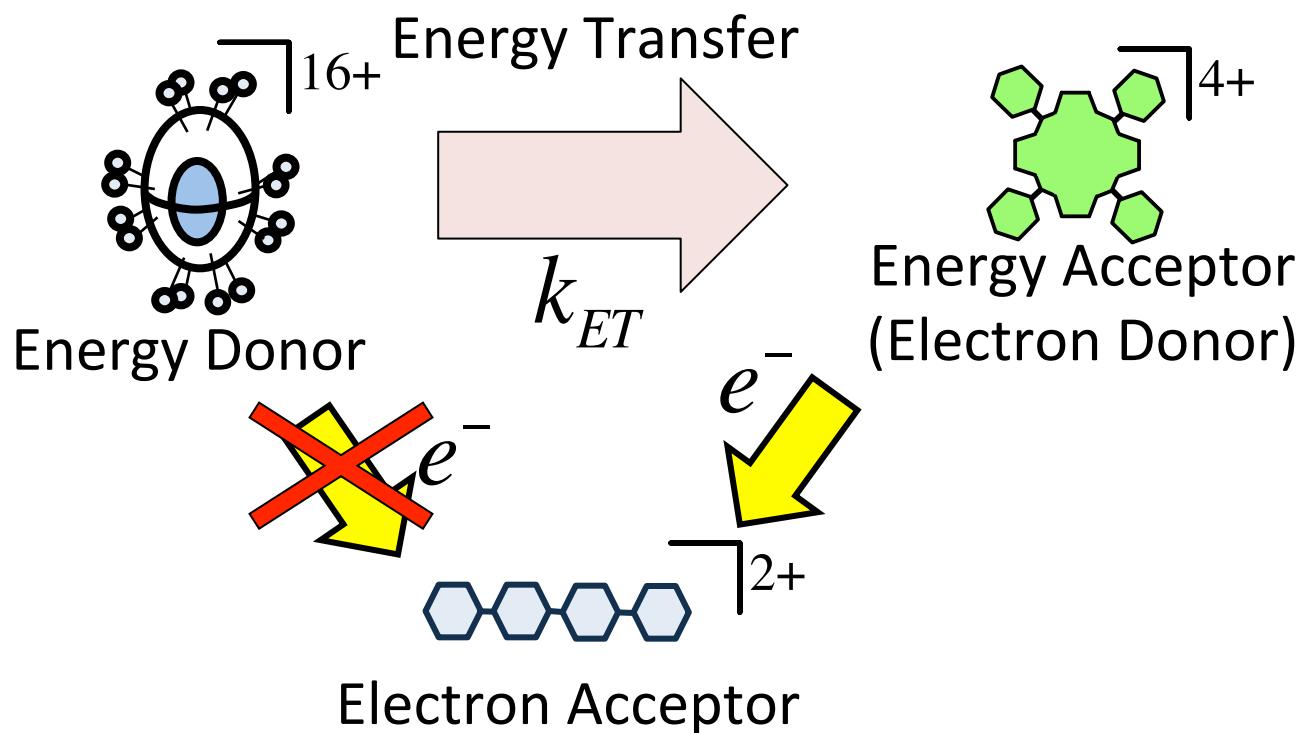
Energy Donor vs. Electron Acceptor



Energy Transfer and Subsequent Electron Transfer



Energy Transfer and Subsequent Electron Transfer on the Clay Surface



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.
- Communication between molecules across molecular wall is possible.

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