전자물리특강

Optical Properties of Organic Semiconductors

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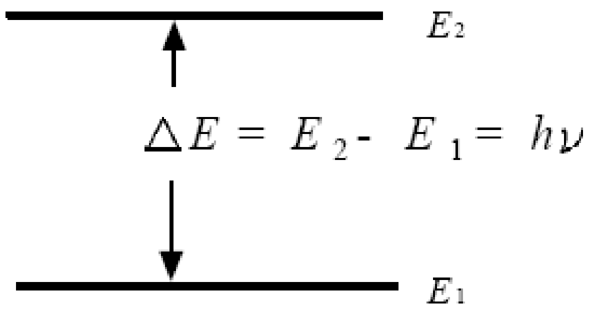
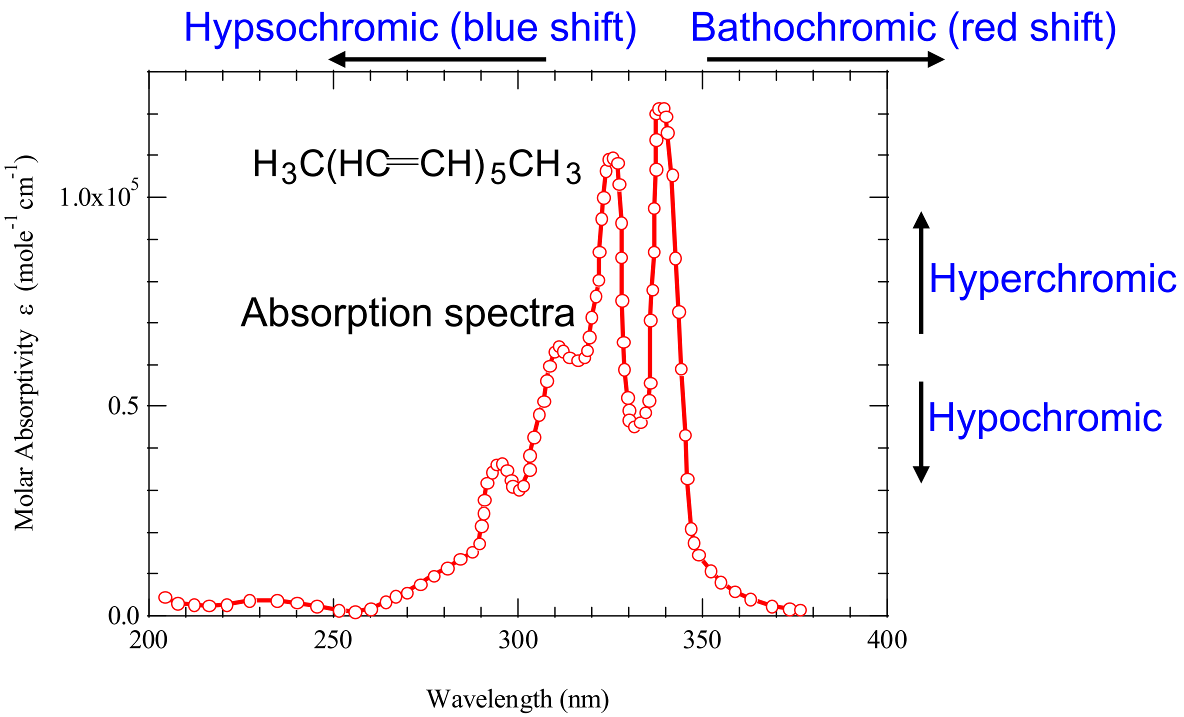
Absorption of Light

UV-Vis absorption



$$\Delta E = E_2 - E_1 = h\nu$$

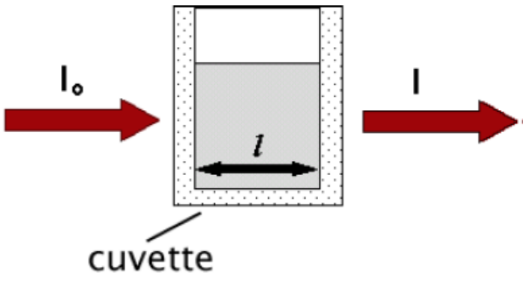


The Beer-Lambert Law:

$$\boxed{Absorbance = \log\left(\frac{I_o}{I}\right) = \varepsilon c l}$$

I_o and I are the intensities entering and leaving the sample, respectively. ε = the molar extinction coefficient or molar absorptivity, c = sample concentration in moles/liter, l = length of light path through the sample in cm.

