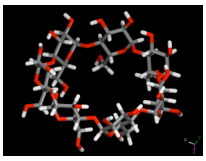
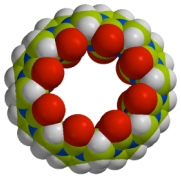
Supramolecular Photophysics

- Manipulating photophysics of organic molecules through weak interactions and confinement
- Use of organic photophysics in understanding supramolecular structures
- Supramolecular organic photohysics: Sensors, molecular motors, etc.

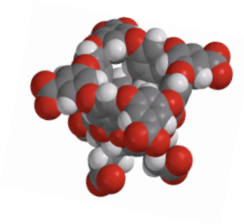
Chemistry in bowls, baskets, cages and cavities



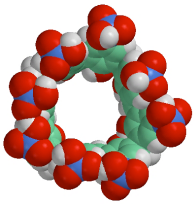
Cyclodextrins



Cucurbiturils

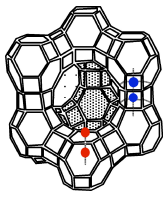


Octa acid(OA)

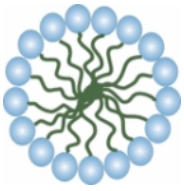


Calixarenes

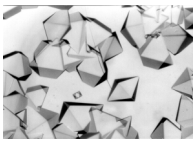
Dendrimers



Zeolites

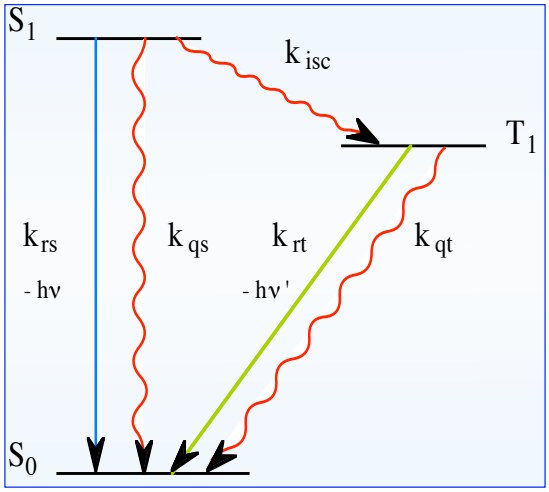


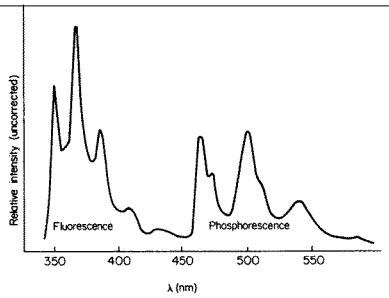
Micelles



Crystals

A brief review of photophysical processes





Fluorescence:

- High radiative rate constant, 10^{-10} to 10^{-8} s^{-1}
- Precursor state (S_1) has short lifetime
- Not susceptible to quenching

Phosphorescence:

- Low radiative rate constant, 10^{-6} to 10 s^{-1}
- Precursor state (T_1) has long lifetime
- Very much susceptible to quenching
- Emission quantum yield depends on S_1 to T_1 crossing

The heavy atom effect on spin transitions

The "heavy atom" effect is an "atomic number" effect that is related to the coupling of the electron spin and electron orbit motions (spin-orbit coupling, SOC).

Most commonly, the HAE refers to the rate enhancement of a spin forbidden photophysical radiative or radiationless transition that is due to the presence of an atom of high atomic number, Z.

The heavy atom may be either internal to a molecule (molecular) or external (supramolecular).

Spin-orbit coupling energies for selected atoms

Table 4.7 Spin–Orbit Coupling in Atoms[a,b]

Atom	Atomic number	ζ (kcal mol^{-1})	Atom	Atomic number	ζ (kcal mol^{-1})
C[c]	6	0.1	I	53	14.0
N[c]	7	0.2	Kr	36	15
O[c]	8	0.4	Xe	54	28
F[c]	9	0.7	Pb	82	21
Si[c]	14	0.4	Hg	80	18
P[c]	15	0.7	Na	11	0.1
S[c]	16	1.0	K	19	0.2
Cl[c]	17	1.7	Rb	37	1.0
Br	35	7.0	Cs	55	2.4

Correlation of Experimental Parameters with Theory

Heavy Atom Effect - Theory

$$P_{S\text{-}T} = \frac{\sum_{i,j} \langle \theta_{S_i} \theta_{T_j} \rangle^2 \langle \phi_S | H_{SO} | \phi_T \rangle^2}{\Delta E_{S\text{-}T}}$$

$$H_{S\text{-}O} \propto \zeta(L \cdot S)$$

$$P_{S\text{-}T} \propto (H_{SO})^2$$

$$P_{S\text{-}T} \propto \zeta^2$$

$P_{S\text{-}T}$ = Transition Probability

ϕ = Electronic Wavefunctions

$\theta_{i,j}$ = Vibrational Wavefunctions

H_{SO} = Spin-Orbit Hamiltonian

S = Spin Angular Momentum

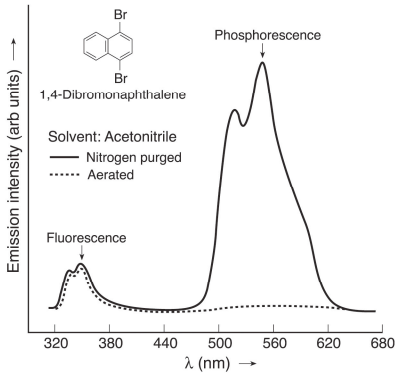
L = Orbital Angular Momentum

ζ = Spin-Orbit Coupling Constant

Examples of internal heavy atom effect

Molecule	k_F^0	k_{ST}	k_P^0	k_{TS}	Φ_F	Φ_P
Naphthalene	10^6	10^6	10^{-1}	10^{-1}	0.55	0.05
1-Fluoronaphthalene	10^6	10^6	10^{-1}	10^{-1}	0.84	0.06
1-Chloronaphthalene	10^6	10^8	10	10	0.06	0.54
1-Bromonaphthalene	10^6	10^9	50	50	0.002	0.55
1-Iodonaphthalene	10^6	10^{10}	500	100	0.000	0.70

Room temperature phosphorescence in solution
Internal heavy atom effect



$^*R(S_1) \xrightarrow{k_{ST}} {}^*R(T_1) \xrightarrow{k_P} S_0 + h\nu_P$

$^*R(S_1) \xrightarrow{k_1}$ not $^*R(T_1)$

$^*R(T_1) \xrightarrow{k_2[Q]}$ not $h\nu_P$

Strategy to record phosphorescence at room temperature through supramolecular approach

