

Molecular Photonics

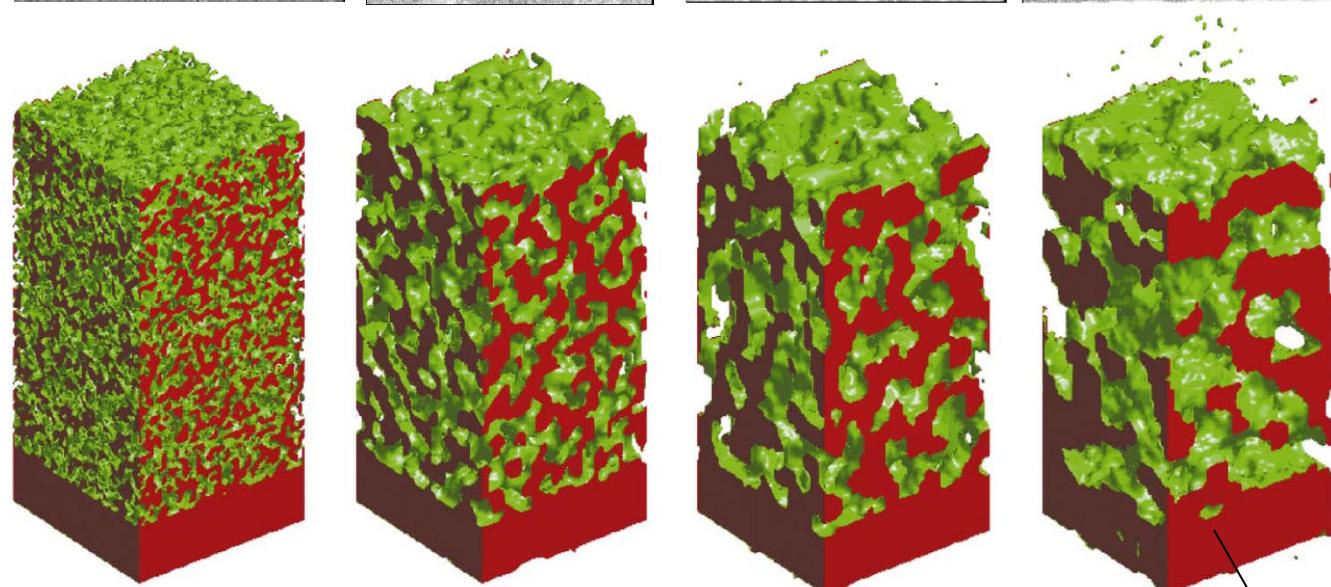
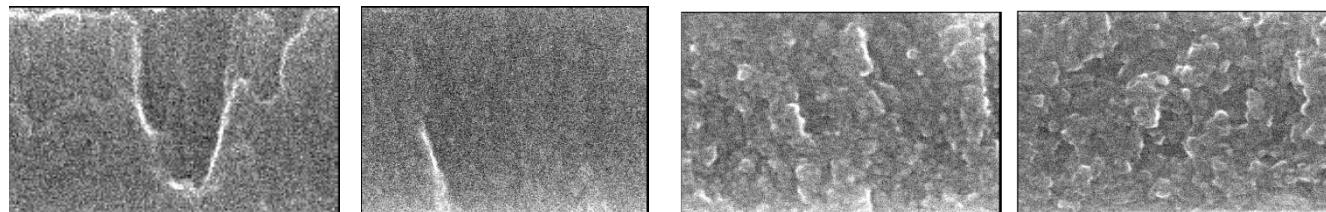
Lecture 3

Motivation I

CuPc:PTCBI (3:4), 1.4% efficiency

Copper phthalocyanine/3,4,9,10-perylene tetracarboxylic bis-benzimidazole

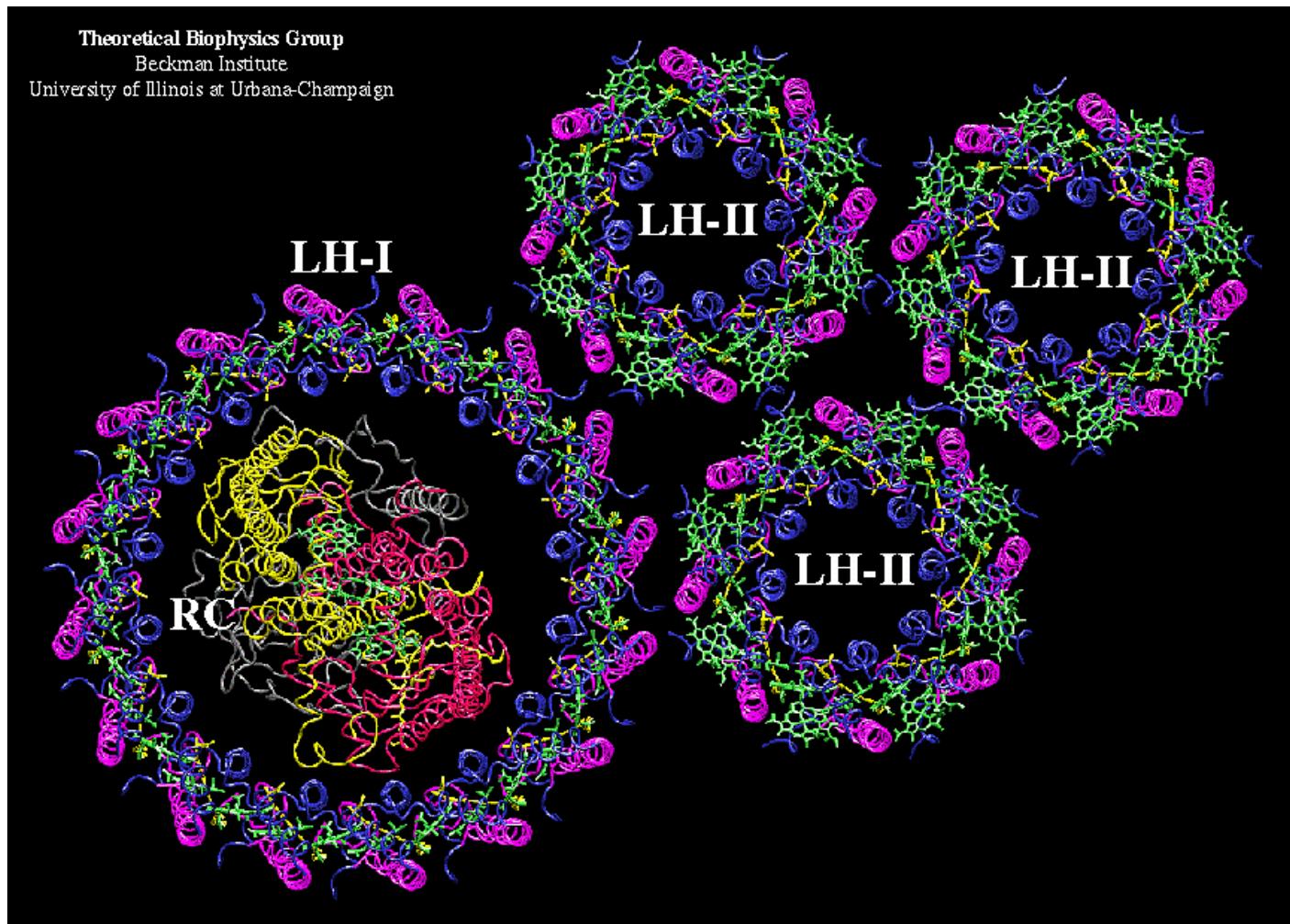
SEM →



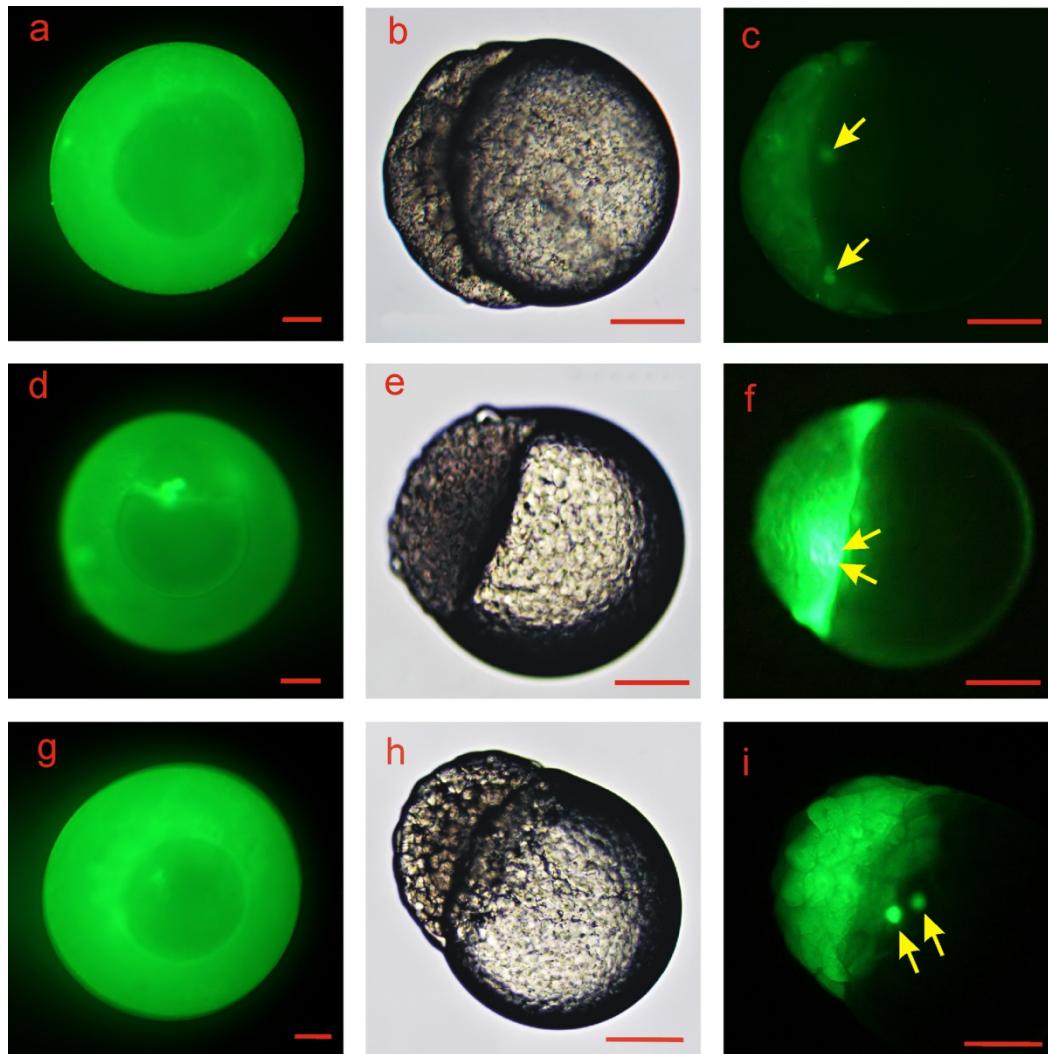
Forrest et al. *Nature* 2003, 425, 158

Most efficient

Motivation II

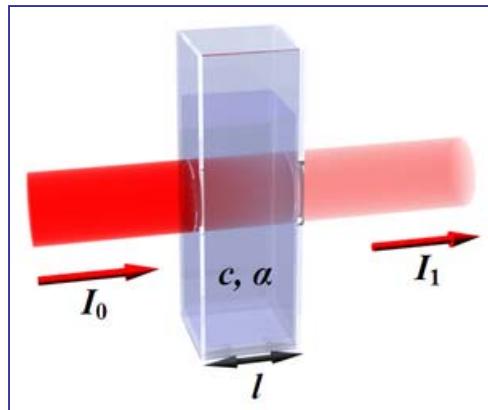


Motivation III – fluorescence probes



Zebrafish embryos at varying developmental stages
permeabilized in the presence of a fluorescent probe

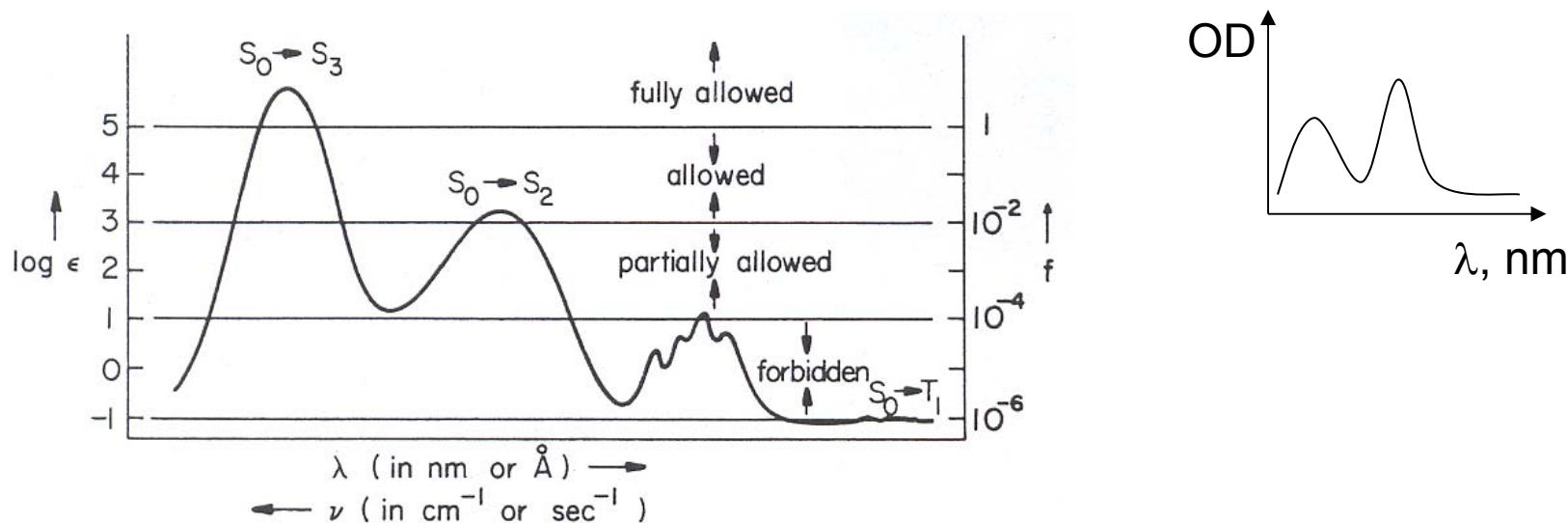
Absorption: Beer-Lambert Law



$$OD = \epsilon \ell c$$

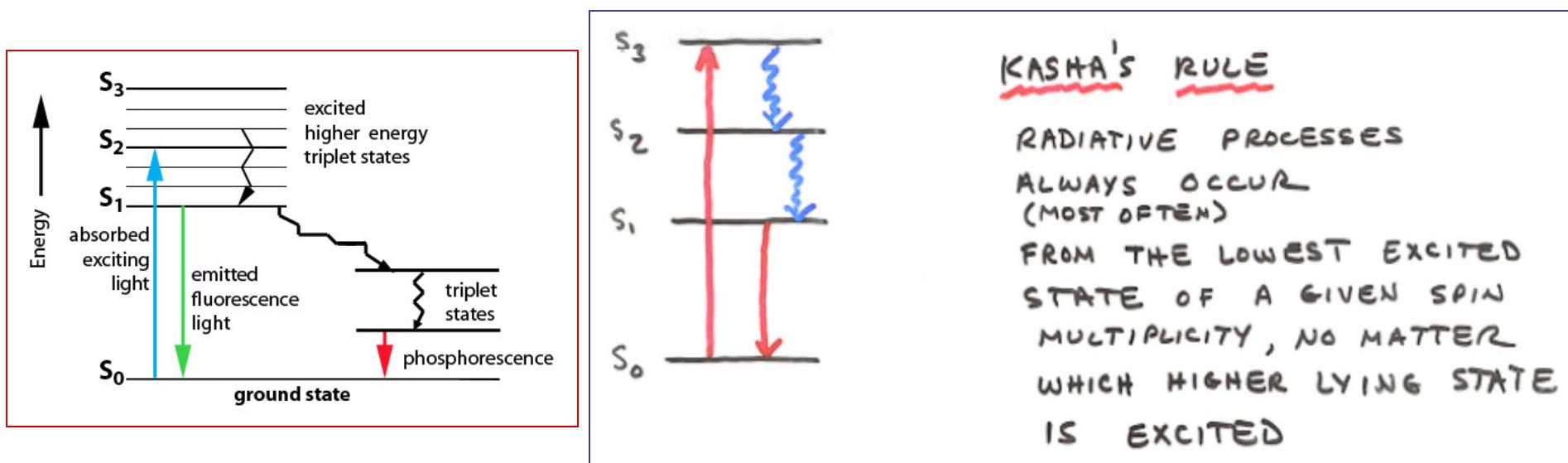
- OD - optical density, $OD = \log \frac{I_0}{I_t}$
where I_0 - intensity of incident light
 I_t - intensity of transmitted light
- ϵ - extinction coefficient
- ℓ - optical path length
- c - concentration

$$\epsilon \equiv [\log (I_0/I_t)]/lc$$



Fluorescence

The **Fluorescence Quantum Yield**, Φ_F , is defined as the ratio of the number of photons emitted to the number of photons absorbed.



Vavilov's Law: Φ_F is independent of the energy of the initially excited state (excitation wavelength). This follows from Kasha's rule.