Molar Absorptivity, $\varepsilon = A / c\, l$, where A= absorbance (Optical Density)



$$\varepsilon \sim 10^{5}\ cm^{-1} \rightarrow \text{solid thickness}\ \ d \sim 10^{-5}\ cm = 100\ nm$$

Selection Rules for Electronic Transition

Fermi Golden Rule

Electric dipole transition rate from *i* to *f* state: $$\Gamma_{i\to f} = \frac{4\pi^2}{\hbar^2 c}\left|\vec{\varepsilon}\cdot<\psi_f\left|\vec{d}\right|\psi_i>\right|^2 I(\omega_{fi})$$

Oscillator strength for the transition $f \propto \left|\vec{\varepsilon}\cdot<\psi_f\left|\vec{d}\right|\psi_i>\right|^2$

Dipole moment operator $\vec{d} = -e\sum_j \vec{r}_j$

- For the allowed transition $\boxed{\Delta l = \pm 1,\ \Delta S = 0}$
- Symmetry selection rule: only *g (even parity)* ↔ *u (odd parity)* transitions are allowed.

 (The vibrational motions may lower the symmetry of a molecule, so that symmetry-forbidden transitions may be observed)

- Spin selection rule: no change in spin multiplicity

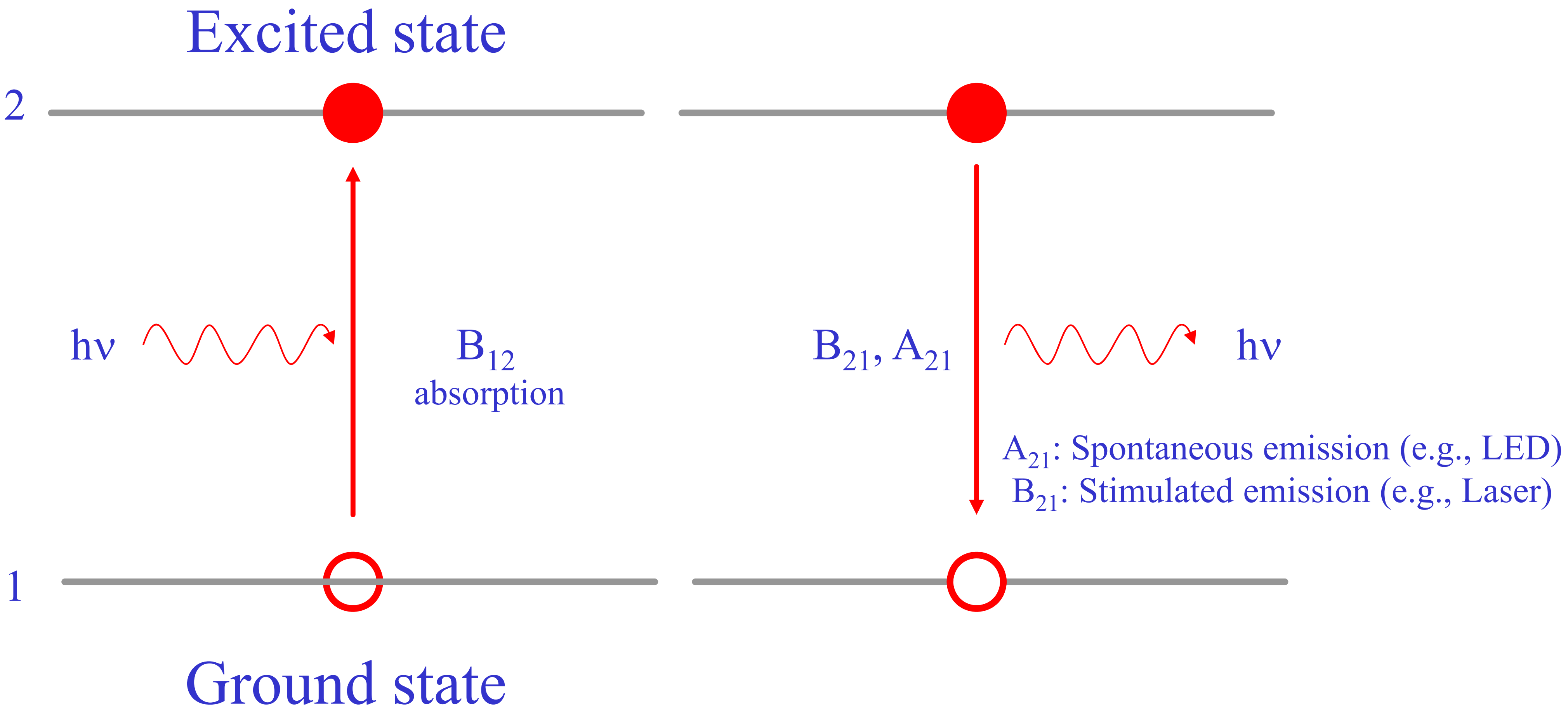
$$\boxed{\mathrm{H_{SO}} = \frac{Ze^2}{2m^2c^2}\frac{1}{r^3}\vec{\mathrm{L}}\cdot\vec{\mathrm{S}} \propto \mathrm{Z}^4}$$