Stage 1

$^*R(S_1) \xrightarrow{k_{ST}} {}^*R(T_1)$

$^*R(S_1) \xrightarrow{k_1} R(S_0)$

Heavy atom effect mainly on k_{ST} so that $k_{ST} > k_1$

Make more triplets through the heavy atom effect

Stage 2

$^*R(T_1) \xrightarrow{k_P} R(S_0) + h\nu_P$

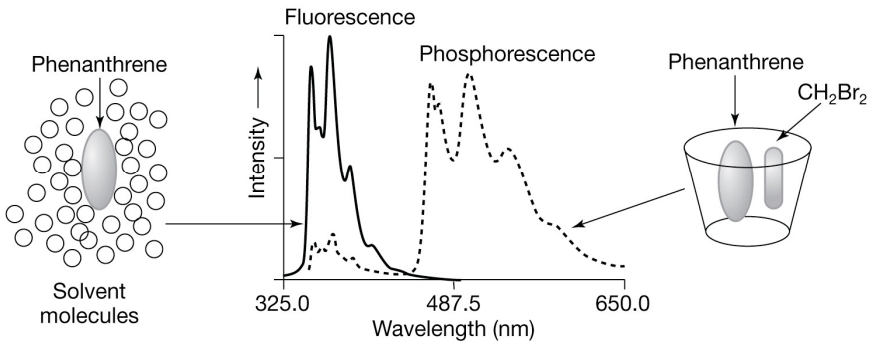
$^*R(T_1) \xrightarrow{k_2[Q]} R(S_0)$

Heavy atom effect mainly on k_P so that $k_P > k_2[Q]$

Make triplets emit faster in competition with quenching processes

Cyclodextrins as hosts

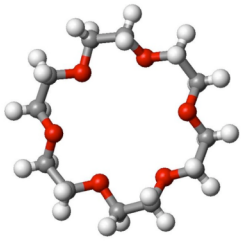
Phenanthrene@Cyclodextrin: effect of CH_2Br_2 as co-guest

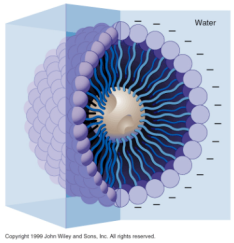


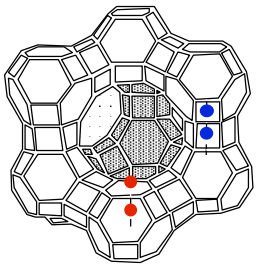
Induced Intersystem Crossing Depends on the SOC: Cations as the heavy atom pertutber

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

Crown ethers, Micelles and Zeolites as hosts







Room temperature phosphorescence in solution
External heavy atom effect: Crown ether apparoach

Table II. Estimates[a,b] of Rate Constants for Excited-State Processes of 1,5-Naphtho-22-crown-6 (**1**) in Alcohol Glass[c] at 77 K with Alkali Metal Chloride Salts Added in 5:1 Molar Excess (Crown at 1.00×10^{-4} *F*)

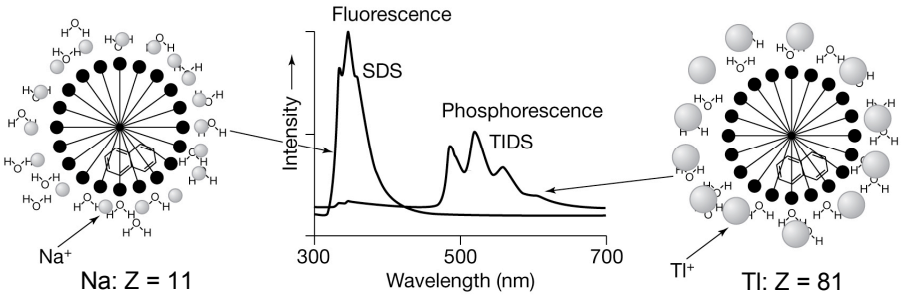
Salt added	$10^{-6}k_f$	$10^{-6}k_{nr}$	$10^{2}k_p$[d]	k_{dt}[d]
None	3.1	25	8.7	0.37
NaCl	2.6	32	6.7	0.41
KCl	2.3	35	5.8	0.39
RbCl	1[e]	52	12.	0.50
CsCl	1[e]	670	81.	1.57

[a] All rate constants in s^{-1}. [b] $k_f = \phi_f\tau_f^{-1}$; $k_{nr} = (1 - \phi_f)\tau_f^{-1}$; $k_p = \phi_p(1 - \phi_f)^{-1}\tau_p^{-1}$; $k_{dt} = \tau_p^{-1} - k_p$. [c] See note 4. [d] With $\phi_f + \phi_{isc} = 1.0$ assumed. [e] Estimated from 77 K UV absorption spectra.

1

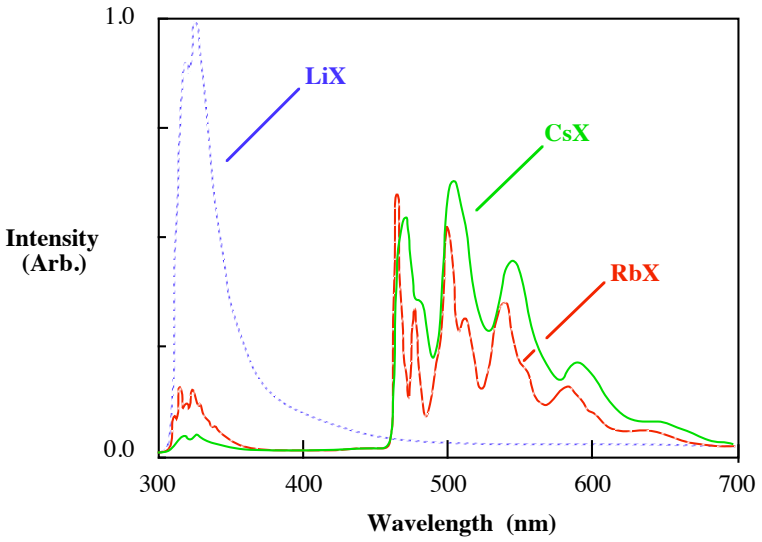
Micelles as hosts

Naphthalene@SDS micelle: effect of heavy atom counterions

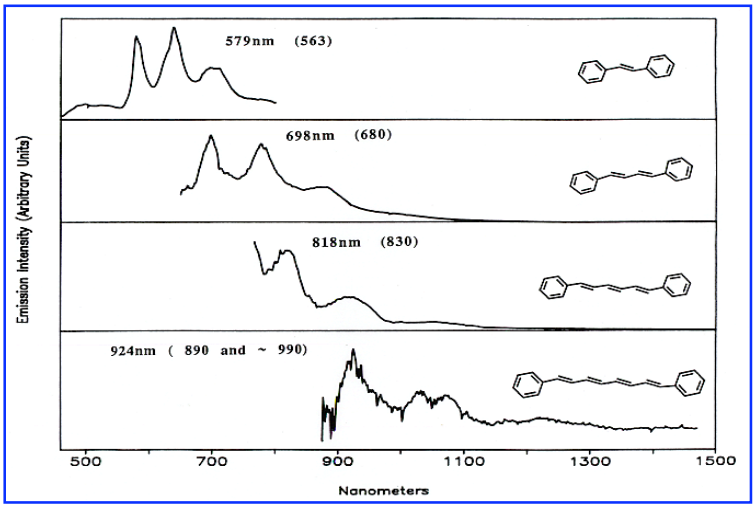


Heavy atom produces more triplets and the triplets produced phosphoresce at a faster rate