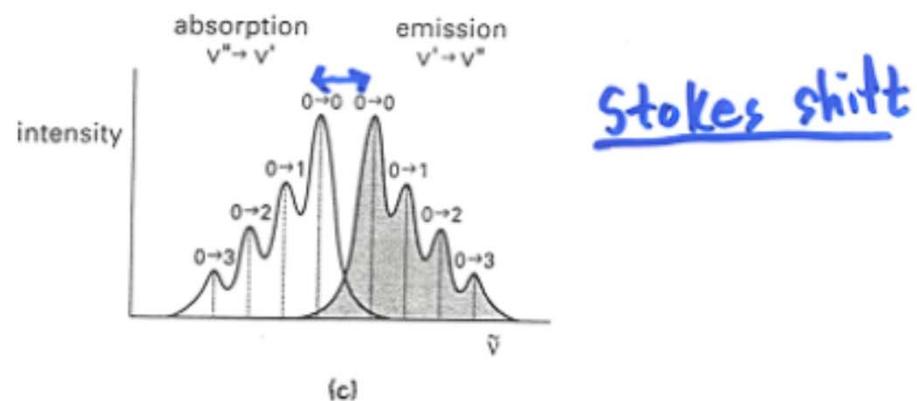
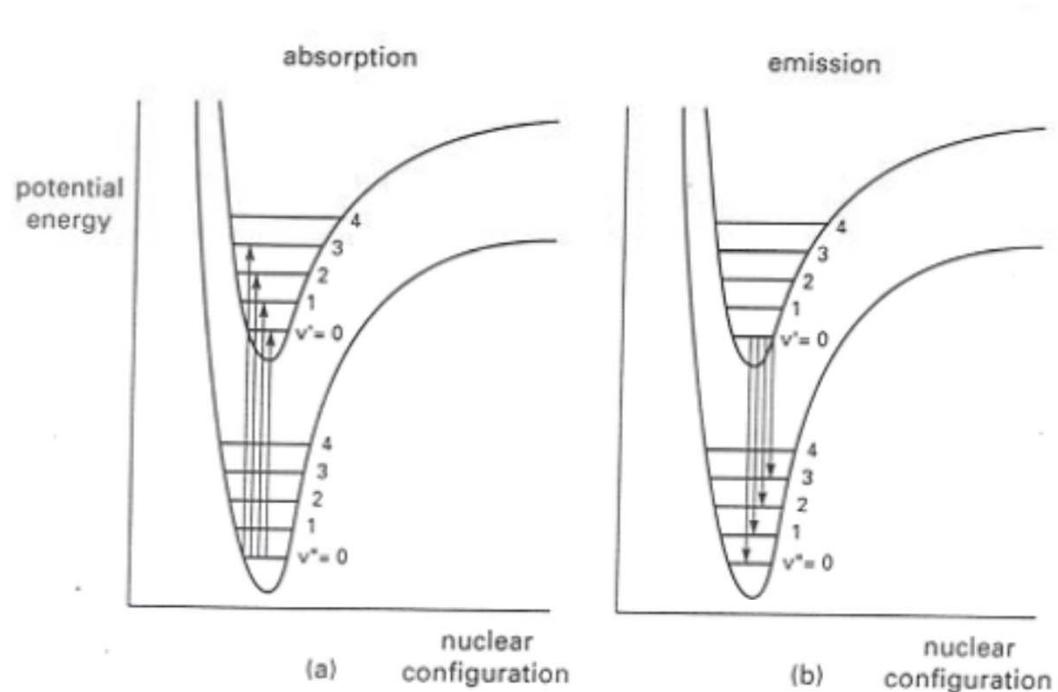
Fluorescence lifetime.

Practical guide on QY determination: S. Fery-Forgues and D. Lavabre, Journal of Chemical Education 1999, 76, 1260

Terminology

- Emission – general term
- Fluorescence – from singlet states
- Phosphorescence – from triplet states
- Luminescence – general for emission of photons

Absorption, emission and Stokes shift



Properties of chromophores

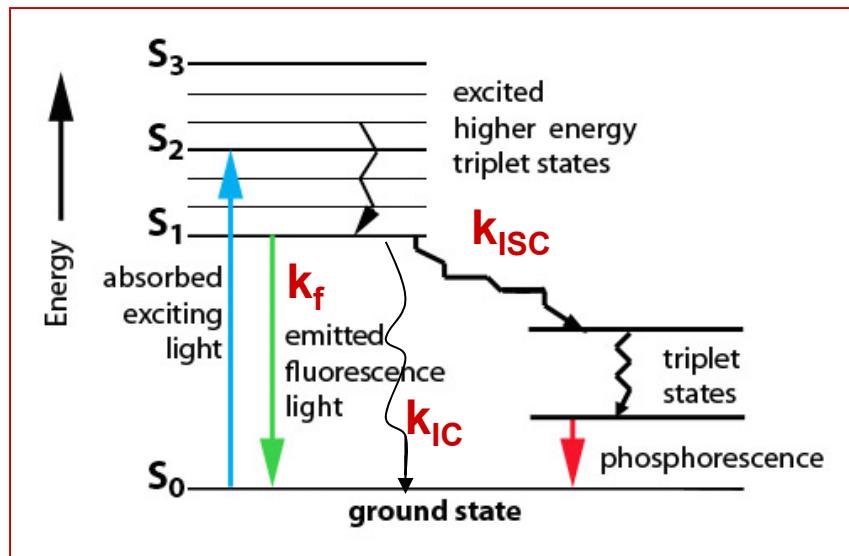
Thus if we wish to produce a bathochromic effect in a molecule (*a*) we may increase the masses of the oscillating system by increasing the number of participating electrons, which may be accomplished by increasing the extent of the conjugating system, as in the polyenes or the phthalocyanines, or (*b*) we may increase the mobility of the electrons. We may now see how this mobility may be increased in the several important classes of substances.

Lewis and Calvin, 1939.

In molecules HOMO-LUMO gap defines the energy of the absorption, while polarizability defines the absorption strength (oscillator strength). Experimental measure of the absorption capability is extinction coefficient.

Emission behavior

Two processes diminish fluorescence:
internal conversion and intersystem crossing



$$\Phi_f = k_f / (k_f + k_{ISC} + k_{IC})$$

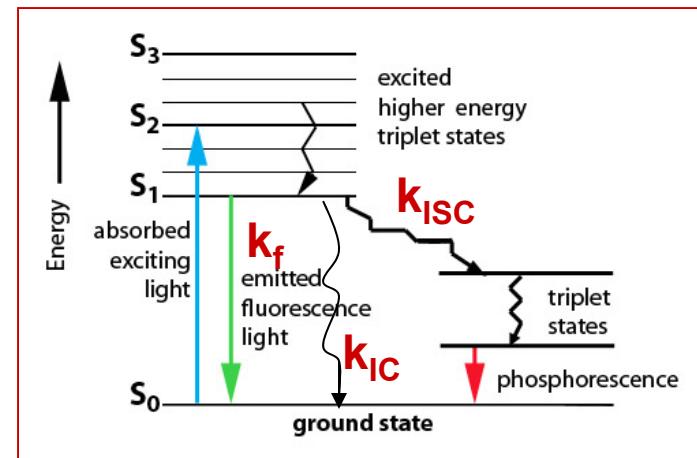
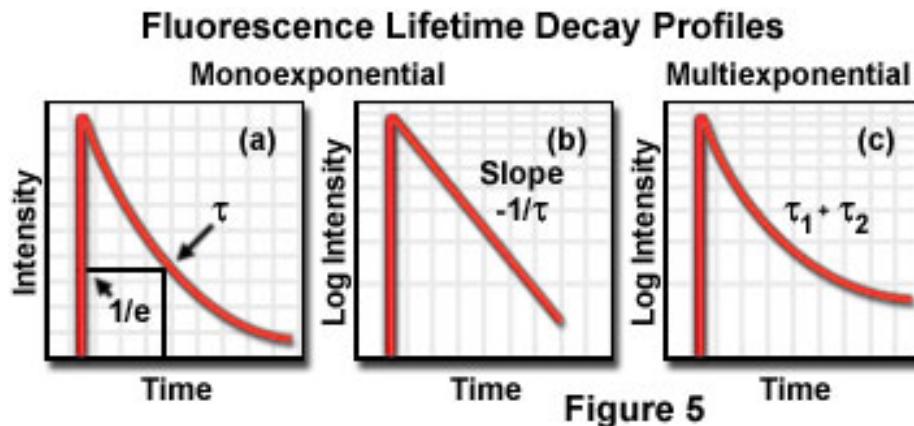
$$\tau_f = 1/k_f$$

$$\tau_{obs} = 1 / (k_f + k_{ISC} + k_{IC})$$

$$\Phi_f = k_f \tau_{obs}$$

$$\Phi_f = \tau_{obs} / \tau_f$$

Lifetime



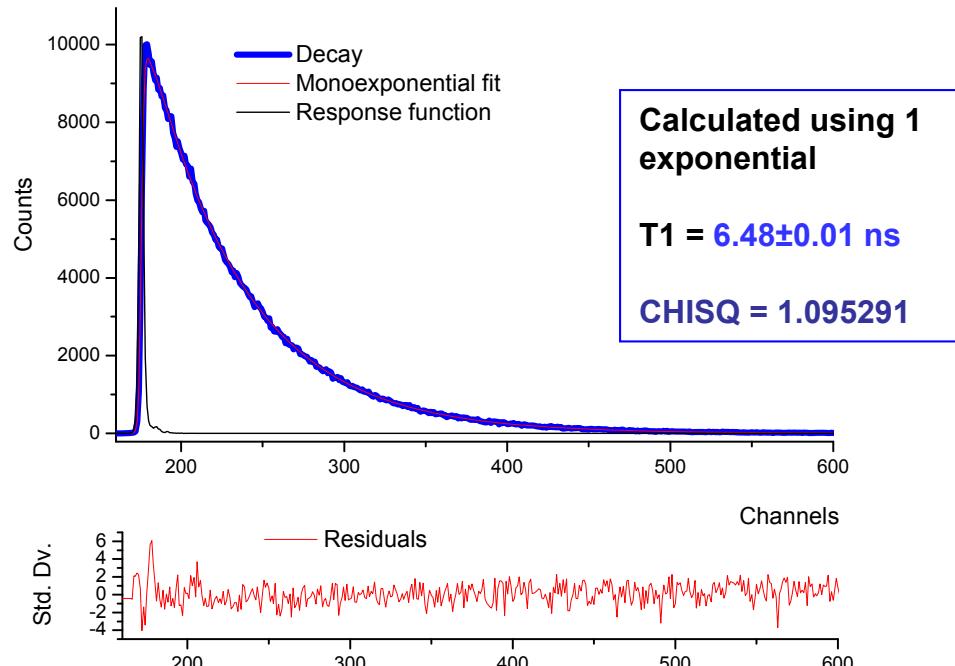
Monoexponential – a particular species (one Jablonski diagram)

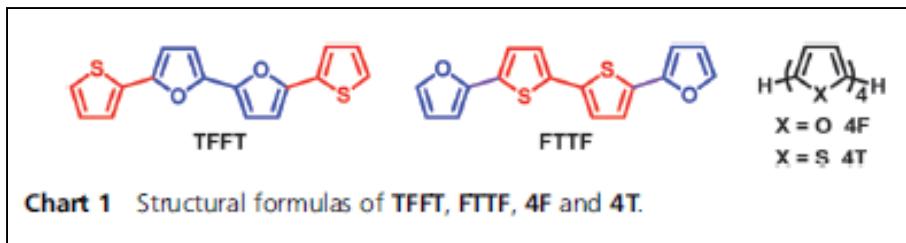
Multiexponential – more than one species (several emitters)

Experimental lifetime:

$$\tau_{\text{obs}} = 1/(k_f + k_{\text{ISC}} + k_{\text{IC}})$$

$$\Phi_f = \tau_{\text{obs}} / \tau_f$$





Bendikov et al.

Chem. Commun., 2013, **49**, 6256–6258

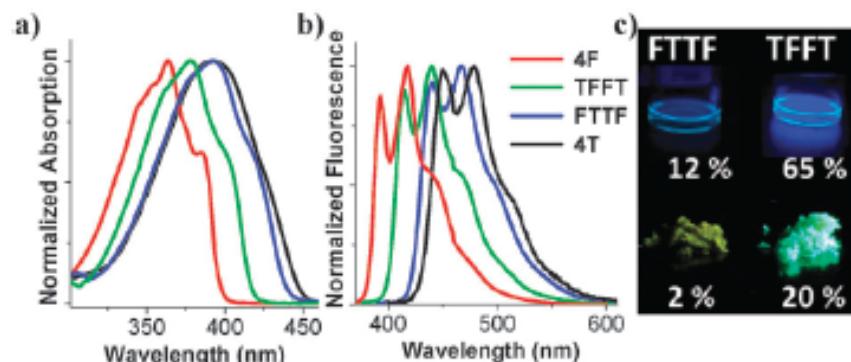


Fig. 2 Normalized (a) absorption and (b) fluorescence spectra of 4F, TFFT, FTTF, and 4T in dioxane. (c) Irradiated (at 365 nm) samples of FTTF and TFFT in dioxane solutions and in solid (crystalline) form. Quantum efficiency values are denoted below each sample.

Table 1 Experimental and calculated properties of TFFT, FTTF, 4F and 4T

	λ_{abs}^a (nm)	$\varepsilon_{\text{max}}^a$ ($\text{cm}^{-1} \text{M}^{-1}$)	λ_{flu}^a (nm)	Φ_f^a	Stokes shift ^a (eV)	Φ_f (solid)	τ_f^a (ns)	k_f^b (ns^{-1})	k_{NR}^c (ns^{-1})	E_{ox}^d (V)	HOMO ^e (eV)	LUMO ^e (eV)
4F	364	37 900	391, 413	0.80^{12}	0.24	0.10	1.48^{12}	0.54	0.14	0.80	-4.73	-1.31
TFFT	378	34 300	415, 440	0.65	0.29	0.20	1.32	0.49	0.27	0.83	-4.81	-1.54
FTTF	393	35 500	441, 467	0.12	0.34	0.02	0.26	0.47	3.38	0.85	-4.88	-1.74
4T	392	36 200	450, 479	0.18^{12}	0.41	0.09	0.38^{12}	0.47	2.16	0.97	-5.01	-1.88

^a Measured in dioxane. ^b Calculated according to the equation $k_f = \Phi_f / \tau_f$. ^c Calculated according to the equation $\Phi_f = k_f / (k_f + k_{\text{NR}})$. ^d Oxidation potentials measured by cyclic voltammetry in propylene carbonate with 0.1 M tetra-*n*-butylammonium tetrafluoroborate, scan rate: 100 mV s⁻¹. ^e Calculated values (B3LYP/6-31G(d)). ^f HLG: HOMO-LUMO gap. ^g The melting point is taken as the peak maximum in DSC curve. ^h From DSC measurements.