 (The spin-orbit coupling allows the mixing of singlet and triplet states)

Eg., Transition from 2p to 1s state in a H atom $\Gamma_{2p\to 1s} \approx 0.6\times 10^9\ s^{-1}$

$$\boxed{\tau = \frac{1}{\Gamma_{2p\to 1s}} \approx 1.6ns}$$

Absorption and Emission of Light



A_{21}: Spontaneous emission (e.g., LED)
B_{21}: Stimulated emission (e.g., Laser)

Absorption and Emission of Light

Consider a molecule with two energy levels 1 and 2.

$$\Gamma_{1\to 2} = B_{12} I(\omega_{fi})$$

The rate of transition B_{12} induced by light of frequency ν

$$\boxed{B_{12} = \frac{2\pi}{3\hbar^2}\left|<\psi_2\middle|\vec{d}\middle|\psi_1>\right|^2}$$

Transition rate for 1 → 2 (absorption): $B_{12}\ I(\nu)\ N_1$

Transition rate for 2 → 1 (emission): $[B_{21}\ I(\nu) + A_{21}]N_2$

N_1 (N_2)= population of the level 1 (level 2).

A_{21} = spontaneous emission from the level 1 to the level 2.

At equilibrium the rate of transition 1↔ 2 must be the same.

$$\frac{N_1}{N_2} = \frac{B_{21} I(\nu) + A_{21}}{B_{12} I(\nu)} = 1 + \frac{A_{21}}{B_{12} I(\nu)} \qquad (1)$$

But at equilibrium, N_1 and N_2 in each level is given by the Boltzmann equation

$$\frac{N_1}{N_2} = \exp(\frac{E_2 - E_1}{kT}) = \exp(\frac{h\nu}{kT}) \qquad (2)$$

Equation 1 and 2 must be equal. Therefore, we can obtain I(ν).

$$I(\nu) = \frac{A_{21}/B_{21}}{(B_{12}N_1/B_{21}N_2) - 1} = \frac{A_{21}/B_{21}}{\frac{B_{12}}{B_{21}} e^{\frac{h\nu}{kT}} - 1} \qquad (3)$$

Absorption and Emission of Light

At equilibrium I(ν) is the radiation density of a black body at temperature T: Planck's radiation law.