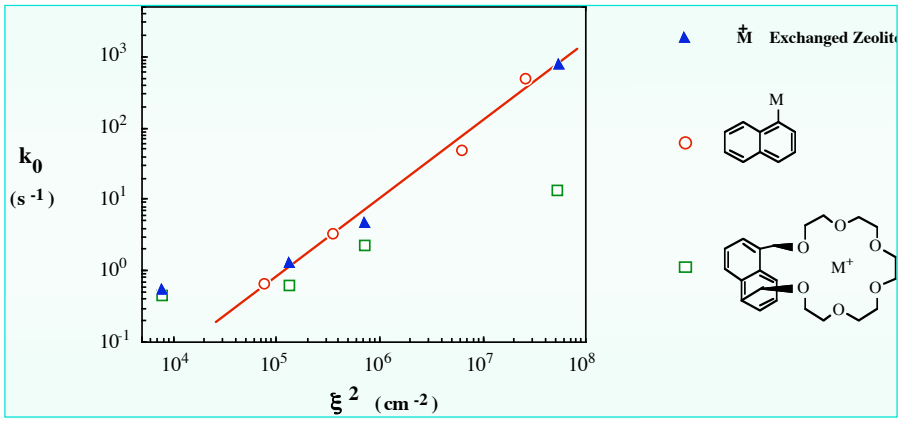
Emission Spectra of Naphthalene Included in MY Zeolites



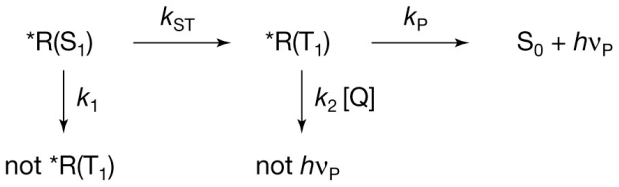
Phosphorescence from Diphenyl Polyenes

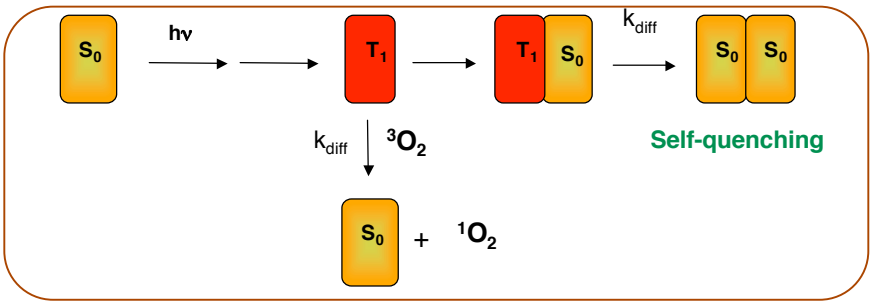


External Heavy Atom Effect on Triplet Decay Rates of Naphthalene

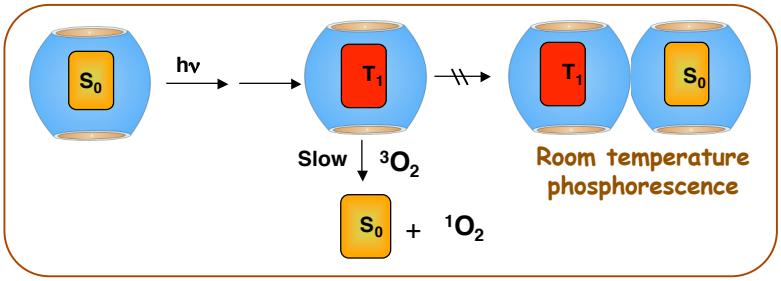


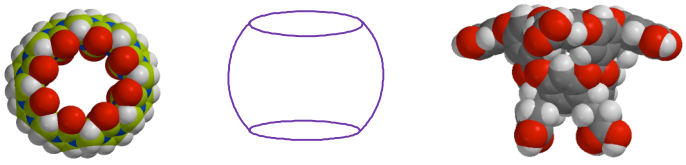
Diffusion controlled self-quenching and oxygen-quenching in solution



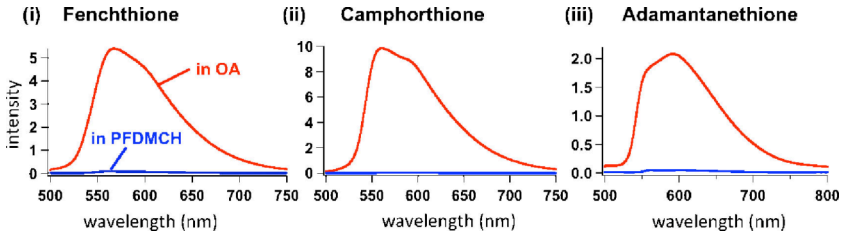


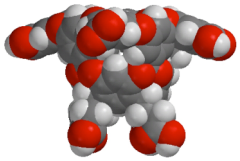
Prevention of self quenching and oxygen quenching with the help of containers

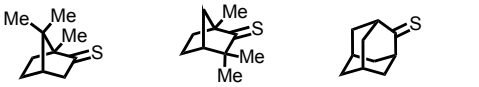




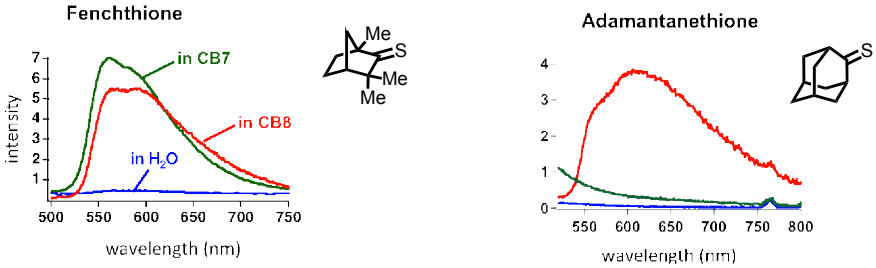
Room temperature phosphorescence from thioketones in solution