$$\Phi_f = k_f / (k_f + k_{\text{ISC}} + k_{\text{IC}})$$

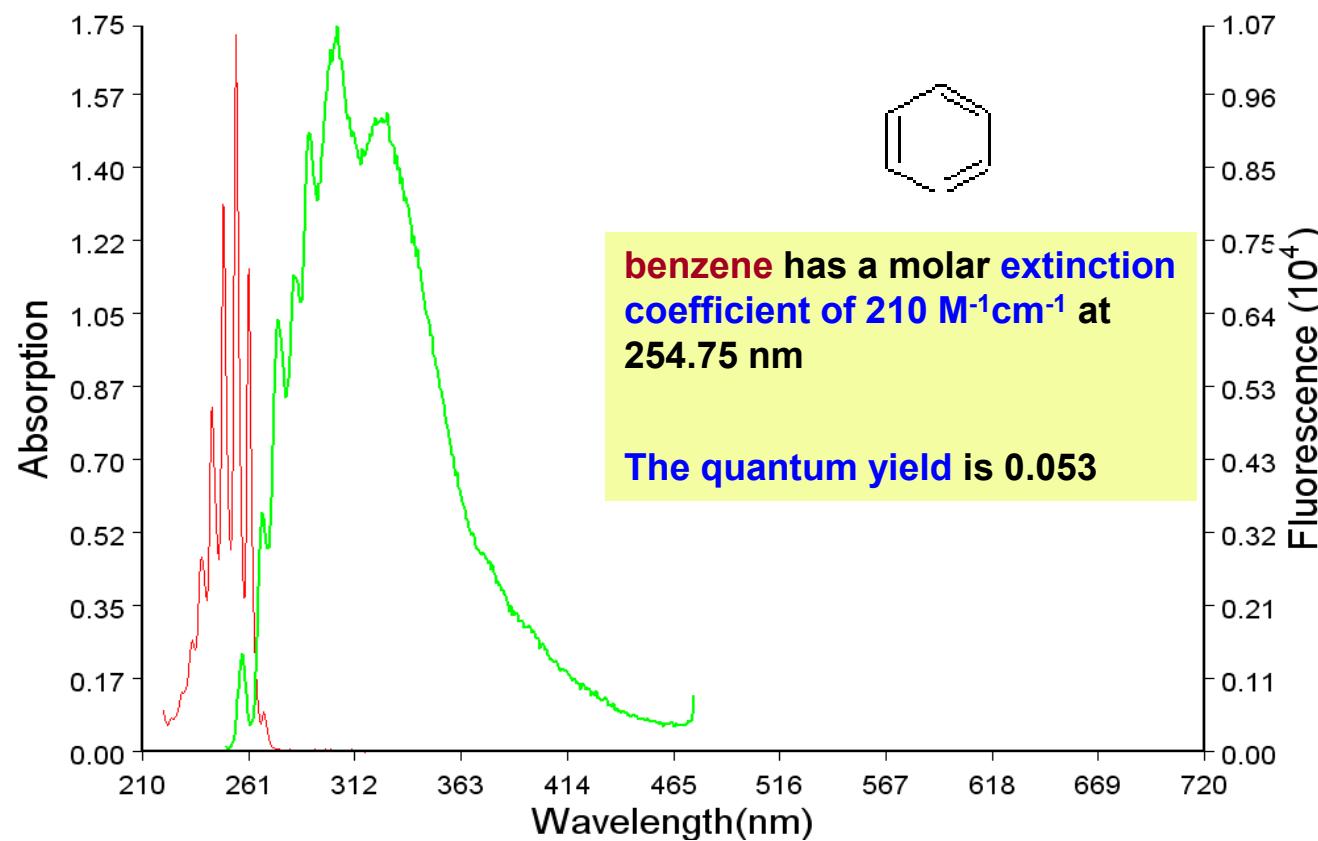
$$\tau_f = 1/k_f$$

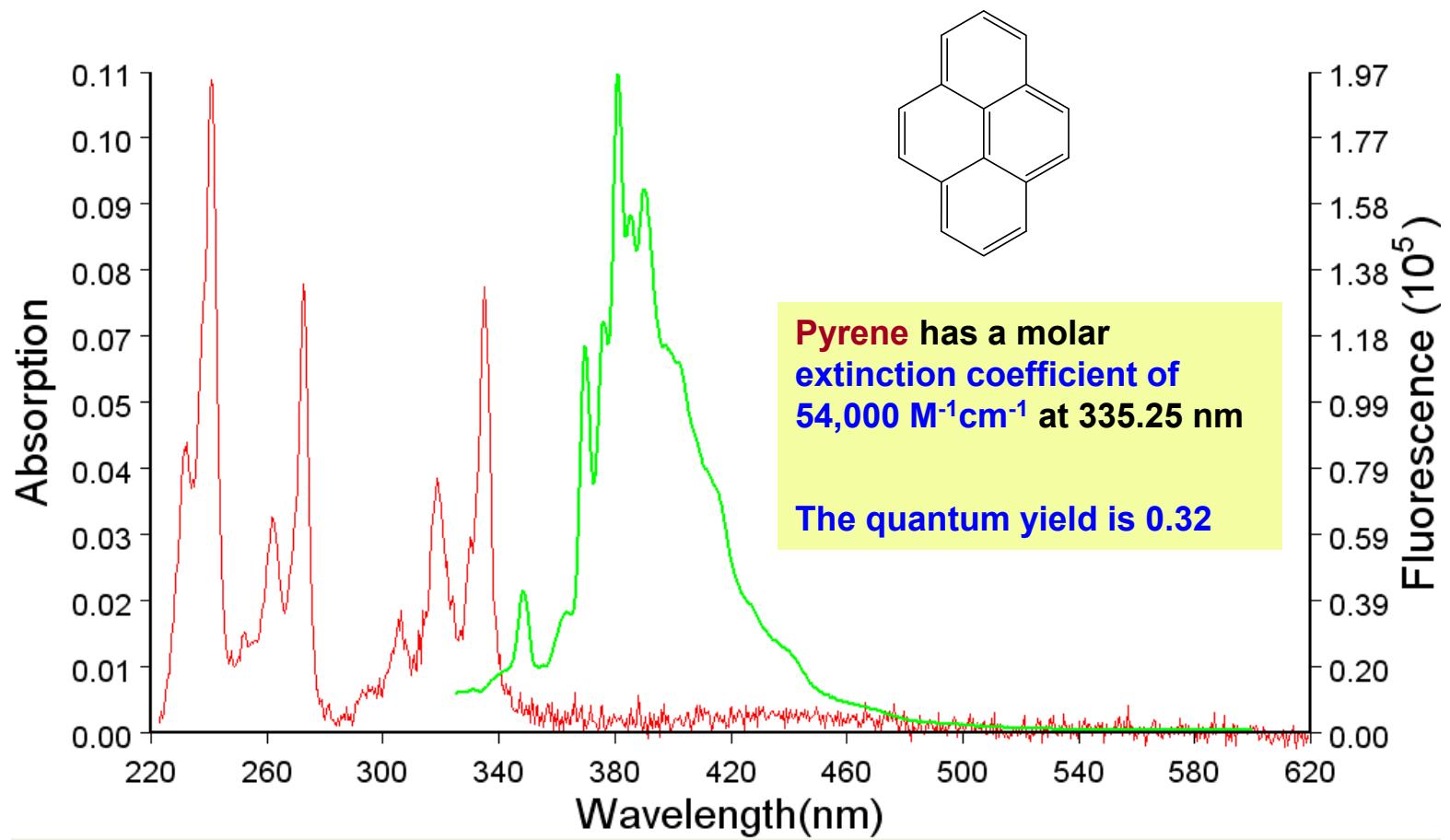
$$\tau_{\text{obs}} = 1/(k_f + k_{\text{ISC}} + k_{\text{IC}})$$

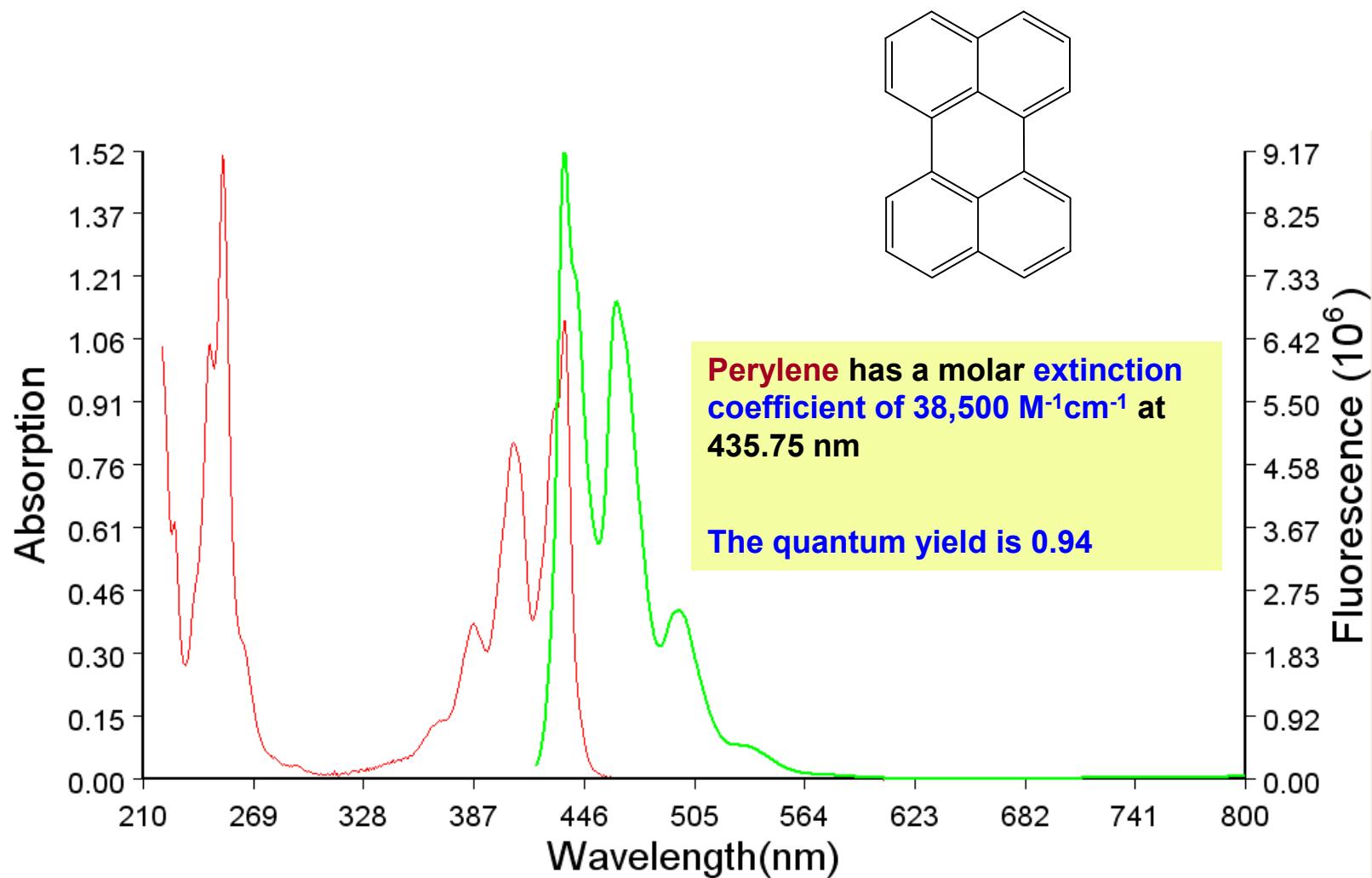
$$\Phi_f = k_f \tau_{\text{obs}}$$

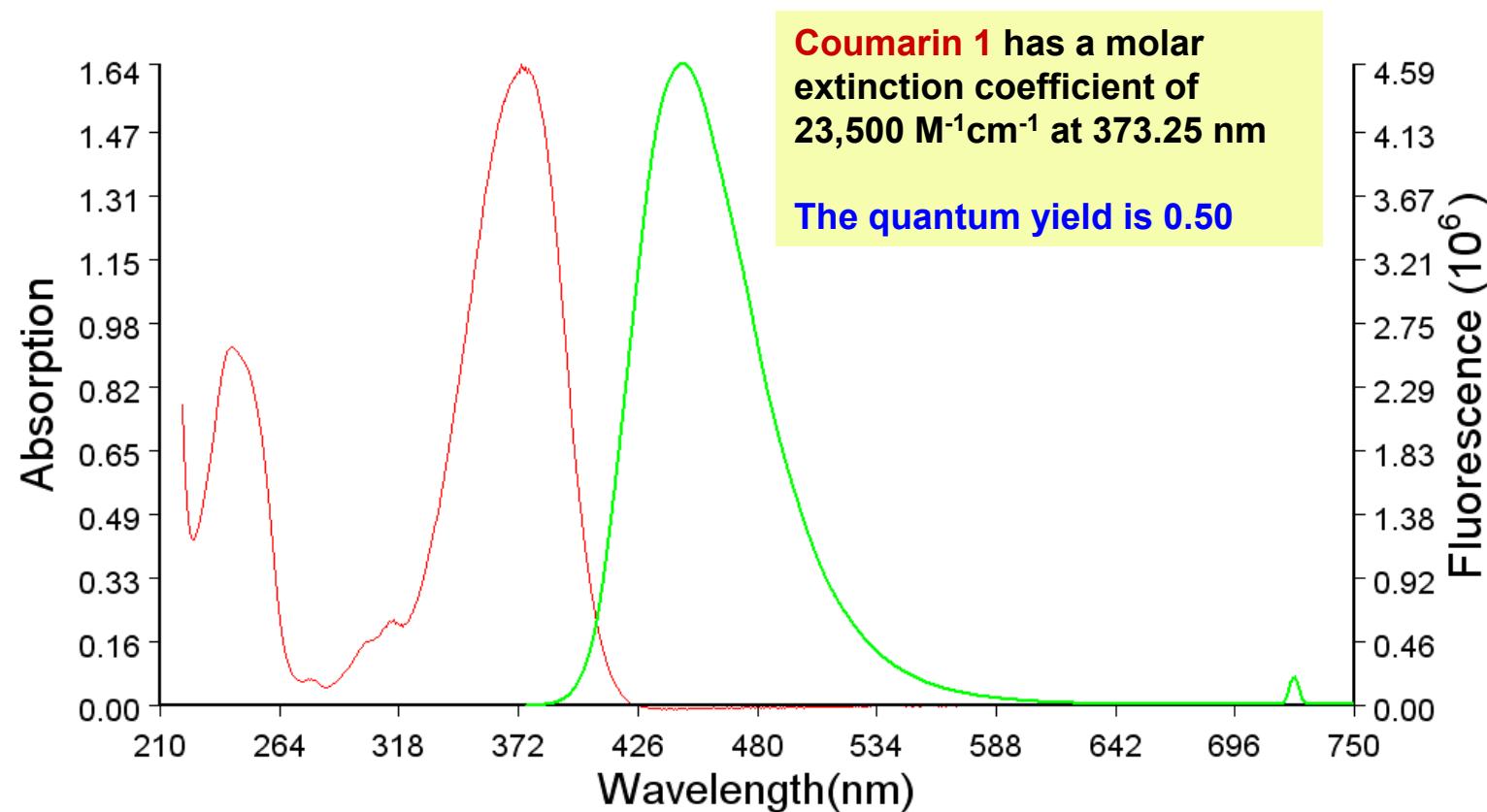
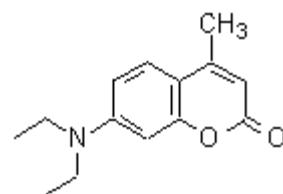
$$\Phi_f = \tau_{\text{obs}} / \tau_f$$

Absorption, fluorescence and structure: experimental data.