$$I(\nu) = \frac{8\pi h\nu^3}{c^3}\frac{1}{e^{\frac{h\nu}{kT}}-1} \qquad (4)$$

By comparing the like terms in equations (3) and (4), the Einstein coefficients can be obtained to give

$$\boxed{B_{12} = B_{21}} \qquad (5)$$

The stimulated emission process occurs at the same rate as the absorption process. And we can get

$$\boxed{\frac{A_{21}}{B_{21}} = \frac{8\pi h\nu^3}{c^3} = \frac{8\pi h}{\lambda^3}} \qquad (6)$$

The rate of spontaneous to stimulated emission increases as ν^3. B_{12} can be measured from the absorption spectrum.

The radiative lifetime:

$$\boxed{\tau_r = \frac{1}{A_{21}} = \frac{c^3}{8\pi h\nu^3 B_{12}} = \frac{\lambda^3}{8\pi h B_{12}}}$$

The stronger the absorption, the shorter the radiative lifetime. And the radiative lifetime decreases with increasing frequency (or decreasing wavelength).

Harmonic oscillator

Schrödinger equation

$$\frac{d^2\psi}{dx^2}+\frac{2m}{\hbar^2}(E-\frac{1}{2}kx^2)\psi=0$$

The *n*-th wave function of the SHO.

$$\psi_n=(\frac{2m\nu}{\hbar})^{1/4}(2^n n!)^{-1/2}H_n(y)e^{-y^2/2}$$

$H_n(y)$: Hermite polynomial

The acceptable solutions are obtained when

$$E_n=(n+\frac{1}{2})\hbar\omega \qquad n=0,1,2,\dots$$

Selection rules : $\Delta n=\pm 1$

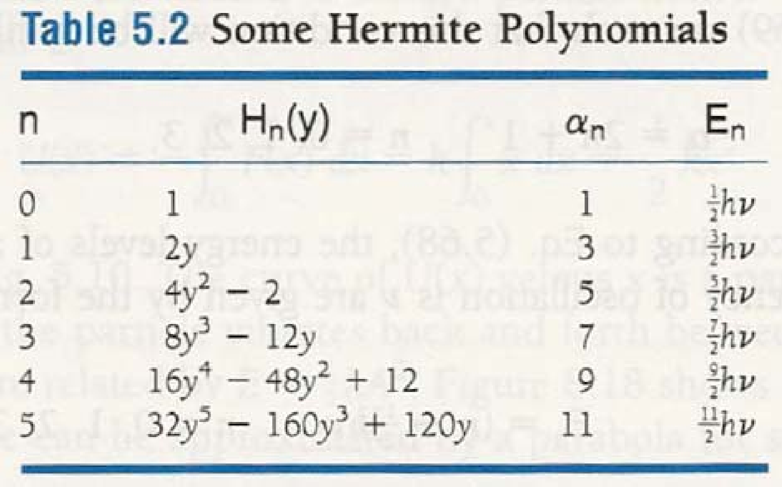
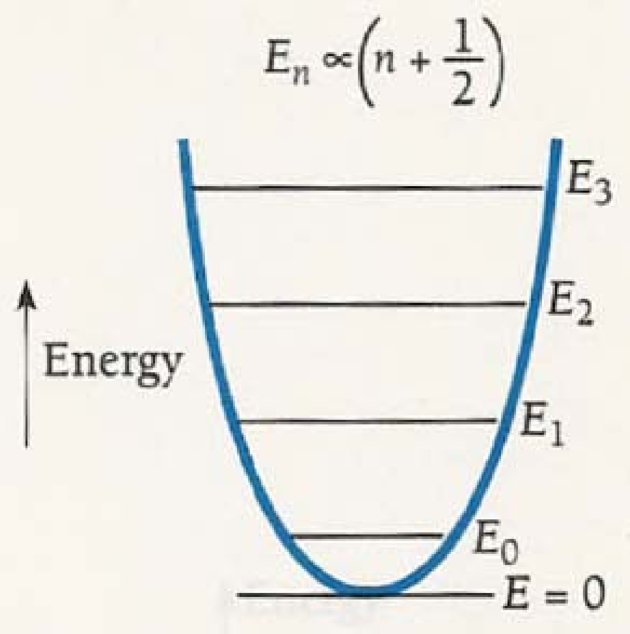