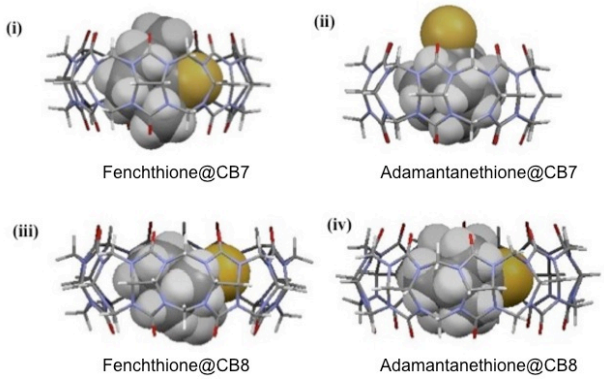






Camphorthione Fenchthione Adamantanethione

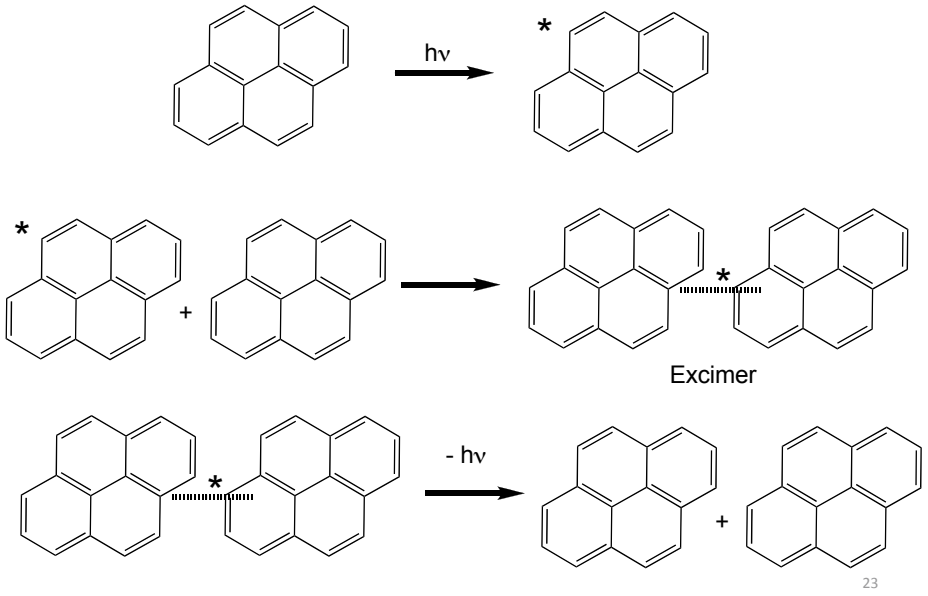




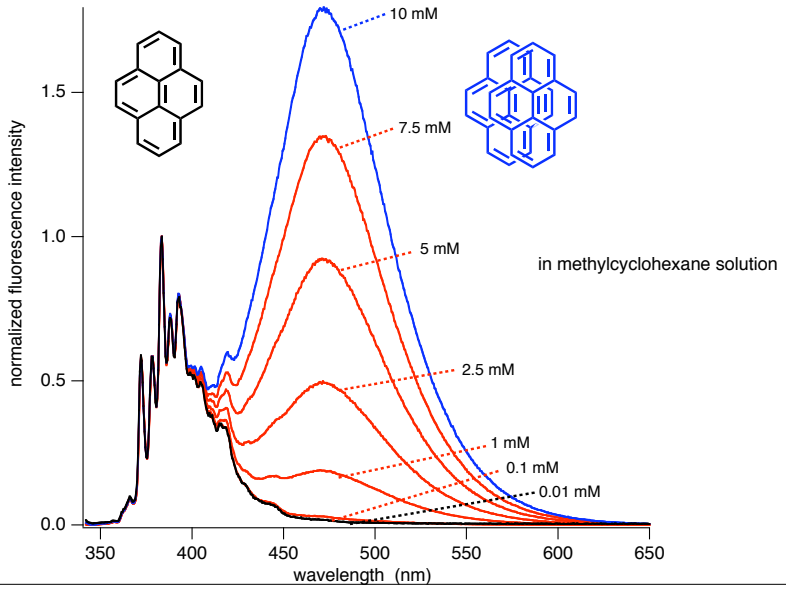
Fenchthione@CB7 Adamantanethione@CB7

Fenchthione@CB8 Adamantanethione@CB8

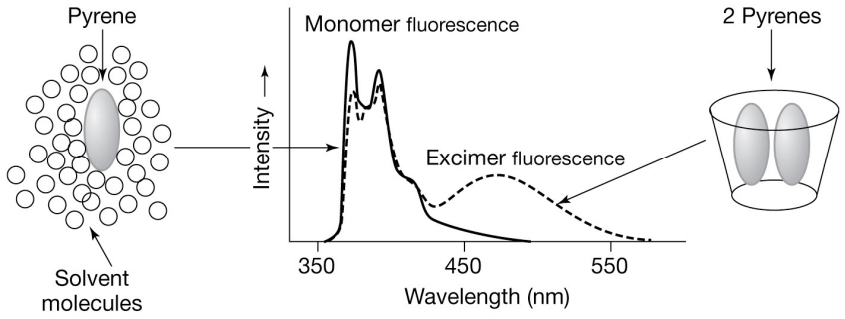
Pyrene as an exemplar of excimer formation



Pyrene Excimer

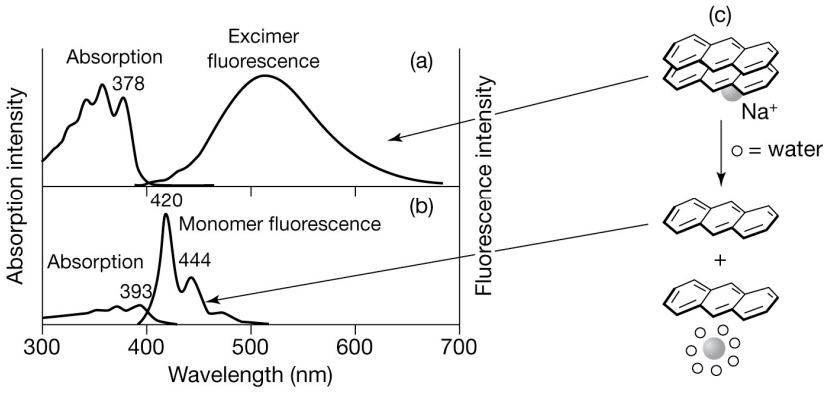


$(Py)_2$@Cyclodextrin: Enhanced excimer formation due to preorganization of two pyrenes in a cyclodextrin cavity