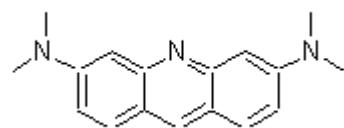






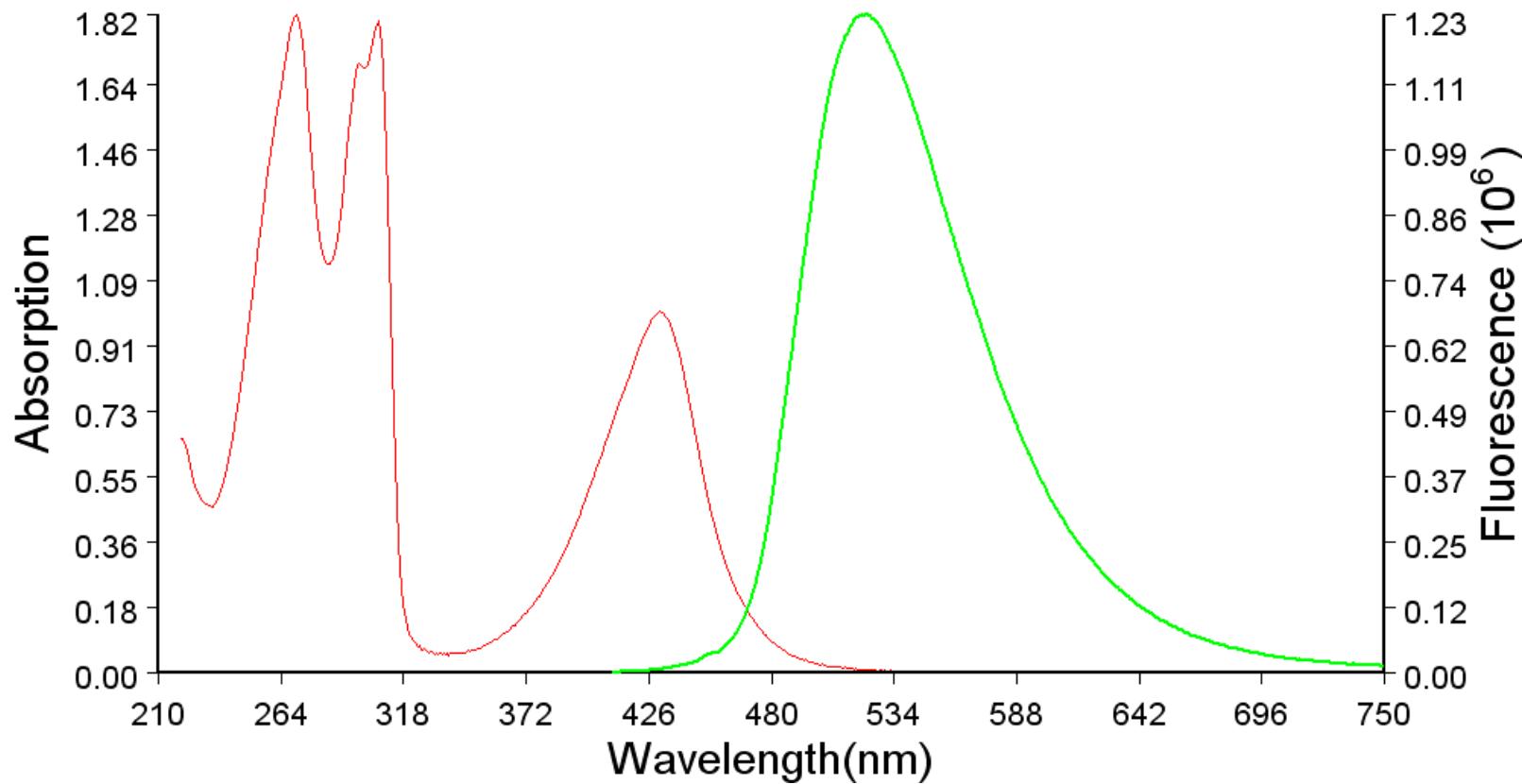


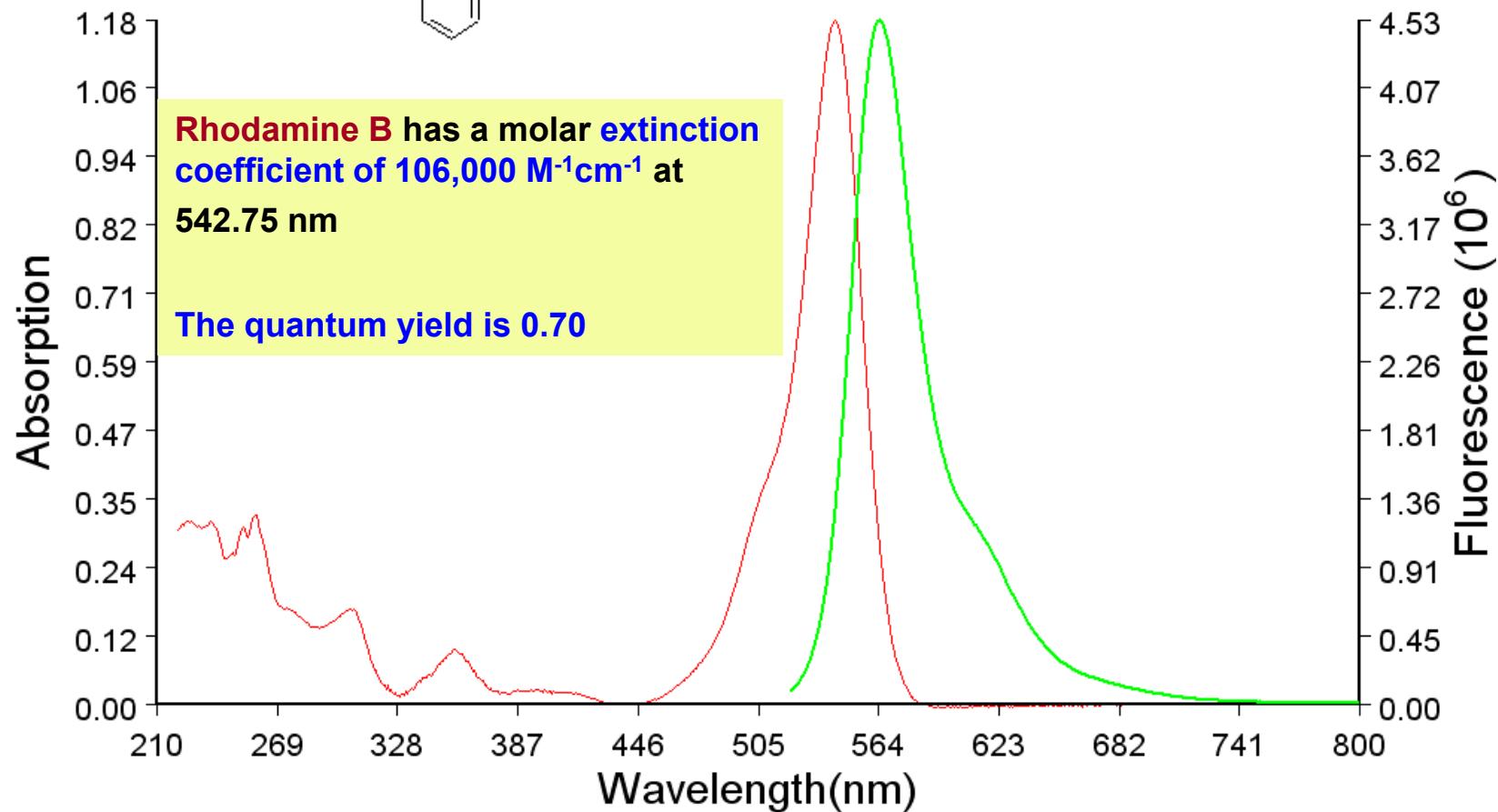
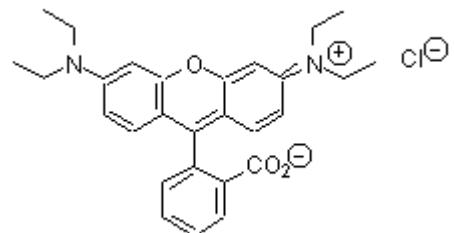
Solvatochromic!!!

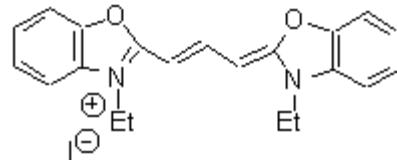


Acridine orange has a molar extinction coefficient of $27,000 \text{ M}^{-1}\text{cm}^{-1}$ at 430.75 nm

The quantum yield is 0.20

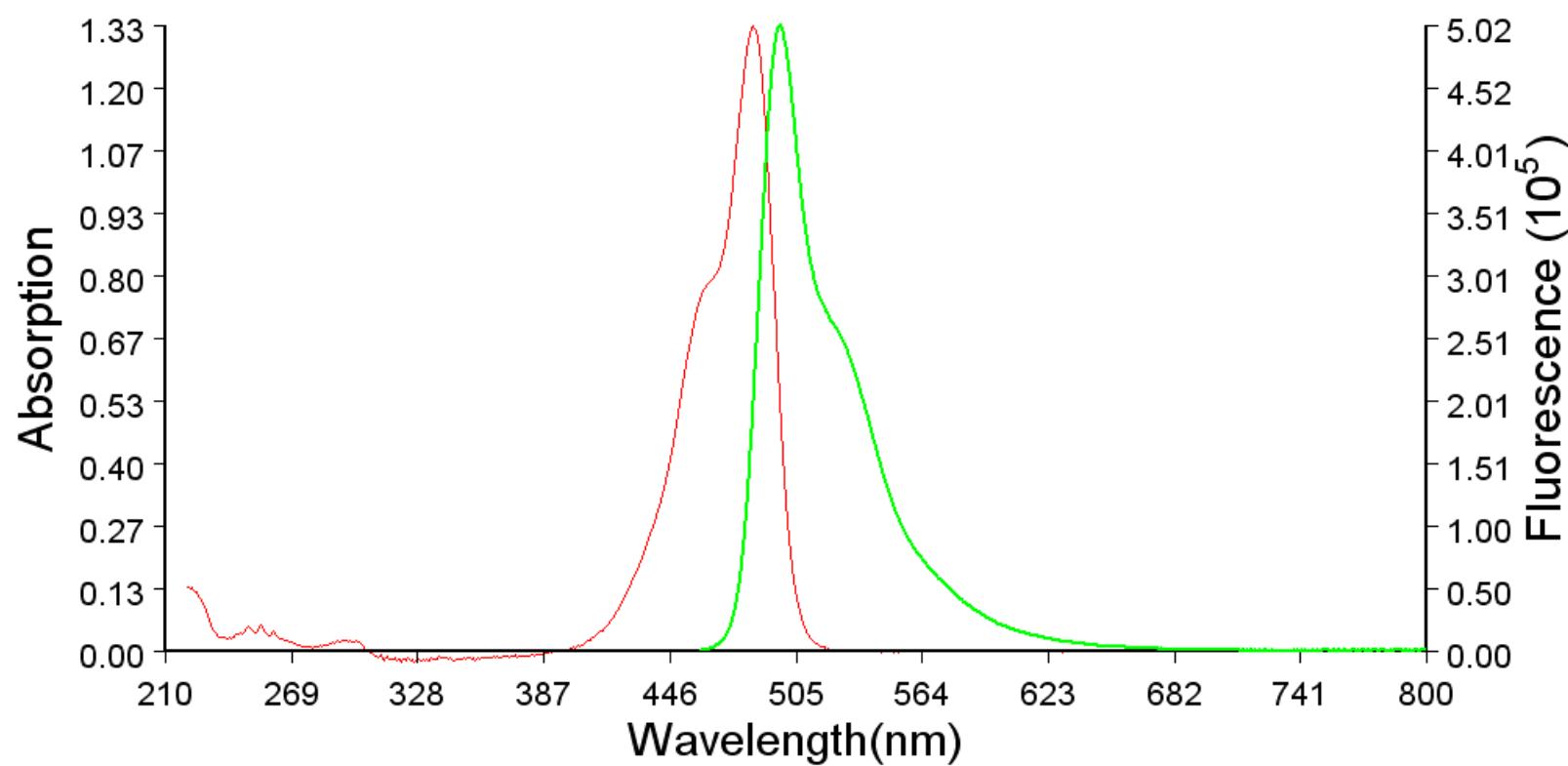


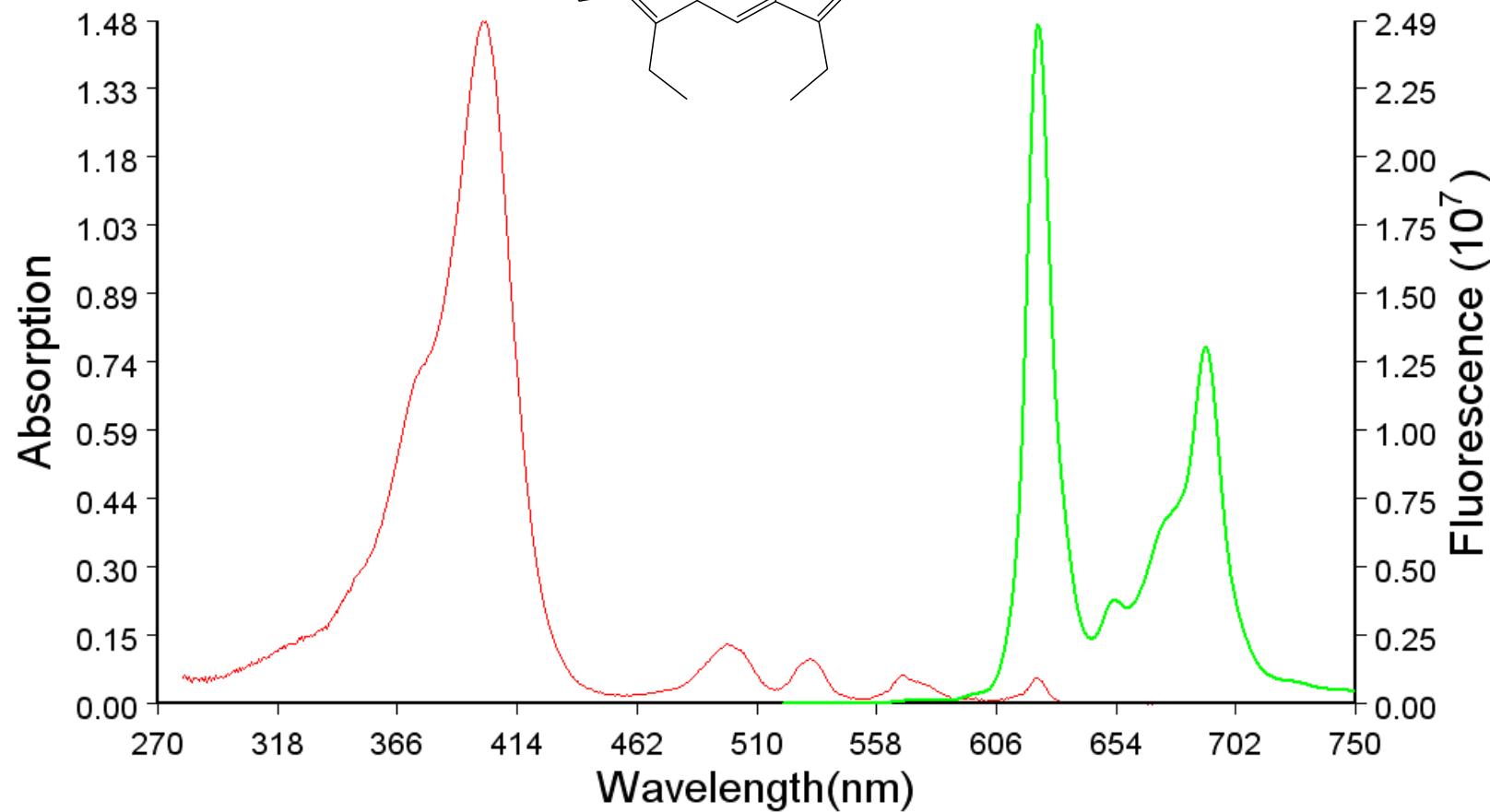




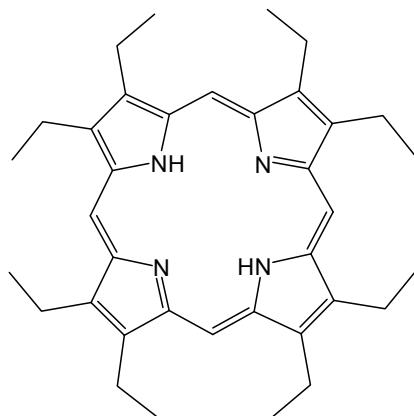
Oxacarbocyanine (C3) dye has a molar extinction coefficient of $149,000 \text{ M}^{-1}\text{cm}^{-1}$ at 485 nm

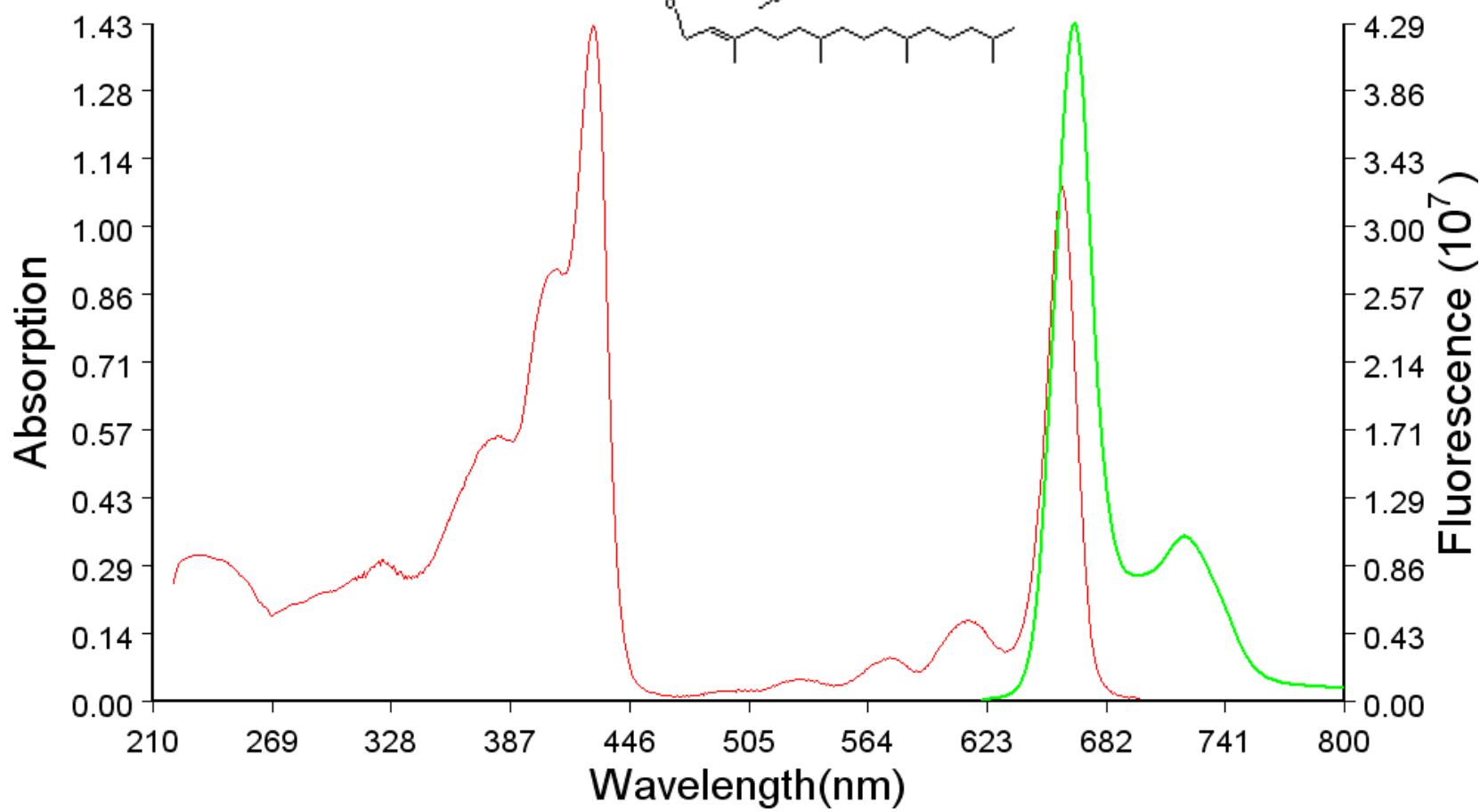
The quantum yield is 0.04





Octaethylporphyrin has a molar extinction coefficient of $159,000 \text{ M}^{-1}\text{cm}^{-1}$ at 400 nm
The quantum yield is 0.13

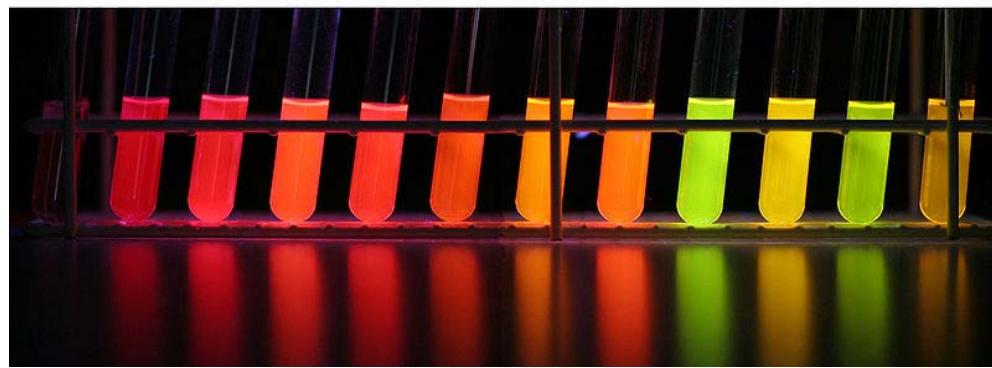
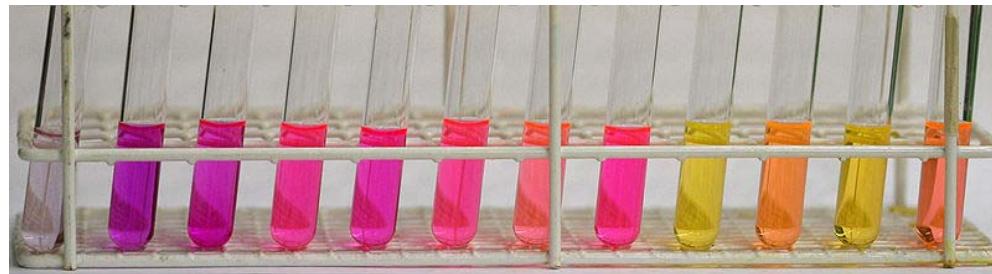