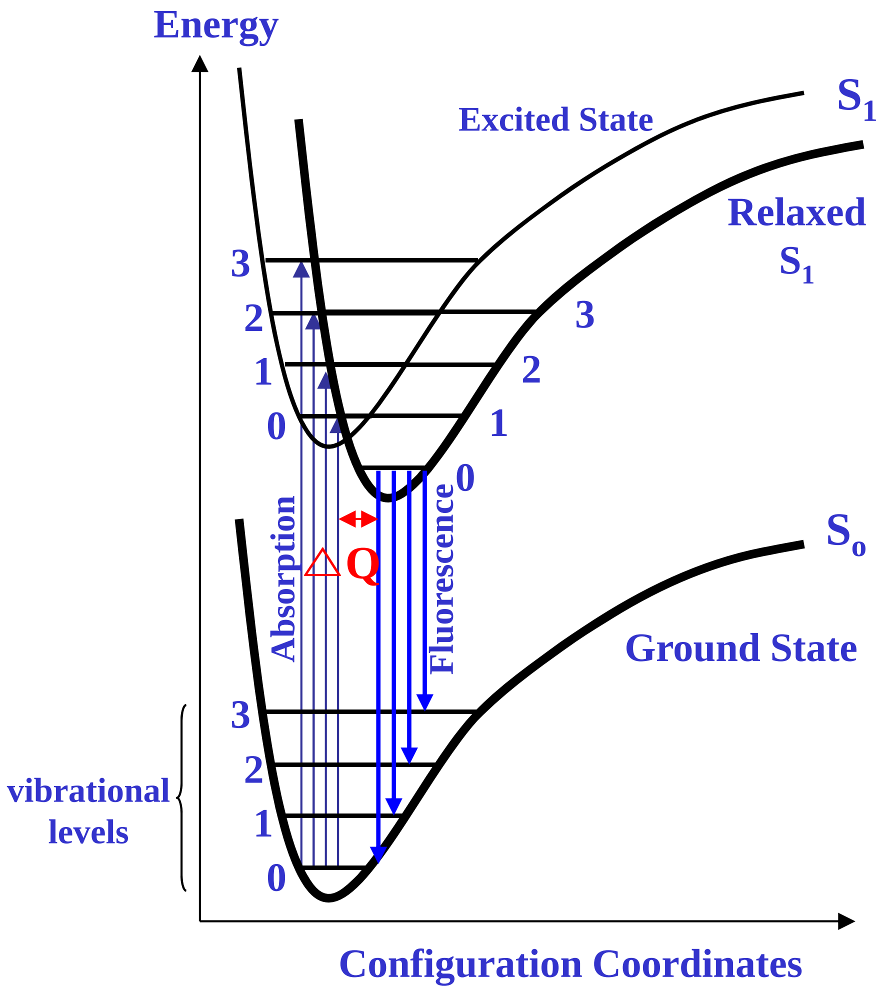
Table 5.2 Some Hermite Polynomials

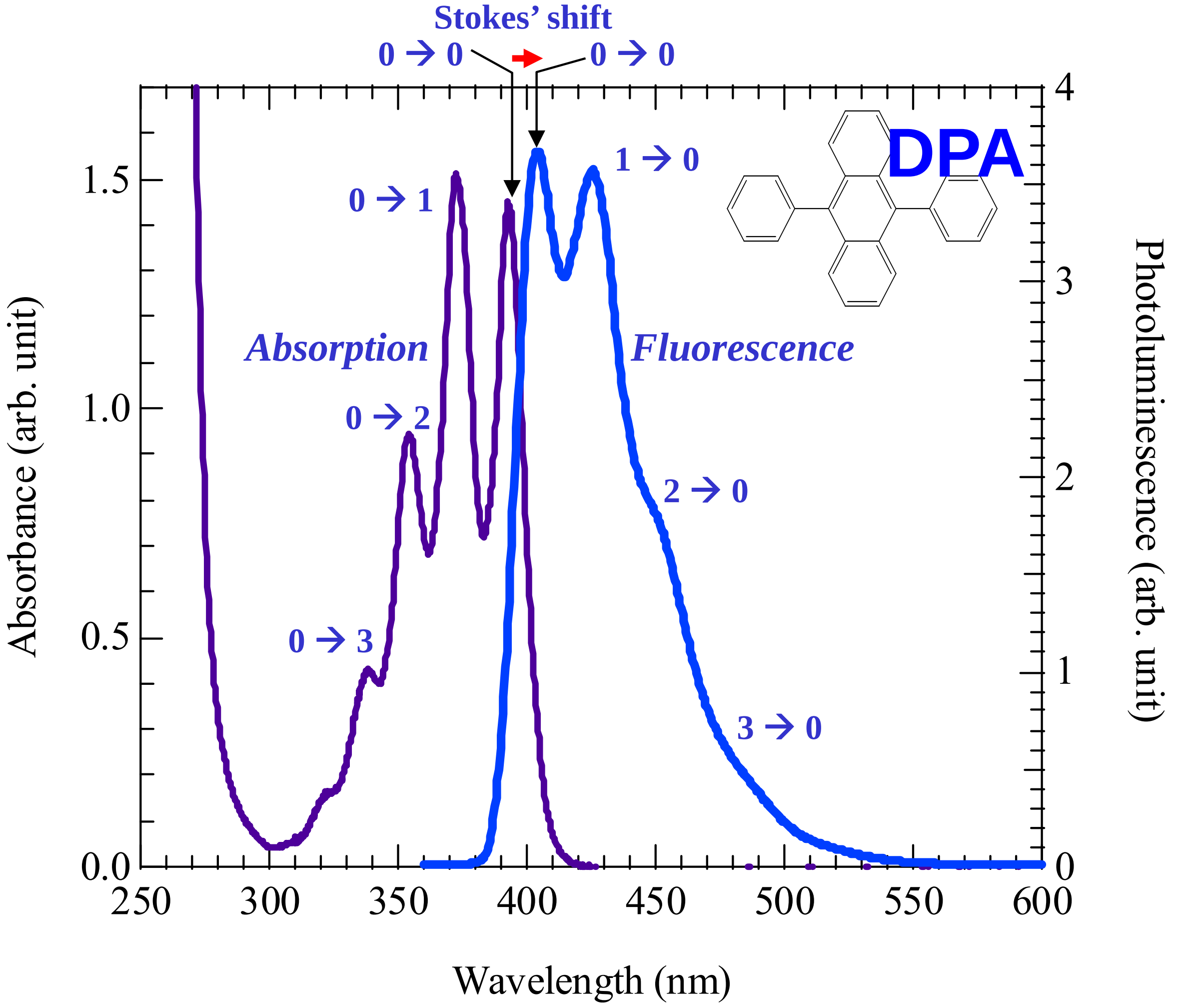
n	$H_n(y)$	α_n	E_n
0	1	1	$\frac{1}{2}h\nu$
1	$2y$	3	$\frac{3}{2}h\nu$
2	$4y^2-2$	5	$\frac{5}{2}h\nu$
3	$8y^3-12y$	7	$\frac{7}{2}h\nu$
4	$16y^4-48y^2+12$	9	$\frac{9}{2}h\nu$
5	$32y^5-160y^3+120y$	11	$\frac{11}{2}h\nu$



A. Beiser, Concepts of Modern Physics, 6th ed., McGraw-Hill, New York, USA, 2003, Chapter 3

Stokes' shift





http://omlc.ogi.edu/spectra/PhotochemCAD/html/diphenyl-anthracene.html

9,10-Diphenylanthracene dissolved in cyclohexane.