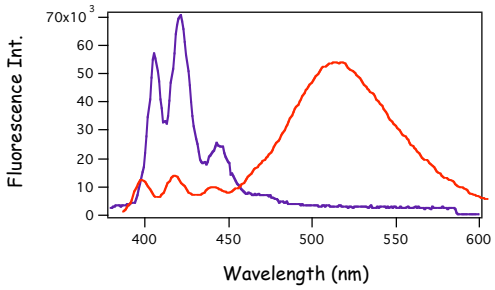


Zeolites as hosts

Anthracene@NaX: Cation controlled aggregation



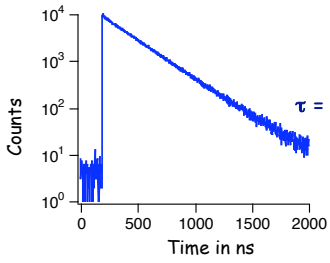
Photophysics of OA-Anthracene Complex



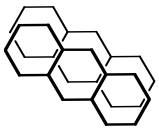
---- Anthracene in water

---- Anthracene in octa acid

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

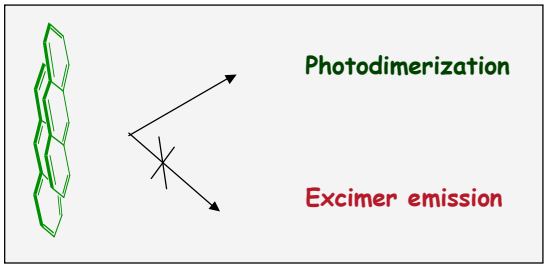


τ = 263 ns

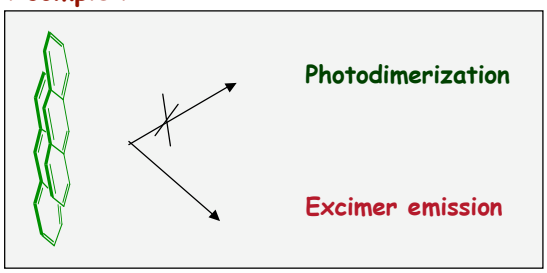


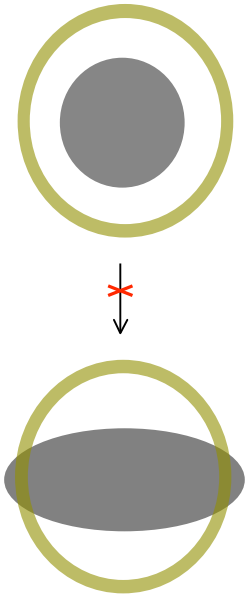
Sandwich excimer – τ 210 - 225 ns

Isotropic solution



OA complex



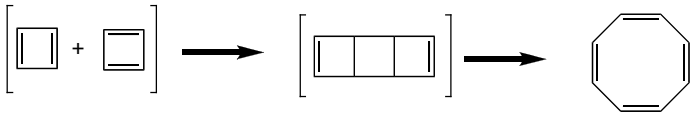


Product too large to fit in

Stabilizing Unstable Molecules

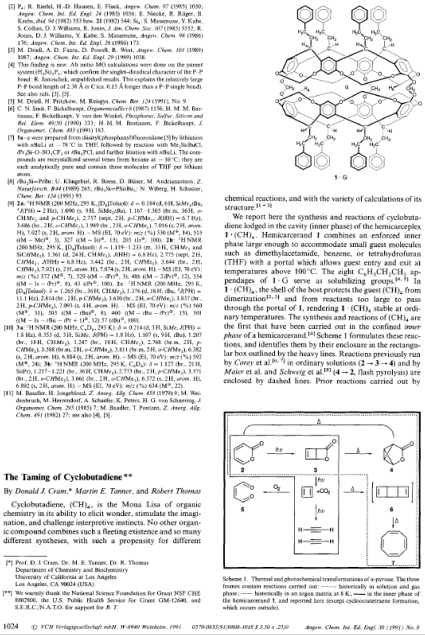
Cram's "taming" of cyclobutadiene

For many years attempts to isolate cyclobutadiene in solution at room temperature failed because one diene undergoes a very rapid Diels-Alder reaction with a second diene molecule (a dimerization)



Cram's idea was to synthesize cyclobutadiene in a host system that would provide supramolecular steric hindrance to prevent dimerization

Cram's breakthrough publication: "The Taming of Cyclobutadiene", Angew. Chem. 30, 1024 (1991)



The Taming of Cyclobutadiene**

By *Donald J. Cram,* Martin E. Tanner, and Robert Thomas*

Cyclobutadiene, $(CH)_4$, is the Mona Lisa of organic chemistry in its ability to elicit wonder, stimulate the imagination, and challenge interpretive instincts. No other organic compound combines such a fleeting existence and so many different syntheses, with such a propensity for different chemical reactions, and with the variety of calculations of its structure.[1–3]

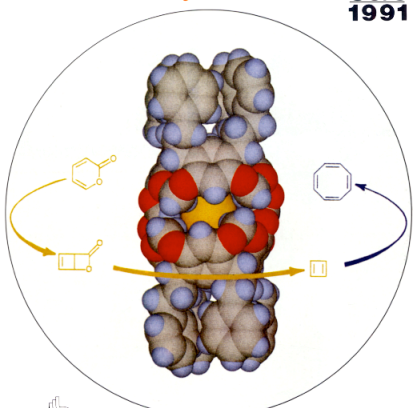
We report here the synthesis and reactions of cyclobutadiene lodged in the cavity (inner phase) of the hemicarcerplex $\mathbf{1}\cdot(CH)_4$. Hemicarcerand **1** combines an enforced inner phase large enough to accommodate small guest molecules such as dimethylacetamide, benzene, or tetrahydrofuran (THF) with a portal which allows guest entry and exit at temperatures above 100 °C. The eight $C_6H_4CH_2CH_2OH$ appendages of **1**·**G** serve as solubilizing groups.[4, 5] In $\mathbf{1}\cdot(CH)_4$, the shell of the host protects the guest $(CH)_4$ from dimerization[6–9] and from reactants too large to pass through the portal of **1**, rendering $\mathbf{1}\cdot(CH)_4$ stable at ordinary temperatures. The synthesis and reactions of $(CH)_4$ are the first that have been carried out in the confined *inner phase* of a hemicarcerand.[10] Scheme 1 formulates these reactions, and identifies them by their enclosure in the rectangular box outlined by the heavy lines. Reactions previously run by *Corey* et al.[6, 7] in ordinary solutions (**2** → **3** → **4**) and by *Maier* et al. and *Schwalg* et al.[8] (**4** → **2**, flash pyrolysis) are enclosed by dashed lines. Prior reactions carried out by

Scheme 1. Thermal and photochemical transformations of α-pyrone. The three frames contain reactions carried out: ····· historically in solution and gas phase; —— historically in an argon matrix at 8 K; ——— in the inner phase of the hemicarcerand **1**, and reported here (except cyclooctatriene formation, which occurs outside).

[*] Prof. D. J. Cram, Dr. M. E. Tanner, Dr. R. Thomas
Department of Chemistry and Biochemistry
University of California at Los Angeles
Los Angeles, CA 90024 (USA)

[**] We warmly thank the National Science Foundation for Grant NSF CHE 8902800, the U.S. Public Health Service for Grant GM-12640, and S.E.R.C./N.A.T.O. for support for *R. T.*

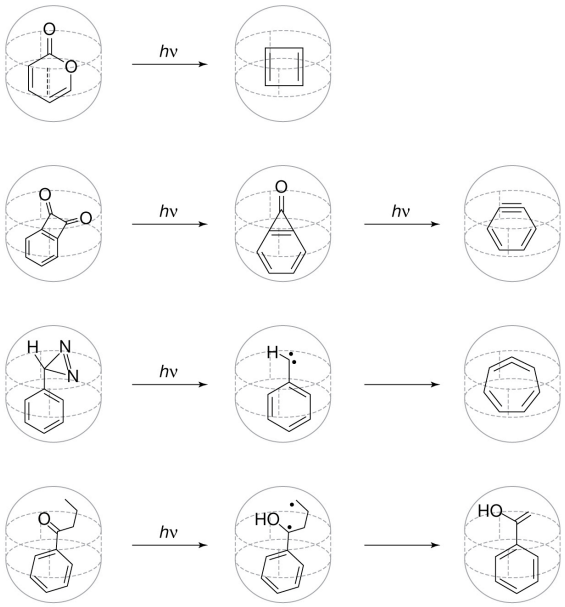
D 3461 E
ANGEWANDTE CHEMIE
A Journal of the Gesellschaft Deutscher Chemiker
International Edition in English
30/8 1991