Chlorophyll a has a molar extinction coefficient of $111,700 \text{ M}^{-1}\text{cm}^{-1}$ at 427.75 nm

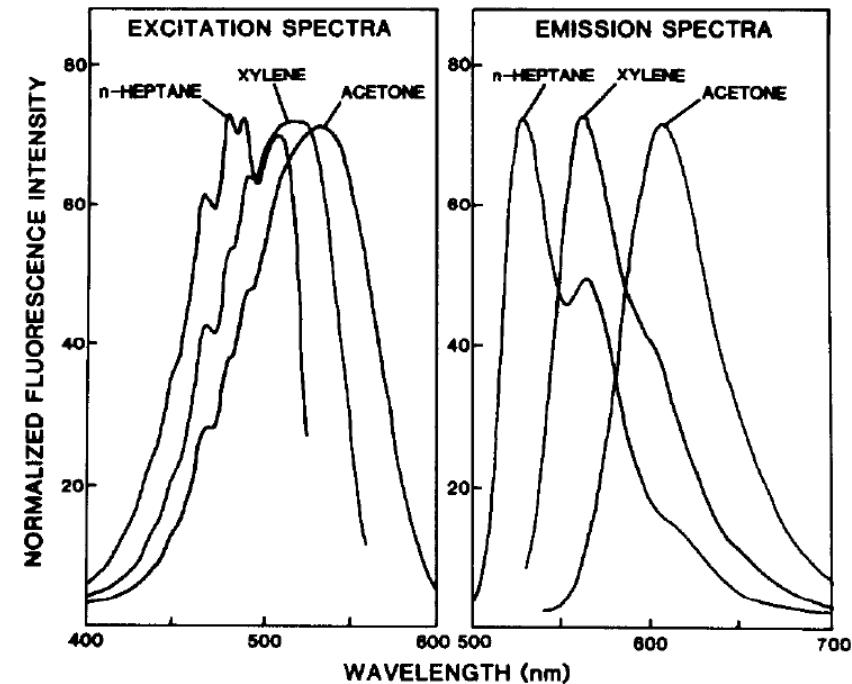
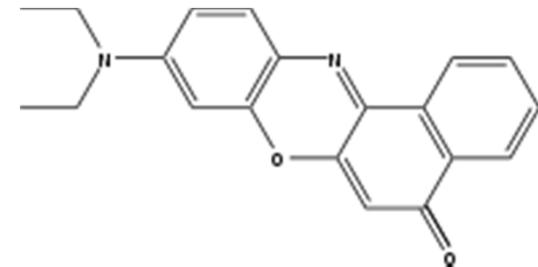
The quantum yield is 0.32

Solvatochromism I



From left to right: 1. [water](#), 2. [methanol](#),
3. [ethanol](#), 4. [acetonitrile](#), 5.
[dimethylformamide](#), 6. [acetone](#), 7. [ethyl acetate](#), 8. [dichloromethane](#), 9. [n-hexane](#), 10. [methyl-tert-butylether](#), 11. [cyclohexane](#), 12. [toluene](#)

Nile Red



Solvatochromism II

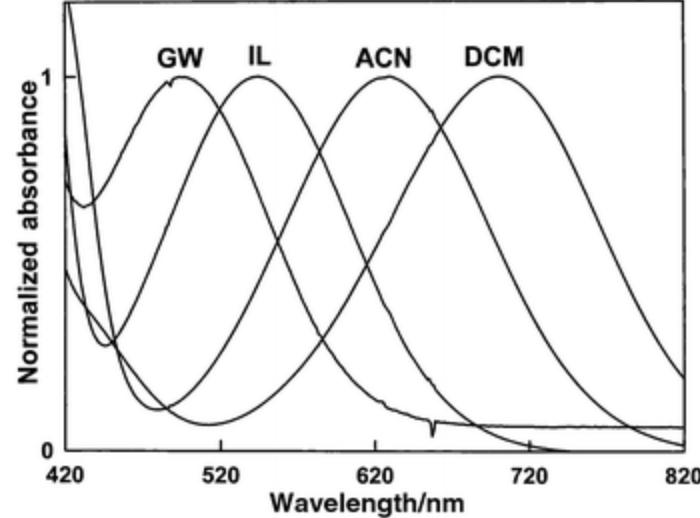
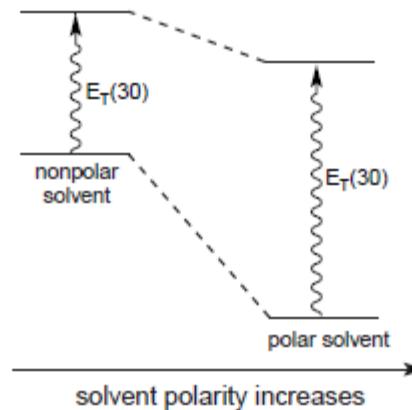
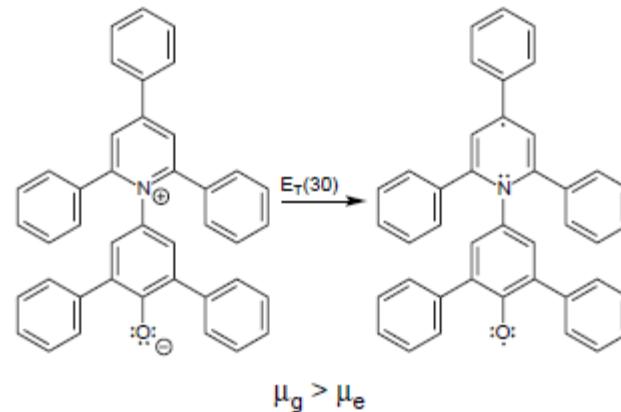


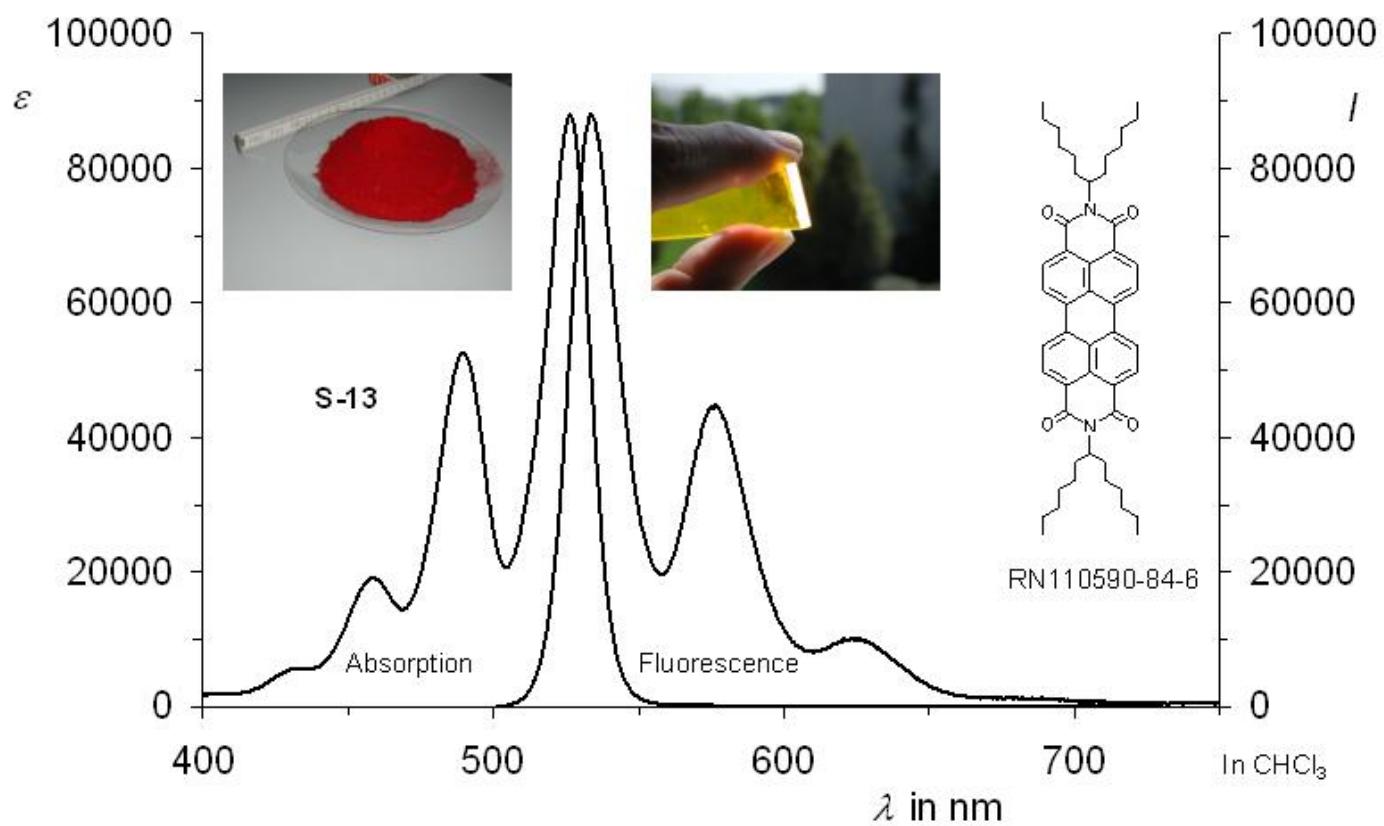
Fig. 3 Longest wavelength intramolecular charge-transfer $\pi\pi^*$ absorption band of Reichardt's betaine dye in 90 wt% glycerol in water (GW), bmimPF₆ (IL), acetonitrile (ACN) and dichloromethane (DCM) under ambient conditions

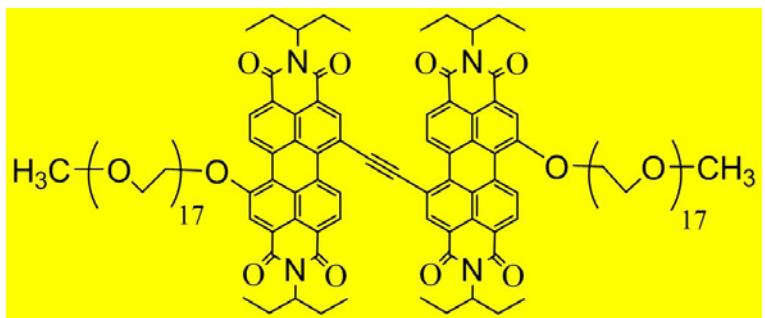
Reichardt's dye



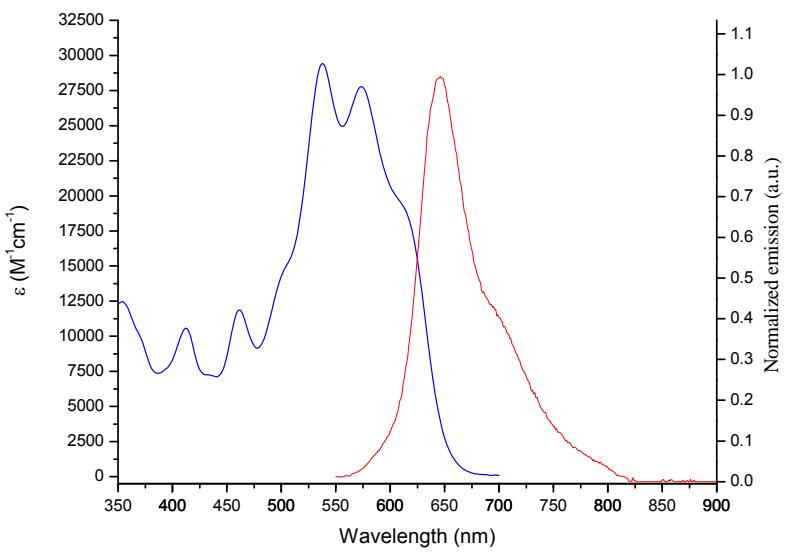
Scheme I

Perylene diimide, QY=1





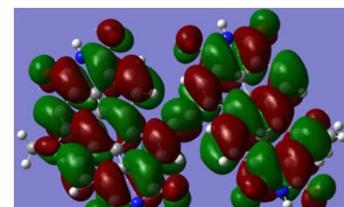
CHCl_3



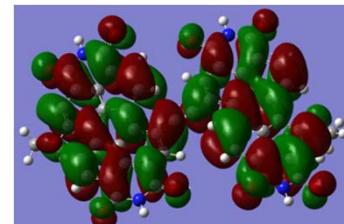
$\text{QY} = 0.06$

TDDFT(B97-1/6-31G*)

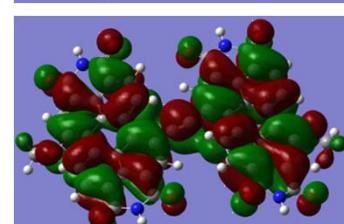
LUMO+1



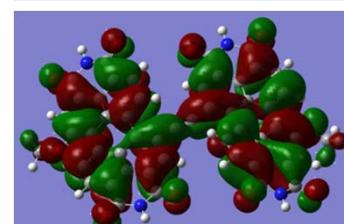
LUMO



HOMO

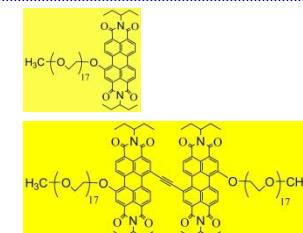
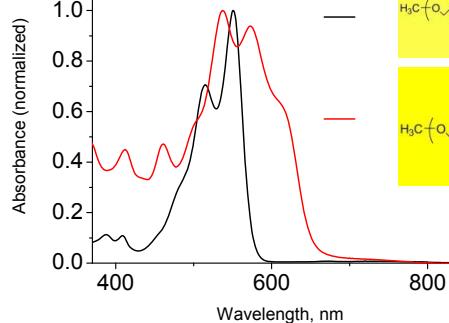