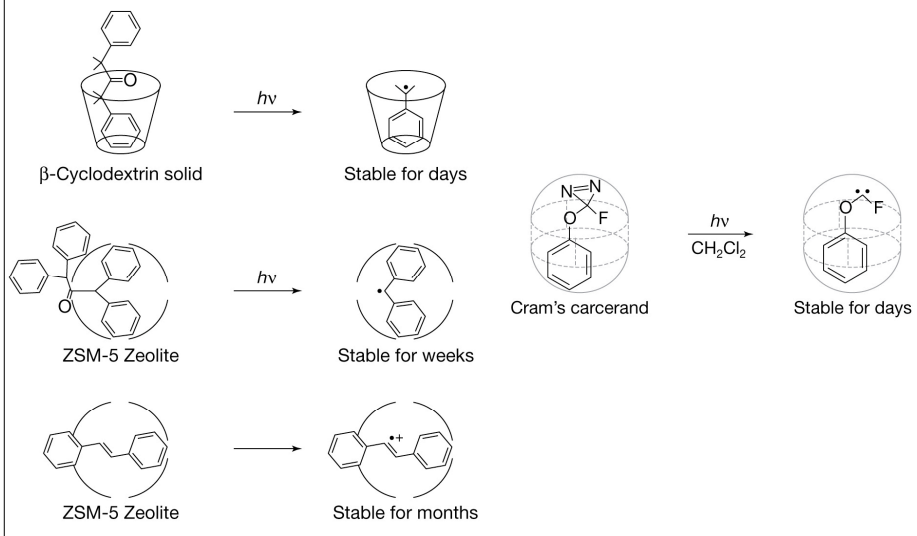
30 Years International Edition
ACIEAY 30 (8) 893–1050 (1991) ISSN 0570–0833
VCH

Now · Now · Now
Highlights
see page 954

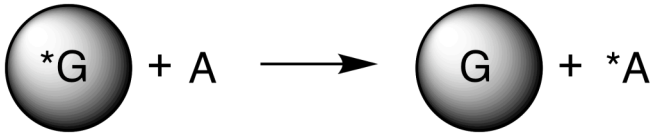
Stabilizing Unstable Molecules



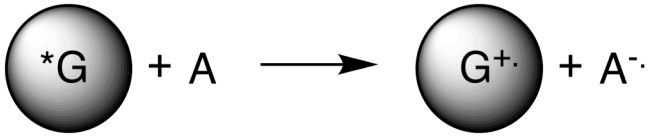
Stabilizing Reactive Intermediates



Energy, electron and spin transfer through the walls of a carcerand



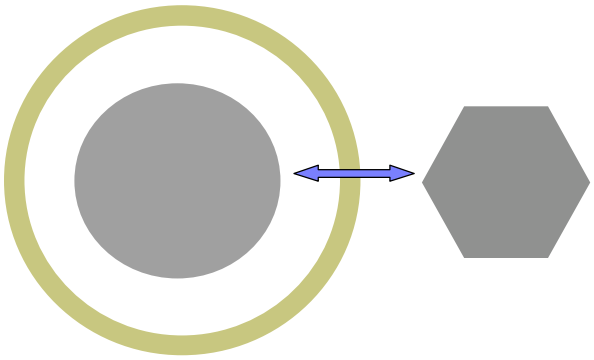
Energy and spin transfer



Electron transfer

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

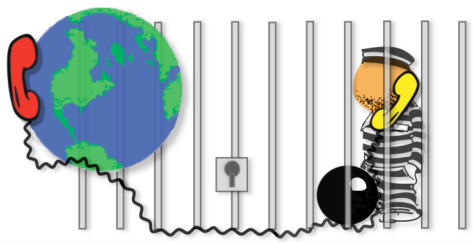
Communication



Electron

Energy

Spin



Biacetyl@carcerand

Can a guest@carcerand undergo electron transfer, spin transfer and energy transfer processes?

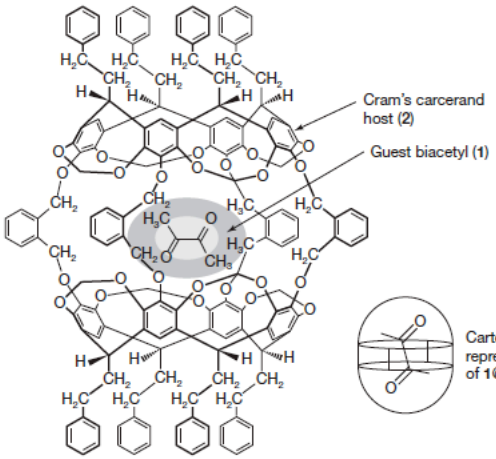
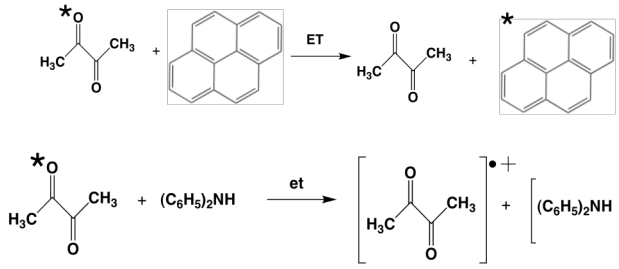


Figure 13.21 Biacetyl (**1**) incarcerated in Cram's carcerand (**2**). The insert to the right is a schematic of the 1@Cram's carcerand (2).

Biacetyl@carcerand can transfer energy and electrons to molecules outside the walls of the carcerand.

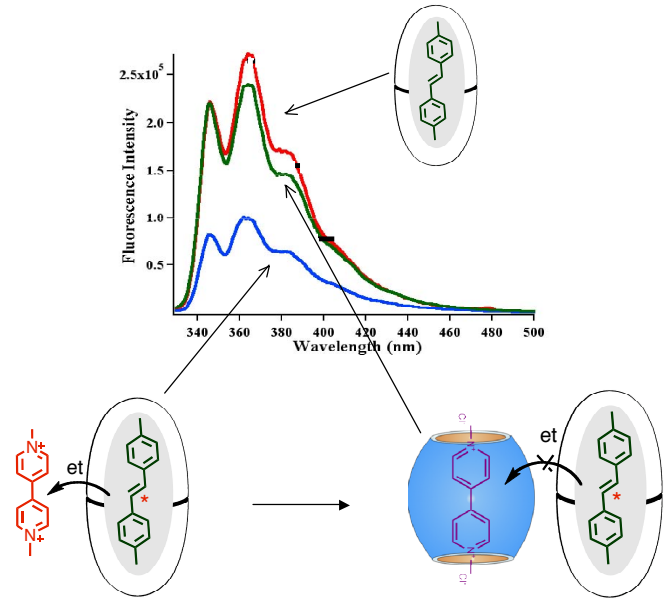


Energy Donor or Electron Acceptor	Energy Acceptor or Electron Donor[a]	Product from **1** Due to ET or et	Product from Py and Amine Due to ET or et	Rate ($M^{-1}\,s^{-1}$)	
1(T_1) (ET)	Py(S_0)	**1**(S_0)	Py(T_1)	$\sim 5 \times 10^9$	
1(T_1)@**2** (ET)	Py(S_0)	**1**(S_0)@**2**	Py(T_1)	$\sim 1 \times 10^6$	Bi@carcerand
1(T_1) (et)	$(C_6H_5)_2NH(S_0)$	$(\mathbf{1}^{\bullet-})$	$[(C_6H_5)_2NH]^{\bullet+}(S_0)$	$\sim 5 \times 10^9$	
1(T_1)@**2** (et)	$(C_6H_5)_2NH(S_0)$	$(\mathbf{1}^{\bullet-})$@**2**	$[(C_6H_5)_2NH]^{\bullet+}(S_0)$	$\sim 3 \times 10^4$	Bi@carcerand

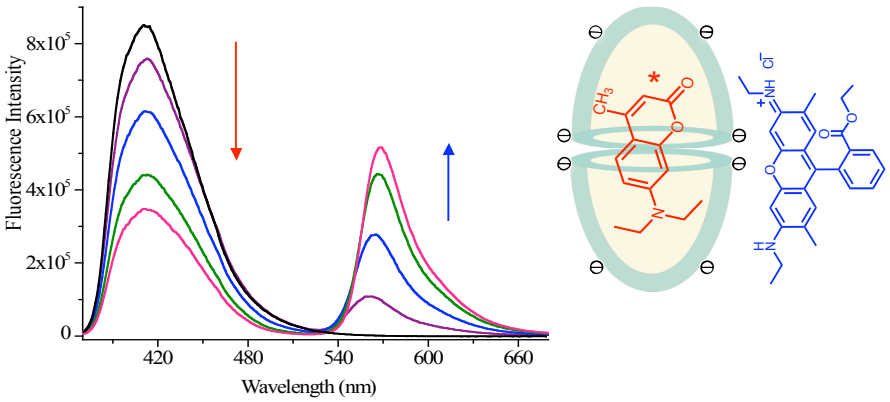
a. Py = pyrene.

ET and et are slowed down by several orders of magnitude (~ 10^{-3}-10^{-4})

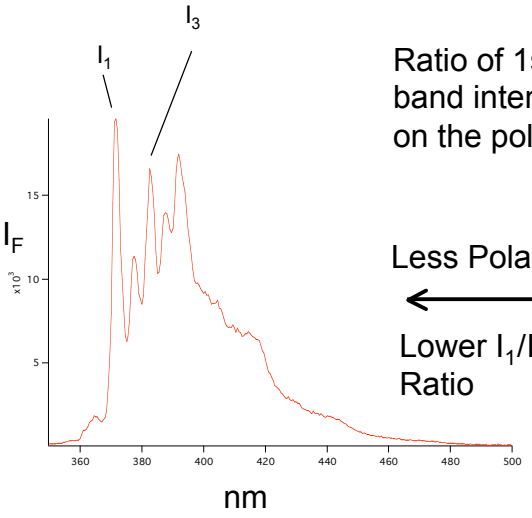
Electron transfer between caged and free molecules



Energy transfer between caged and free molecules



Fluorescence Response to Solvent Polarities



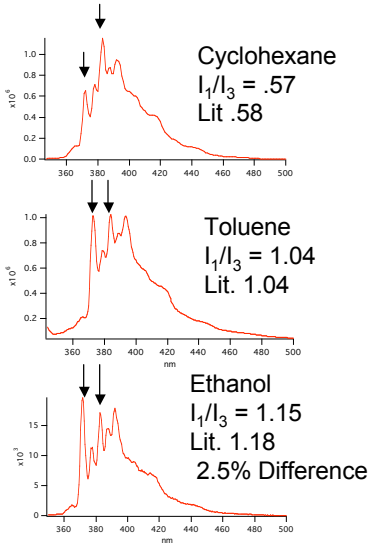
Ratio of 1st to 3rd vibrational band intensities is dependent on the polarity of the solvent.

Less Polar ⟷ More Polar

Lower I_1/I_3 Ratio

Higher I_1/I_3 Ratio

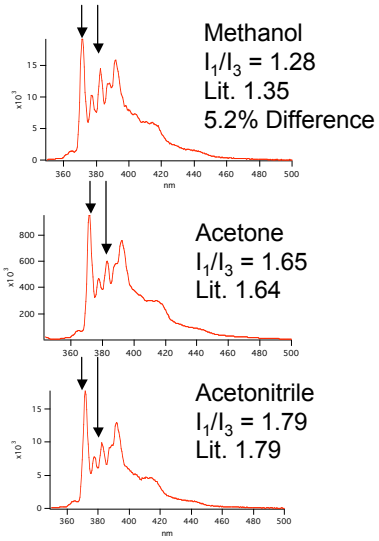
Comparison of pyrene emission in different solvents



Cyclohexane
I_1/I_3 = .57
Lit .58

Toluene
I_1/I_3 = 1.04
Lit. 1.04

Ethanol
I_1/I_3 = 1.15
Lit. 1.18
2.5% Difference



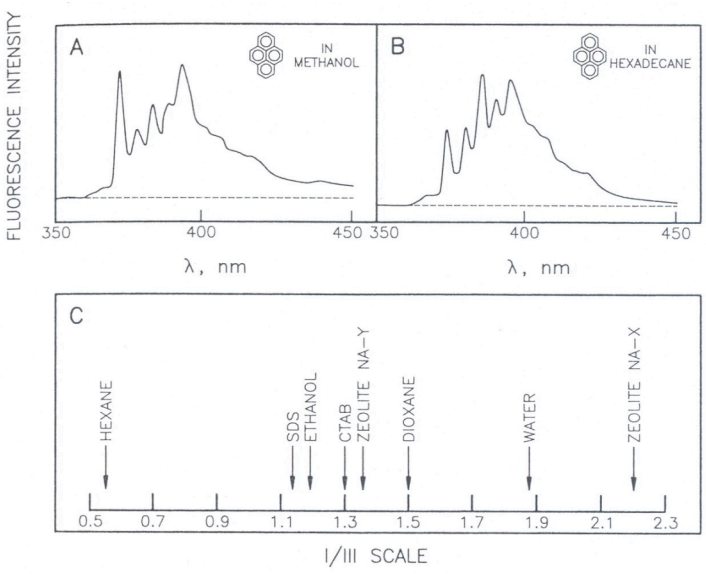
Methanol
I_1/I_3 = 1.28
Lit. 1.35
5.2% Difference

Acetone
I_1/I_3 = 1.65
Lit. 1.64

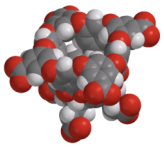
Acetonitrile
I_1/I_3 = 1.79
Lit. 1.79

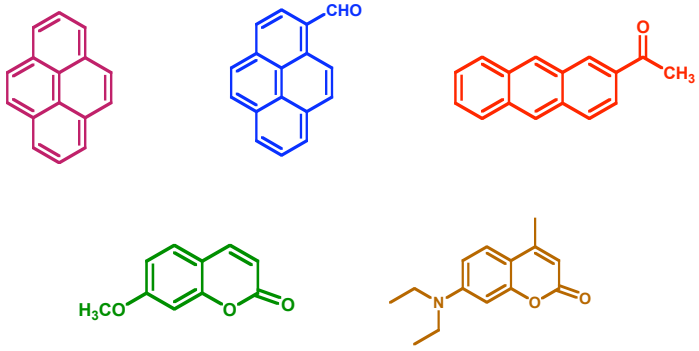
Pyrene fluorescence provides a means of measuring the polarity of a host as the environment experienced by a guest