HOMO-1

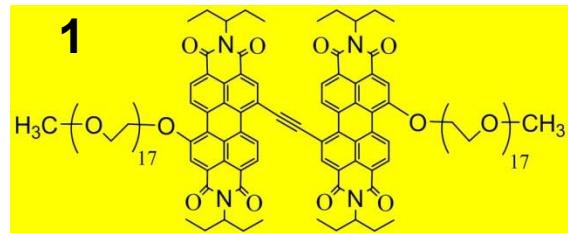


1.8790 eV
659.85 nm
 $f=0.6583$

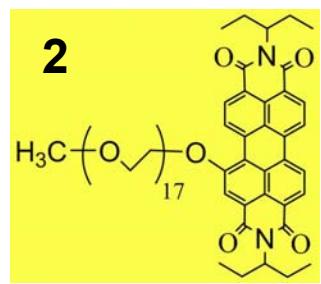
2.4680 eV
502.36 nm
 $f=0.4036$



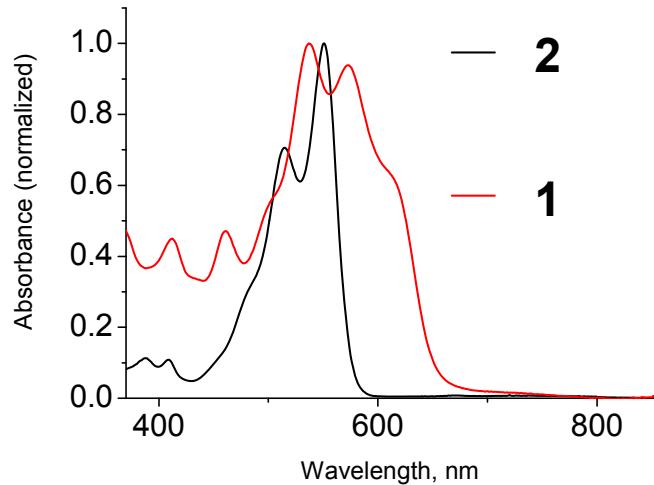
Energy gap law



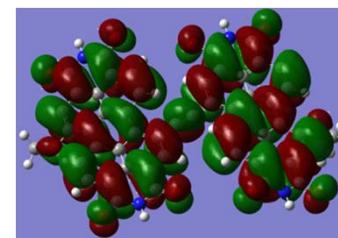
QY = 6%



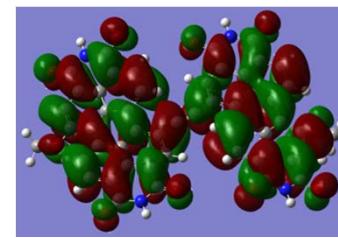
QY = 85%



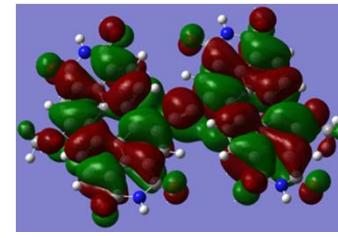
LUMO+1



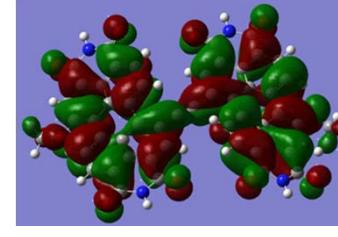
LUMO



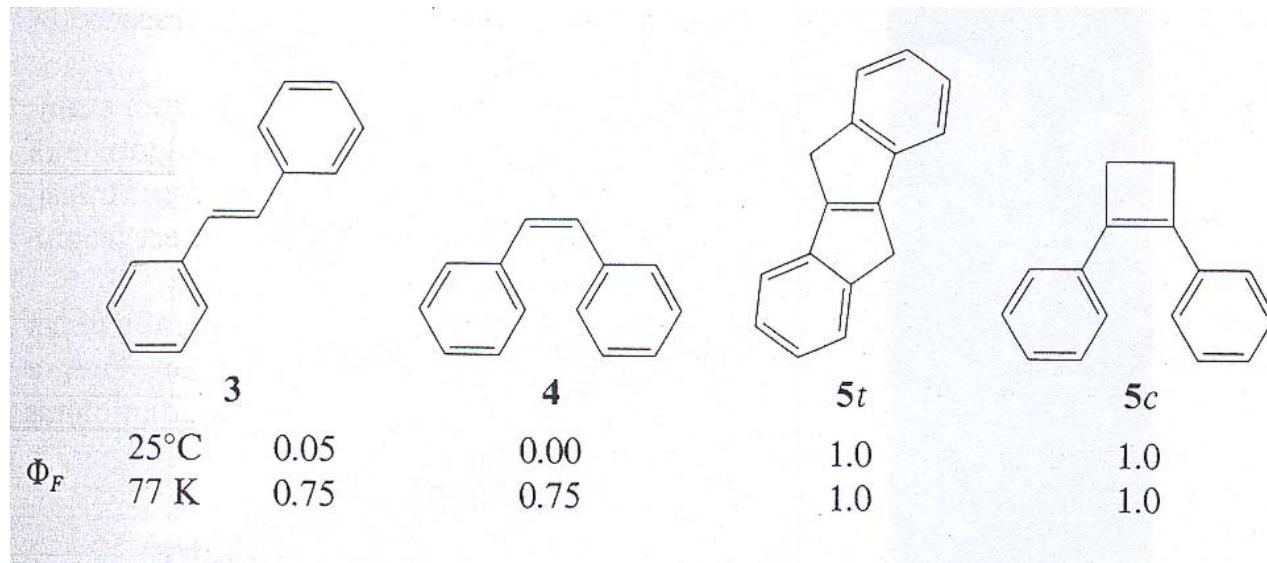
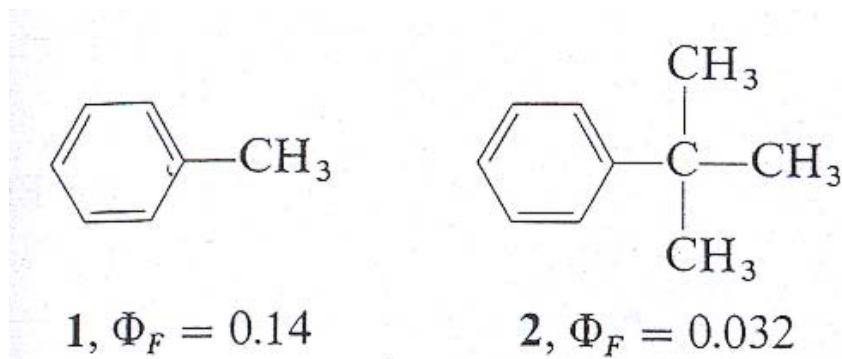
HOMO



HOMO-1



Molecular flexibility and QY

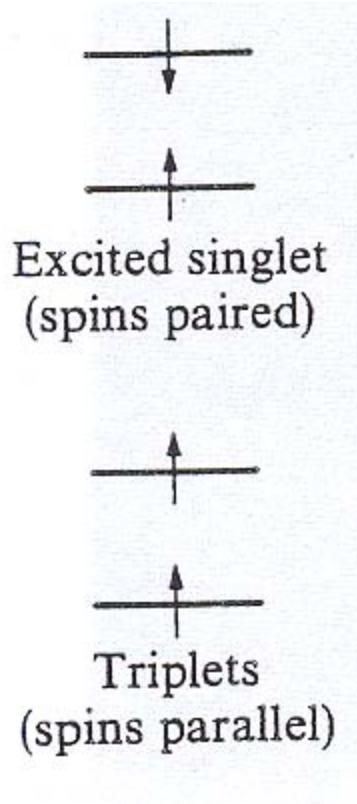


Quantum yields

Table 5.5 Some Examples of Fluorescence Quantum Yields and Other Emission Parameters

Compound	Φ_F^a	ε_{\max}	k_F^0	k_{ST}	Configuration of S_1
Benzene	~0.2	250	2×10^6	10^7	π, π^*
Naphthalene	~0.2	270	2×10^6	5×10^6	π, π^*
Anthracene	~0.4	8500	5×10^7	$\sim 5 \times 10^7$	π, π^*
Tetracene	~0.2	14000	2×10^7	$\sim 10^8$	π, π^*
9,10-Diphenylanthracene	~1.0	12600	$\sim 5 \times 10^8$	$< 10^7$	π, π^*
Pyrene	~0.7	510	$\sim 10^6$	$< 10^5$	π, π^*
Triphenylene	~0.1	355	$\sim 2 \times 10^6$	$\sim 10^7$	π, π^*
Perylene	~1.0	39500	$\sim 10^8$	$< 10^7$	π, π^*
Stilbene ^b	~0.05	24000	$\sim 10^8$	$\sim 10^9$	π, π^*
1-Chloronaphthalene	~0.05	~300	$\sim 10^6$	5×10^8	π, π^*
1-Bromonaphthalene	~0.002	~300	$\sim 10^6$	$\sim 10^9$	π, π^*
1-Iodonaphthalene	~0.000	~300	$\sim 10^6$	$\sim 10^{10}$	π, π^*
Benzophenone ^c	~0.000	~200	$\sim 10^6$	$\sim 10^{11}$	n, π^*
Biacetyl ^d	~0.002	~20	$\sim 10^5$	$\sim 10^8$	n, π^*
Diaza[2.2.2]bicyclooctane ^e	~1.0	~200	$\sim 10^6$	$< 10^5$	n, π^*
Acetone ^f	~0.001	~20	$\sim 10^5$	$\sim 10^9$	n, π^*
Perfluoroacetone ^g	~0.1	~20	$\sim 10^5$	$\sim 10^7$	n, π^*
3-Bromoperylene ^h	~1.0	~40,000	$\sim 10^8$	$< 10^6$	π, π^*
Pyrene-3-carboxaldehyde ⁱ	~0.25	~70,000	$\sim 10^8$	$\sim 10^8$	$\pi, \pi^* (?)$
Cyclobutanone ^j	~0.0001	~20	$\sim 10^5$	$\sim 10^9$	n, π^*
Diaza[2.2.1]bicycloheptane ^e	~0.0001	400	$\sim 10^6$	$\sim 10^6$	n, π^*

Triplets and Singlets



Singlets are normally higher in energy than triplets. This results from the better correlation of electronic motion in triplet states that minimizes electronic repulsion.

Or in other words:

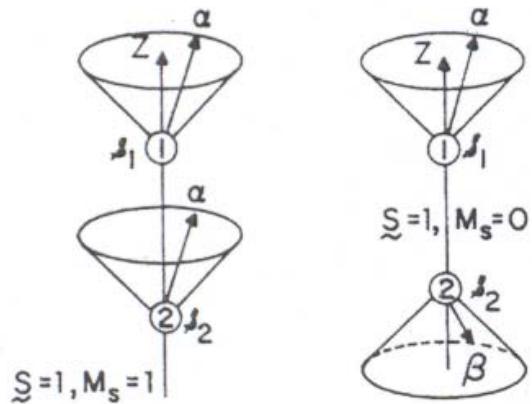
Pauli Principle: Unpaired electrons avoid one another and thereby correlate their motion to minimize electronic collisions (repulsion). – **Purely quantum mechanical phenomenon**

Singlet to triplet transitions (intersystem crossing) – we will talk about it later

Vectorial Model

The electron may be viewed as an electrically charged particle that generates a magnetic angular momentum as a result of rotation or *spin* around an axis.

THE TRIPLET STATE



$$\langle \mathbf{s}_1 | \mathbf{s}_2 \rangle = \alpha\alpha$$

T_+

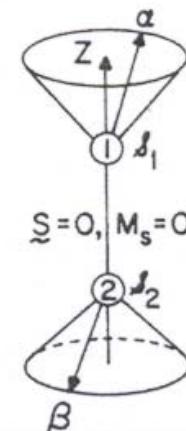
$$\langle \mathbf{s}_1 | \mathbf{s}_2 \rangle = \alpha\beta$$

T_0

$$\langle \mathbf{s}_1 | \mathbf{s}_2 \rangle = \beta\beta$$

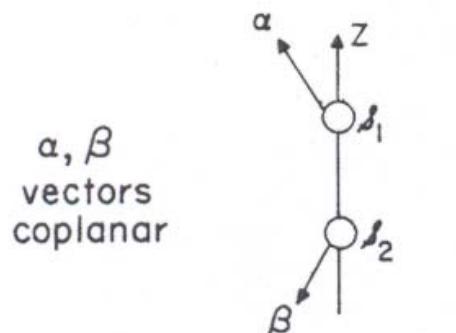
T_-

THE SINGLET STATE

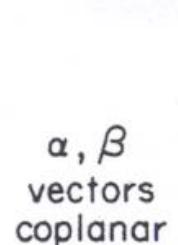


$$\langle \mathbf{s}_1 | \mathbf{s}_2 \rangle = -\alpha\beta$$

S

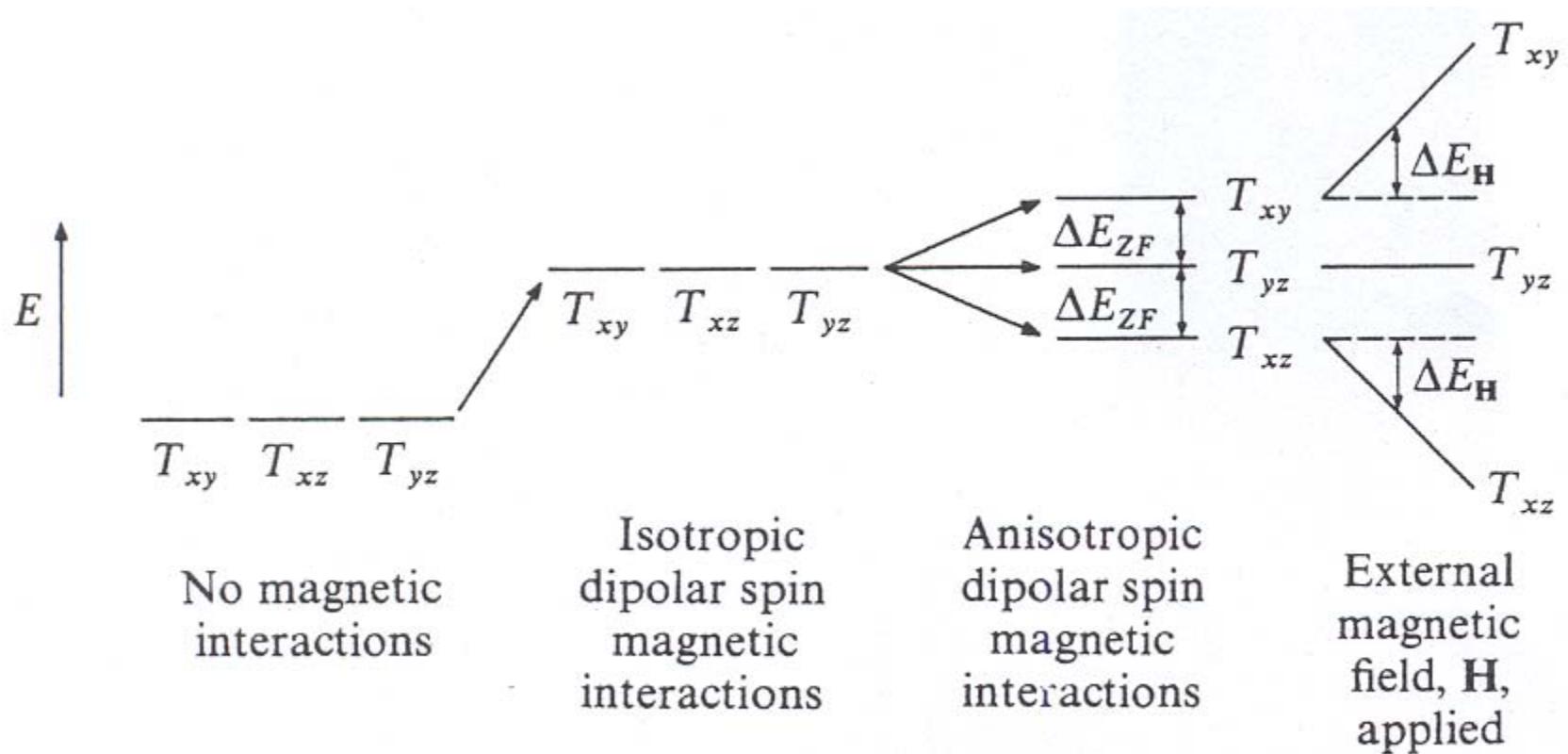


$$\begin{aligned} \text{in phase } &= T_0 \\ &= \alpha(1)\beta(2) + \beta(1)\alpha(2) \end{aligned}$$



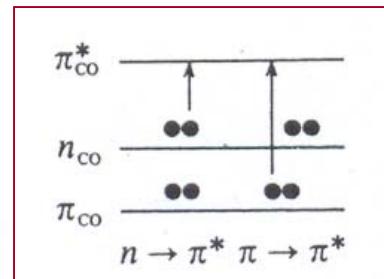
$$\begin{aligned} \text{out of phase } &= S \\ &= \alpha(1)\beta(2) - \beta(1)\alpha(2) \end{aligned}$$

Typical triplet behavior



Singlet-Triplet energy difference, formaldehyde case

$$E(S_0) = 0 \quad \text{by definition}$$



(2.9)

$$E(S_1) = E(n, \pi^*) + K(n, \pi^*) + J(n, \pi^*)$$

(2.10)

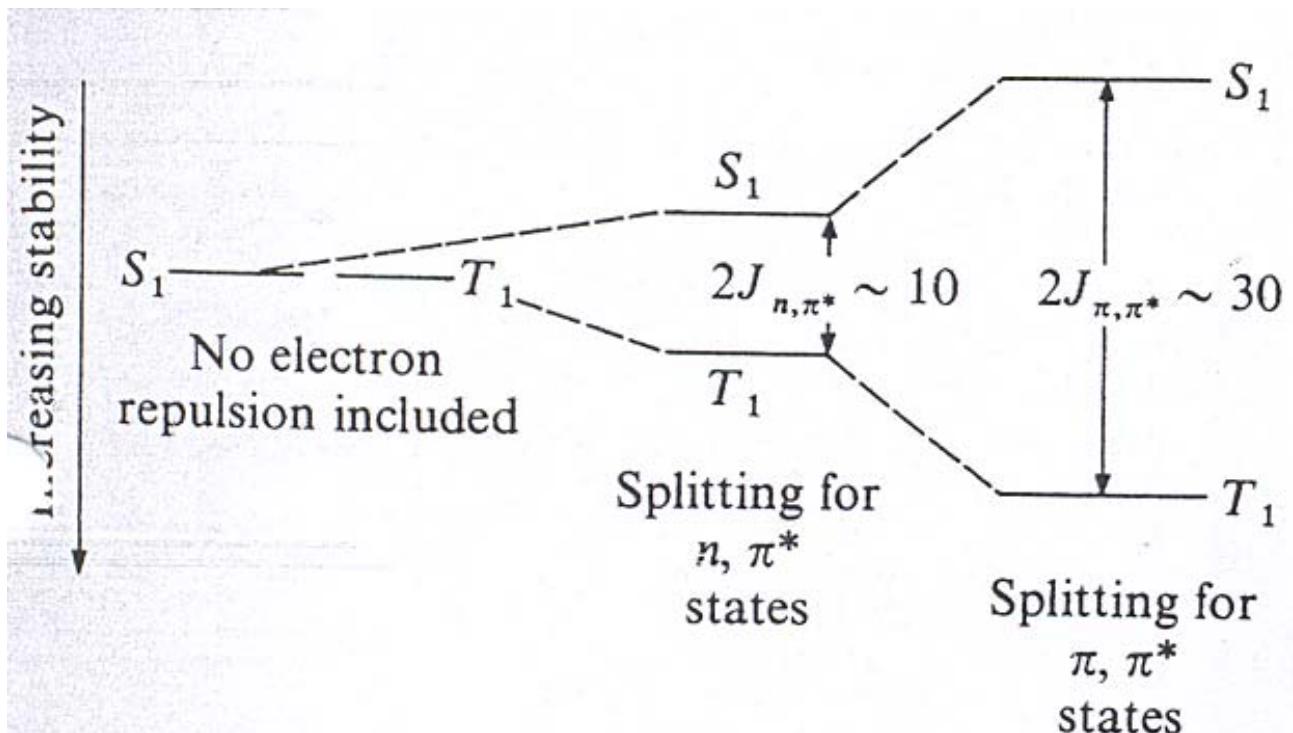
$$E(T_1) = E(n, \pi^*) + K(n, \pi^*) - J(n, \pi^*)$$

(2.11)

where J is the matrix element that measures electron repulsion due to electron exchange and K is the matrix element that measures electron repulsion due to Coulombic interactions. Both J and K are positive (energy enhancing) quantities. Note that

$$\underline{\Delta E_{\text{ST}} = E(S_1) - E(T_1) = 2J(n, \pi^*) > 0} \quad \text{Singlet-Triplet splitting} \quad (2.12)$$

and since J must be positive we conclude that $E(S_1) > E(T_1)$ in general.



Formaldehyde case

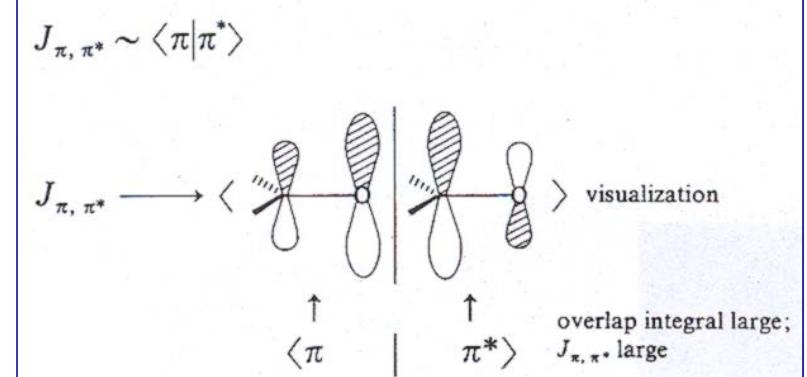
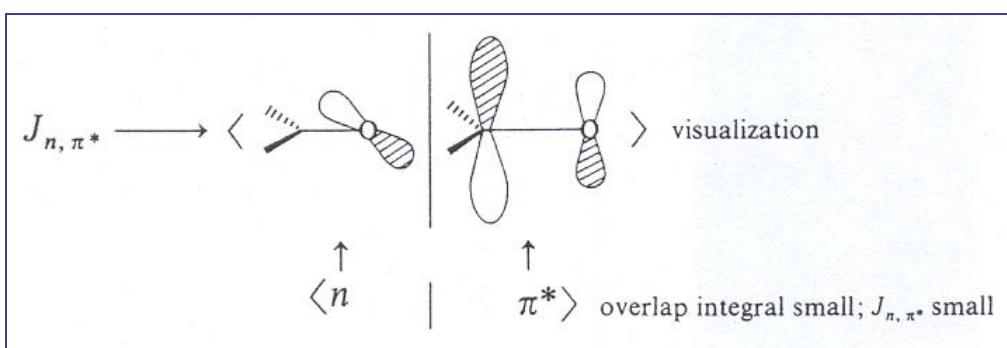
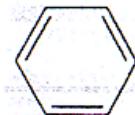


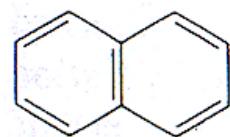
Table 2.1 Singlet-Triplet Splittings

Molecule	Configuration ($S_1 - T_1$)	$\Delta E (S_1 - T_1)$ in kcal/mole
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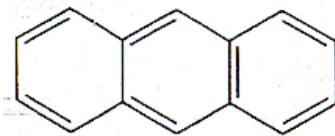
$\text{CH}_2=\text{CH}_2$	π, π^*	70
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	π, π^*	70
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	π, π^*	40
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	π, π^*	35
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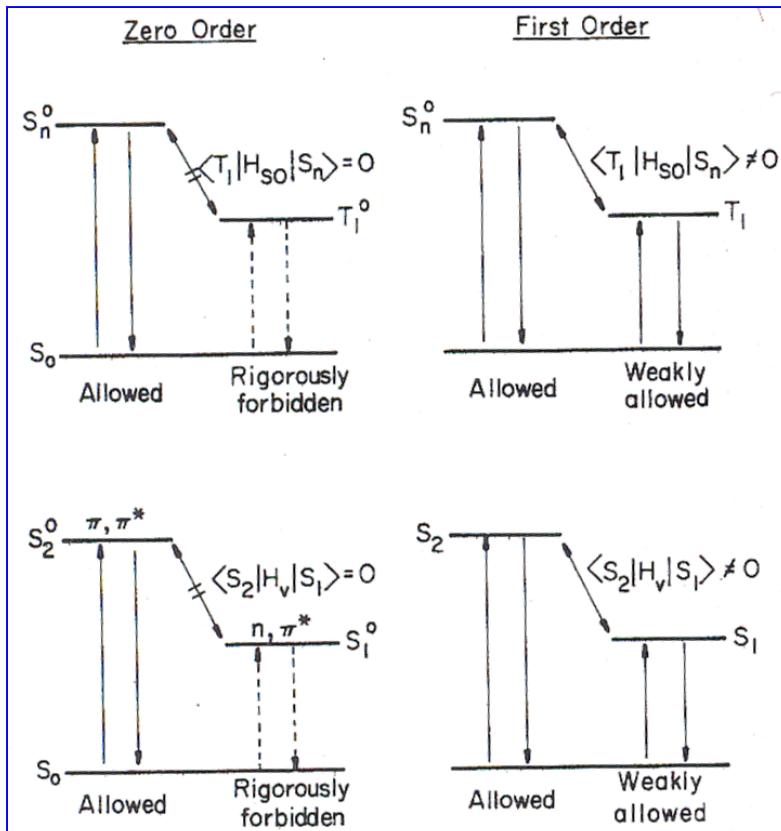
$\text{CH}_2=\text{O}$	n, π^*	10
------------------------	------------	----

$(\text{CH}_3)_2\text{C}=\text{O}$	n, π^*	7
------------------------------------	------------	---

$\text{Ph}_2\text{C}=\text{O}$	n, π^*	7
--------------------------------	------------	---

Spin-orbit coupling, Mixing

Energy gap law



$$\text{Mixing coefficient} \rightarrow \lambda = \left| \frac{\langle \psi_a | H | \psi_b \rangle}{E_a - E_b} \right| \begin{array}{l} \leftarrow \text{Matrix element} \\ \leftarrow \text{Energy separation} \end{array}$$

$$\text{First Order } n, \pi^* \rightarrow S_1 = n, \pi^* + \left| \frac{\langle n, \pi^* | H | \pi, \pi^* \rangle}{E_{\pi, \pi^*} - E_{n, \pi^*}} \right| \pi, \pi^*$$

1. Direct electronic coupling of T_1 with S_n , i.e.,

$$\langle T_1 | H_{so} | S_n \rangle \neq 0 \quad (5.28)$$

2. Indirect electronic coupling of T_1 and S_n via an intermediate triplet T_n , i.e.,

$$\langle T_1 | H_{so} | S_n \rangle = 0 \quad (5.29)$$

$$\langle T_n | H_{so} | S_n \rangle \neq 0 \quad \text{and} \quad \langle T_n | H_e | T_1 \rangle \neq 0 \quad (5.30)$$

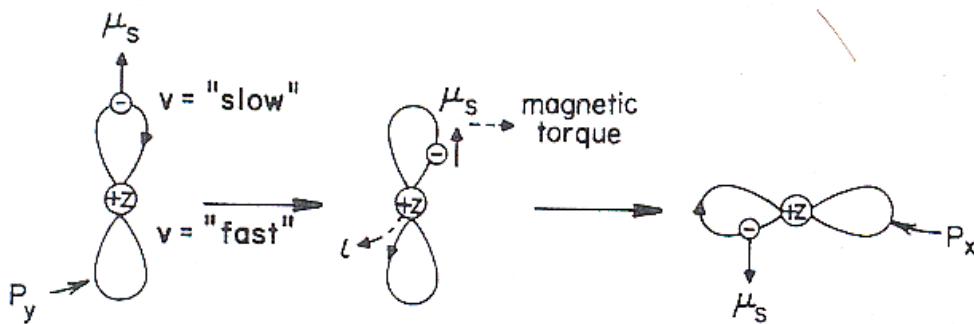
3. The “turning on” of mechanisms (1) and (2) via vibrational motions of the molecule, i.e.,

$$\langle T_1 | H_{so} | S_n \rangle = 0 \quad \text{but} \quad \langle T_1^v | H_{so} | S_n \rangle \neq 0 \quad (5.31)$$

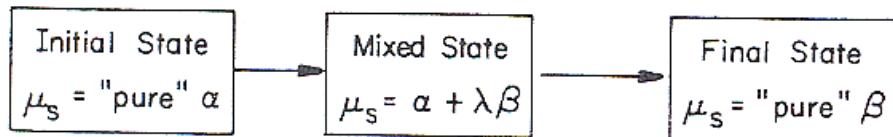
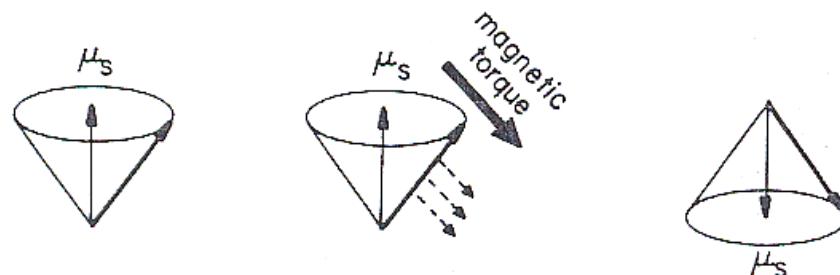
$$\langle T_n | H_e | T_1 \rangle = 0 \quad \text{but} \quad \langle T_n^v | H_e | T_1^n \rangle \neq 0 \quad (5.32)$$

Singlet-triplet transitions: Multiplicity mixing by spin-orbit coupling

SPIN - ORBITAL DESCRIPTION



VECTOR MODEL DESCRIPTION

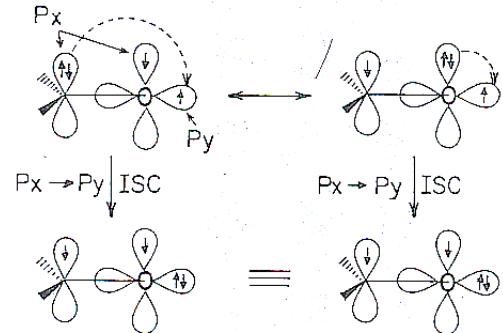


NB: spin changed but orbital changed too – conservation of momentum.

To get a spin flip, a mechanism should exist that allows some kind of orbital flip i.e. *electron jumps from one orbital to another one with different momentum ($p_y \rightarrow p_x$)*

Orbital flip, heavy nucleus, the closest overlap of orbitals participating in the flip

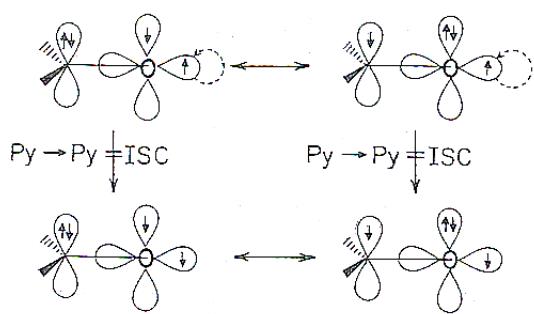
Selection Rules



$$S_1 = \pi(\downarrow) n(\uparrow) \pi^*(\uparrow) = {}^1(n, \pi^*)$$

↓
SPIN FLIP ALLOWED

$$T_1 = \pi(\downarrow) n(\uparrow) \pi^*(\downarrow) = {}^3(\pi, \pi^*)$$



$$S_1 = n(\uparrow) \pi^*(\downarrow) = {}^1(n, \pi^*)$$

↓
SPIN FLIP FORBIDDEN

$$T_1 = n(\downarrow) \pi^*(\downarrow) = {}^3(n, \pi^*)$$

Figure 6.8

Qualitative orbital description of the basis for the allowed ${}^1(n, \pi^*) \rightarrow {}^3(\pi, \pi^*)$ and the forbidden ${}^1(n, \pi^*) \rightarrow {}^3(n, \pi^*)$ intersystem crossings.

El-Sayed's rules:

$n, \pi^* \rightleftharpoons n, \pi^*$	Forbidden
$n, \pi^* \rightleftharpoons \pi, \pi^*$	Allowed
$\pi, \pi^* \rightleftharpoons \pi, \pi^*$	Forbidden
$T_1 \rightleftharpoons S_0$ Transitions	Allowed
$n, \pi^* \rightarrow n^2$	Allowed
$\pi, \pi^* \rightarrow \pi^2$	Forbidden

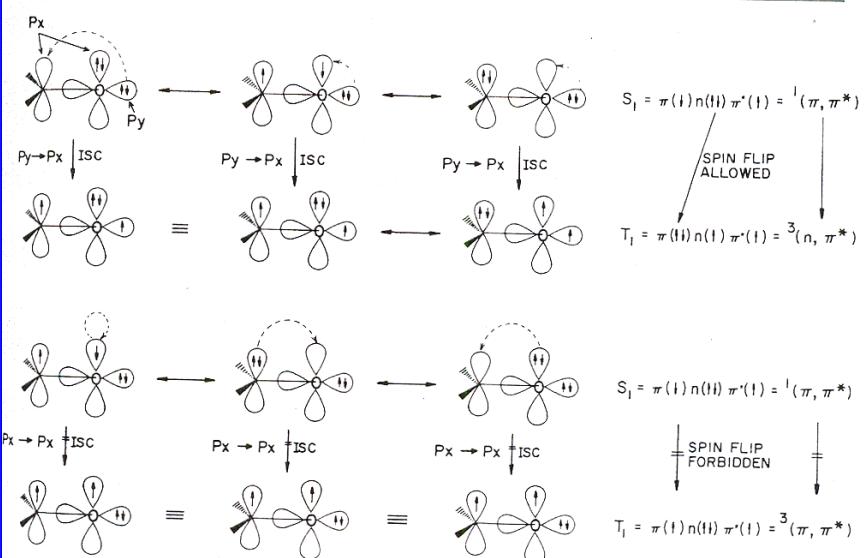


Figure 6.9

Qualitative orbital description of the allowed ${}^1(\pi, \pi^*) \rightarrow {}^3(n, \pi^*)$ and the forbidden ${}^1(\pi, \pi^*) \rightarrow {}^3(\pi, \pi^*)$ intersystem crossings.



Mostafa A. El-Sayed ([Arabic](#): مصطفى السيد) (born 8 May 1933 - [Zifta](#), Egypt) is an [Egyptian-American](#) chemical physicist, a leading nanoscience researcher, a member of the [National Academy of Sciences](#) and a [US National Medal of Science](#) laureate. He is also known for the spectroscopy rule named after him, the *El-Sayed* rule.

He earned his [B.Sc.](#) from [Ain Shams University](#) Faculty of Science in the 1953. El-Sayed earned his doctoral degree from [Florida State University](#) working with [Michael Kasha](#), the last student of the legendary [G. N. Lewis](#). He spent time as a researcher at [Harvard University](#), [Yale University](#) and the [California Institute of Technology](#) before joining the faculty of the [University of California at Los Angeles](#) in 1961. He is currently the Julius Brown Chair and Regents Professor of Chemistry and Biochemistry at the [Georgia Institute of Technology](#). He heads the [Laser Dynamics Lab](#) there.
El-Sayed is a former editor-in-chief of the [Journal of Physical Chemistry](#)

Heavy atom effect

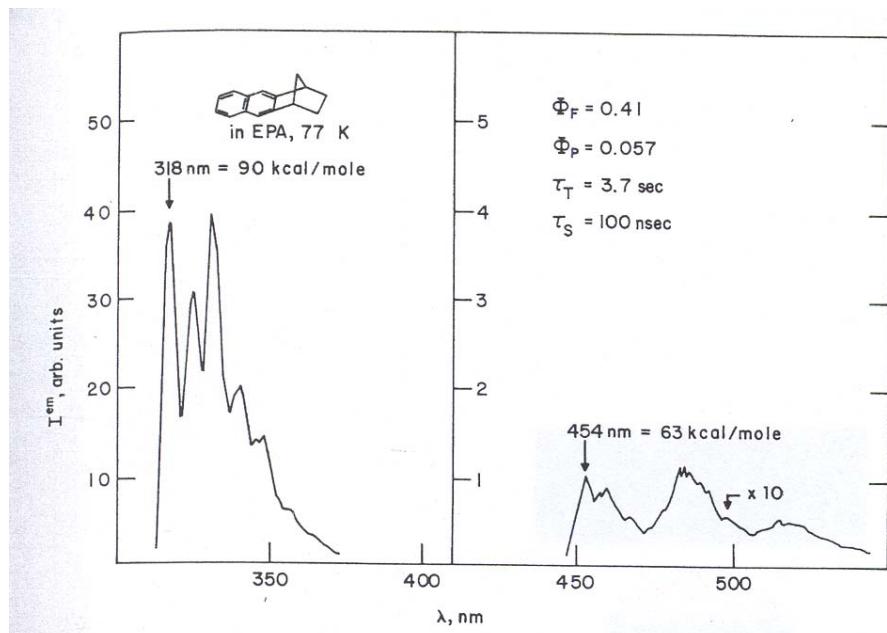


Figure 5.16

Total emission spectrum of naphthonorbornene at 77 K.

Phosphorescence lifetime is longer, since it is a forbidden transition.