Pyrene as a polarity probe



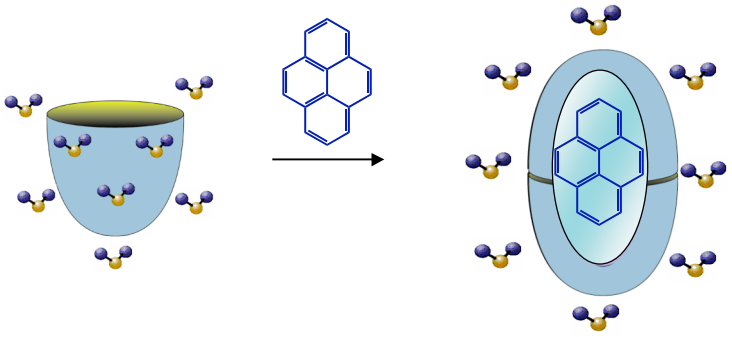
Octa acid's interior micropolarity probed





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

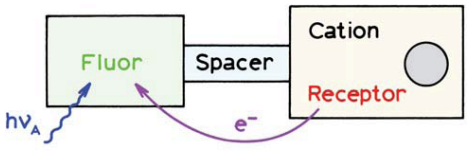
Interior of octa acid is benzene-like



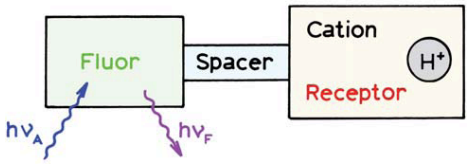
'Dry' and 'Non-polar'

Hydrogen Oxygen

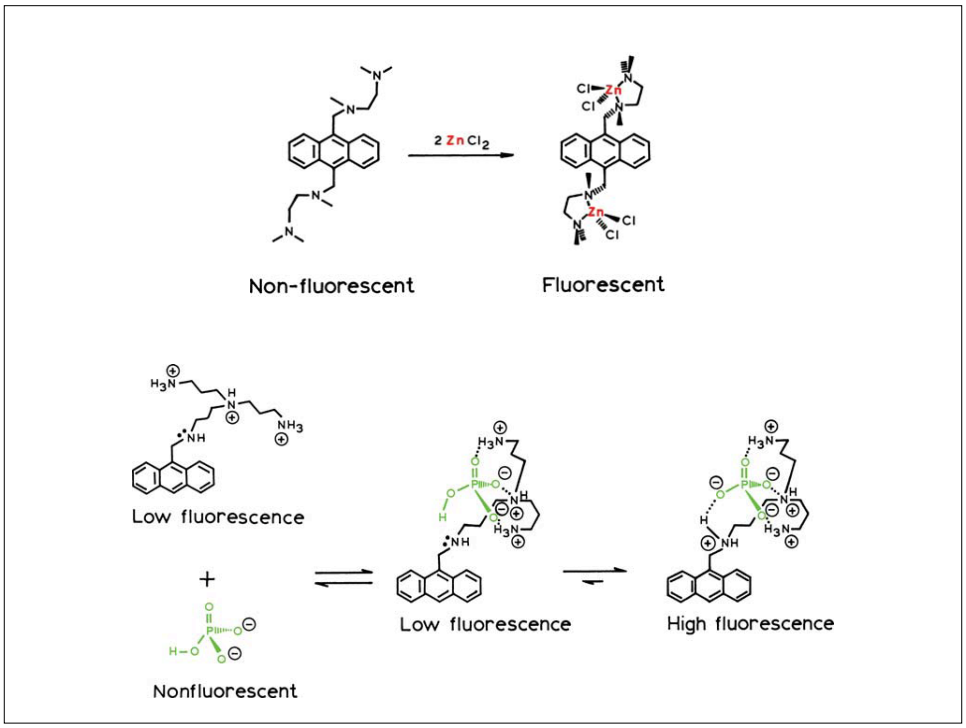
Supramolecular Sensors



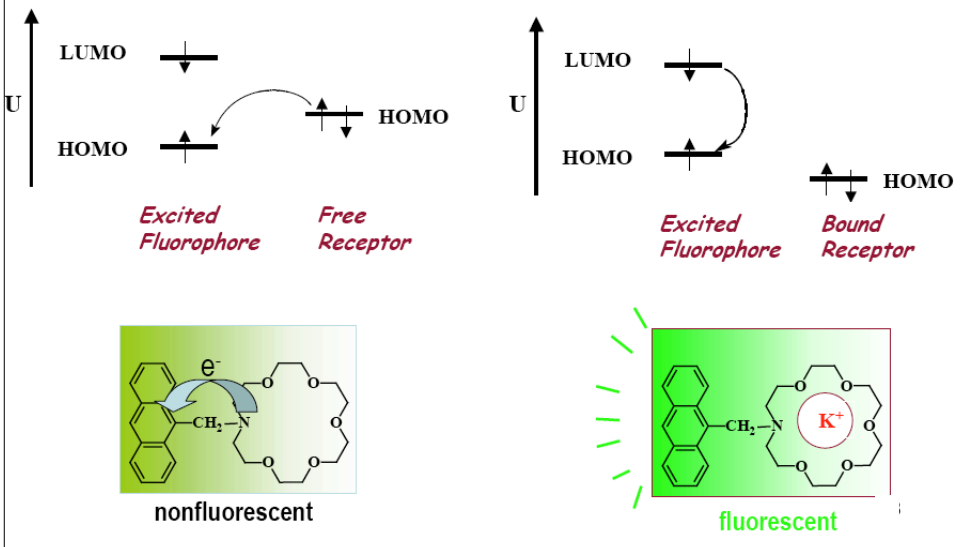
Nonfluorescent



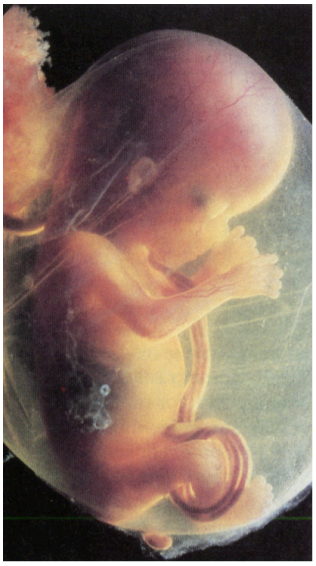
Fluorescent

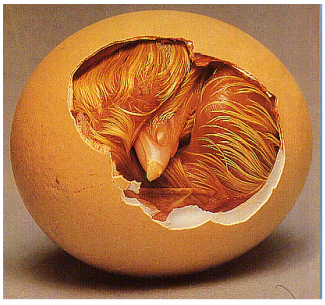


Mechanism of PET Signaling



Chemistry in Confined Spaces





Container Chemistry at Backyard