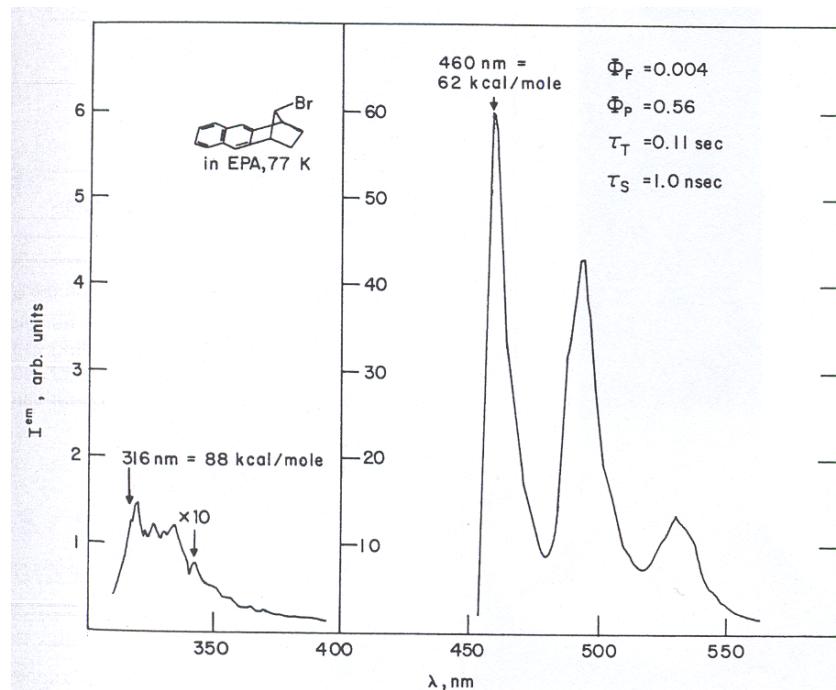
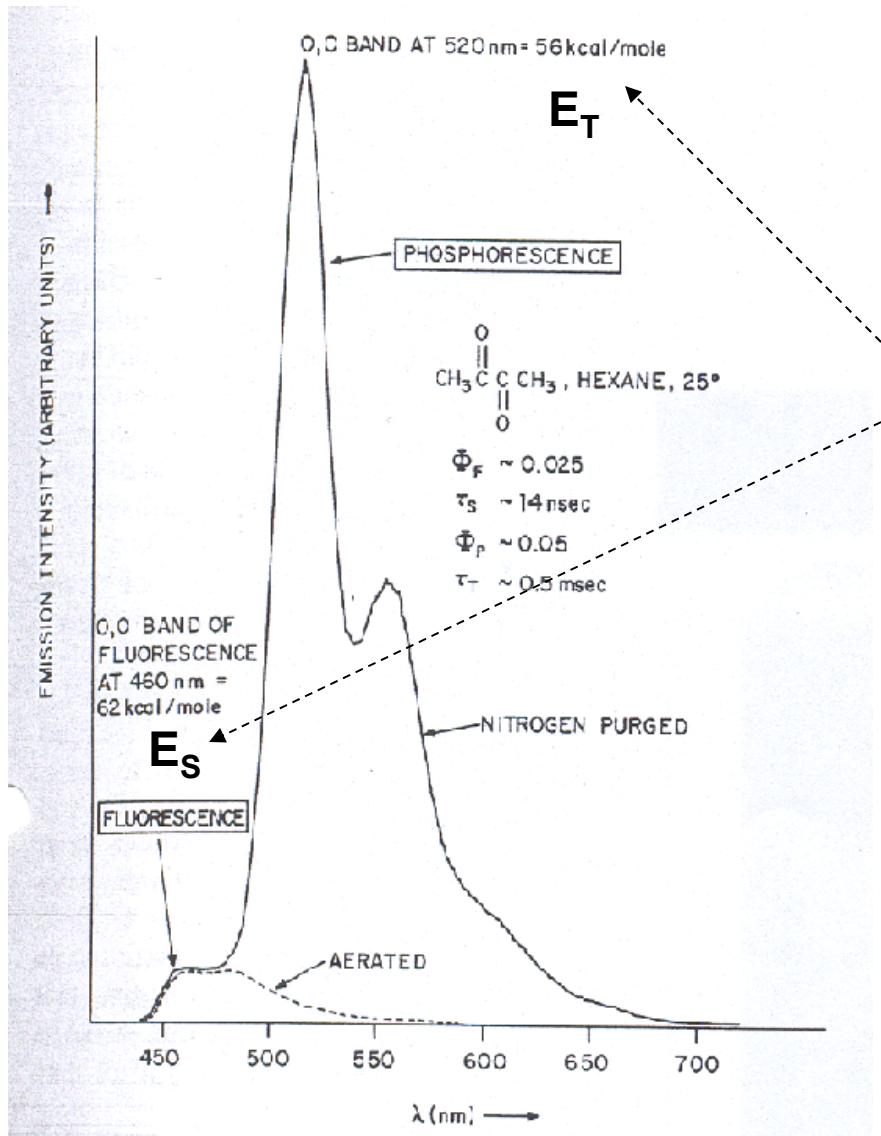


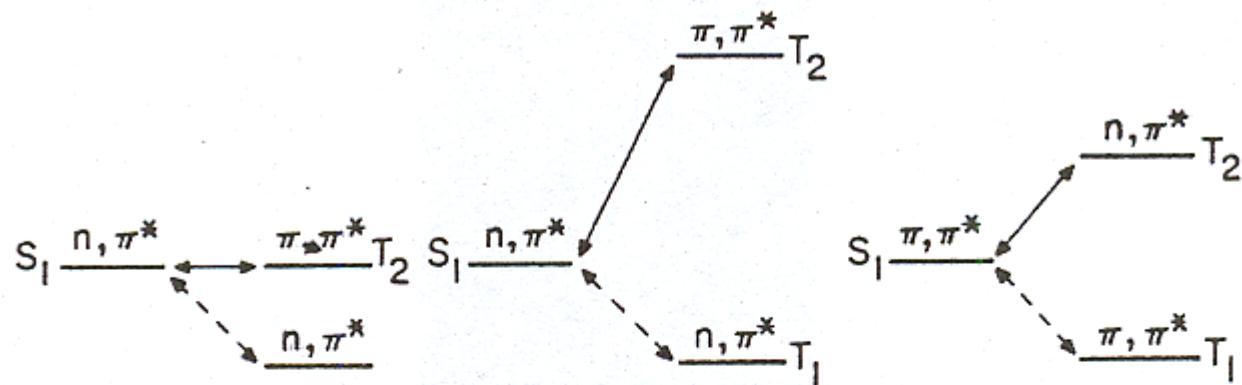
Figure 5.17

Total emission spectrum of 7-anti-bromonaphthonorbornene at 77 K.

Influence of O₂ on triplets.



The first vibronic band, or onset of fluorescence or phosphorescence corresponds to 0-0 transition. It is used to define singlet (E_S) or triplet (E_T) state energy.

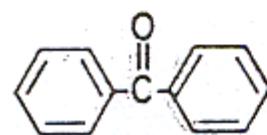


$$k_{ST} \sim 10^{11} - 10^{10} \text{ sec}^{-1}$$

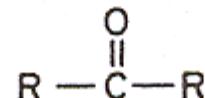
$$k_{ST} \sim 10^9 - 10^8 \text{ sec}^{-1}$$

$$k_{ST} \sim 10^7 - 10^6 \text{ sec}^{-1}$$

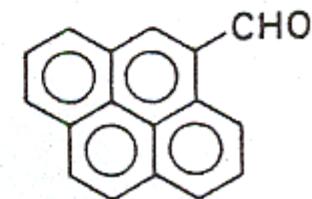
"FAST"



"INTERMEDIATE"



"SLOW"



Examples

1. Fluorescence occurs from S_1 to S_0 ; phosphorescence occurs from T_1 to S_0 ; S_n and T_n emissions are rare (Kasha's rule).
2. The quantum yield of fluorescence and the quantum yield of phosphorescence are independent of initial excitation energy (Vavilov's rule).
3. The sum of $\Phi_F + \Phi_{ST} \cong 1$ (Ermolev's rule).

Table 6.2 Quantum Yields for Fluorescence and Intersystem Crossing of Organic Molecules^a

Molecule (Configuration of S_1)	Φ_F	Φ_{ST}	$1 - (\Phi_F + \Phi_{ST})^b$	$E_{S_1}^c$
Benzene (π, π^*)	0.05	0.25	0.70	110
1,4-Dimethylbenzene (π, π^*) ^d	0.35	0.65	<0.05	100
Naphthalene (π, π^*)	0.20	0.80	<0.05	92
Anthracene (π, π^*)	0.70	0.30	<0.05	76
Tetracene (π, π^*)	0.15	0.65	0.20	60
Pentacene (π, π^*)	0.10	0.15	0.75	50
Azulene (π, π^*)	0.000	—	Low	50
Acetone (n, π^*)	0.001	~1.0	0.05	85
Diacetyl (n, π^*)	0.002	~1.0	0.05	65
Benzophenone (n, π^*)	0.000	~1.0	0.05	75
5-Methyl-2-heptanone (n, π^*) ^e	0.000	0.10	0.90	85
Cyclobutanone (n, π^*) ^f	0.000	0.00	1.0	80
1,3-Pentadiene (n, π^*) ^g	0.000	0.00	1.0	100



Table 6.3 Representative Values of Intersystem Crossing Rates ($S_1 \rightarrow T_1$), Singlet-Triplet Energy Gaps.^a

Molecule	k_{sr} (sec ⁻¹) ^a	ΔE_{sr}	(kcal/mole) ^a
Naphthalene	10^6	30	$S_1(\pi, \pi^*) \rightarrow T_1(\pi, \pi^*)$
Anthracene	10^8	2–3	$S_1(\pi, \pi^*) \rightarrow T_2(\pi, \pi^*)$
Pyrene	10^6	30	$S_1(\pi, \pi^*) \rightarrow T_1(\pi, \pi^*)$
Triphenylene	5×10^7	20	$S_1(\pi, \pi^*) \rightarrow T_1(\pi, \pi^*)$
1-Bromonaphthalene	10^9	30	$S_1(\pi, \pi^*) \rightarrow T_1(\pi, \pi^*)$
9-Acetoanthracene ^b	$\sim 10^{10}$	~ 5	$S_1(\pi, \pi^*) \rightarrow T_2(n, \pi^*)$
Perylene	$< 10^8$	~ 30	$S_1(\pi, \pi^*) \rightarrow T_1(\pi, \pi^*)$
3-Bromoperylene ^c	$< 10^8$	30	$S_1(\pi, \pi^*) \rightarrow T_1(\pi, \pi^*)$
Acetone ^d	5×10^8	5	$S_1(n, \pi^*) \rightarrow T_1(n, \pi^*)$
Benzophenone ^e	10^{11}	5	$S_1(n, \pi^*) \rightarrow T_2(\pi, \pi^*)$
Benzil	5×10^8	5	$S_1(n, \pi^*) \rightarrow T_1(n, \pi^*)$
Biacetyl	7×10^7	5	$S_1(n, \pi^*) \rightarrow T_1(n, \pi^*)$
9,10-Dibromoanthracene ^f	$\sim 10^8$	30	$S_1(\pi, \pi^*) \rightarrow T_1(\pi, \pi^*)$
		5	$S_1(\pi, \pi^*) \rightarrow T_2(\pi, \pi^*)$
[2.2.2]-diaza-bicyclooctane ^g	$\sim 10^6$	25	$S_1(n, \pi^*) \rightarrow T_1(n, \pi^*)$

Example: heavy atom

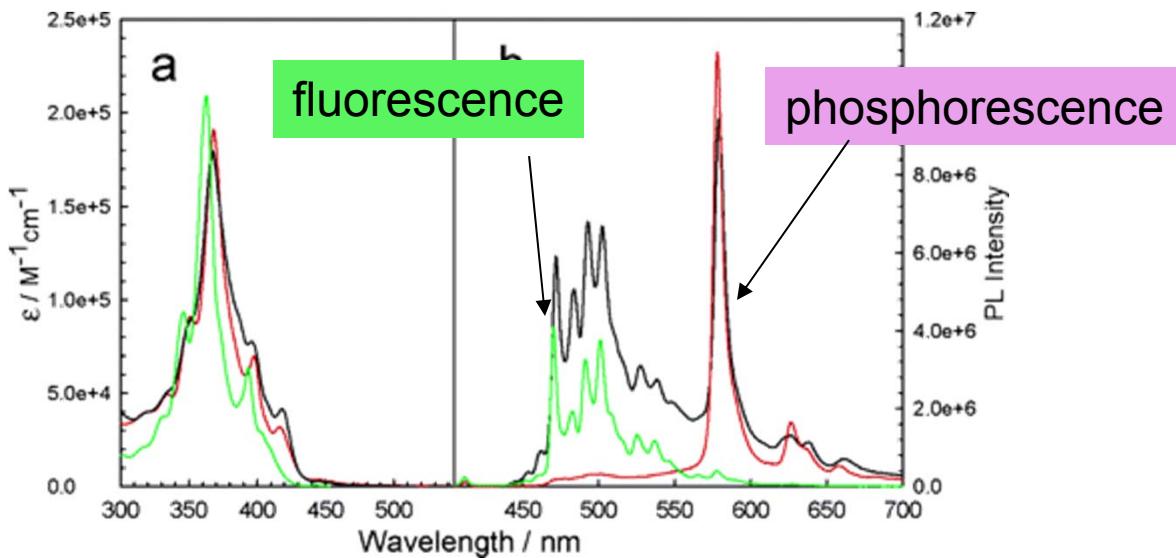
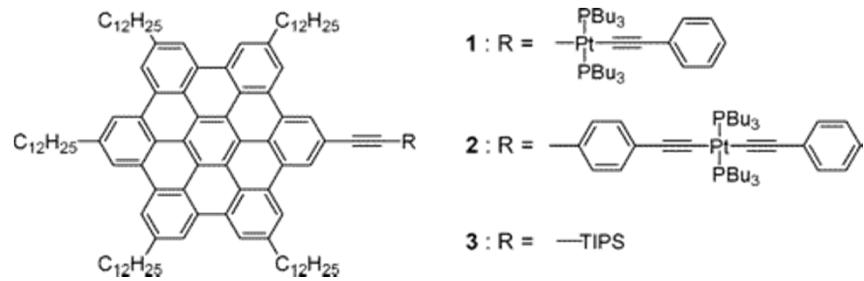
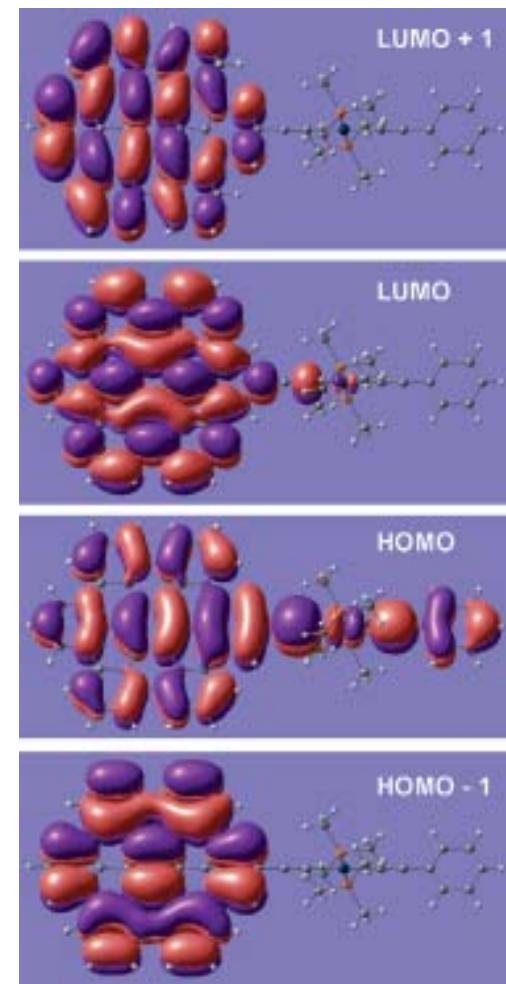
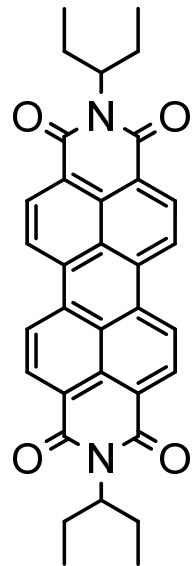


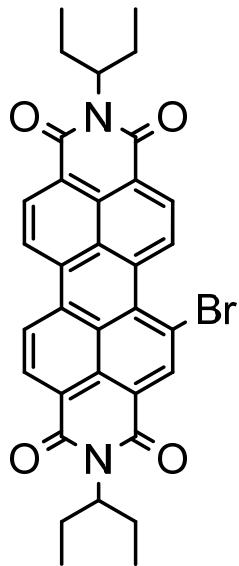
Figure 1 (a) Absorption and (b) photoluminescence spectra of **1** (red), **2** (black), and **3** (green) in THF solution. Photoluminescence spectra were obtained in argon-deoxygenated solution



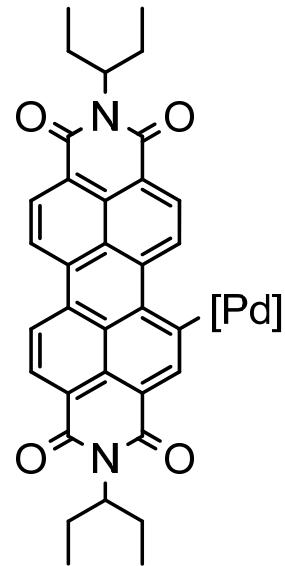
The real life is hard...



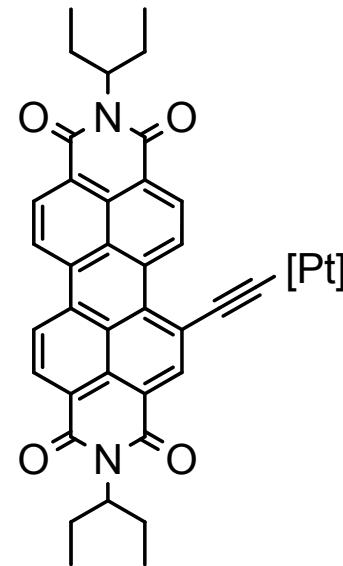
QY=1



QY=0.8



QY=0.6
 $\Phi_{ST}=0.2$



QY~0
 $\Phi_{ST}=1$