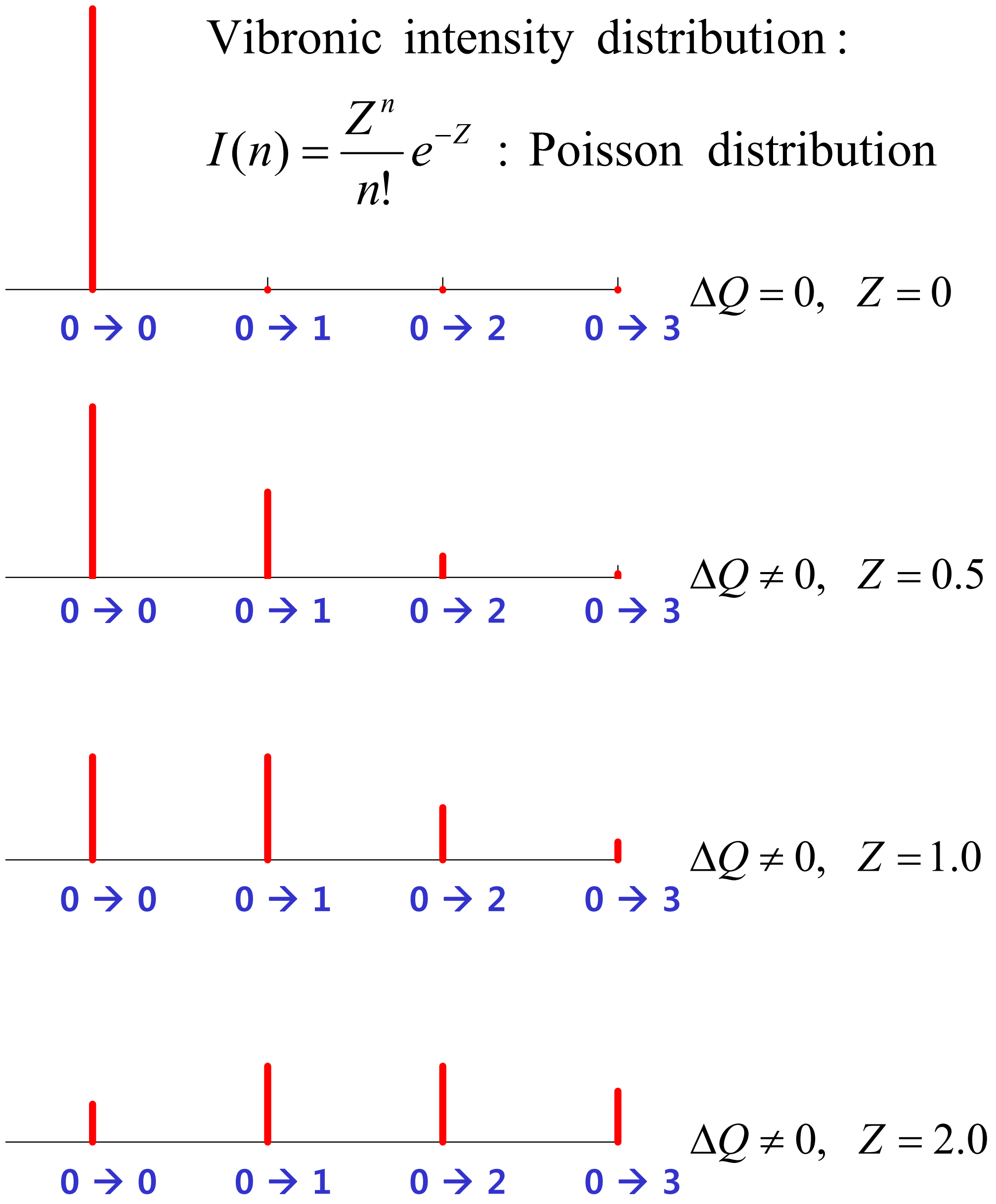
Franck-Condon intensity distribution

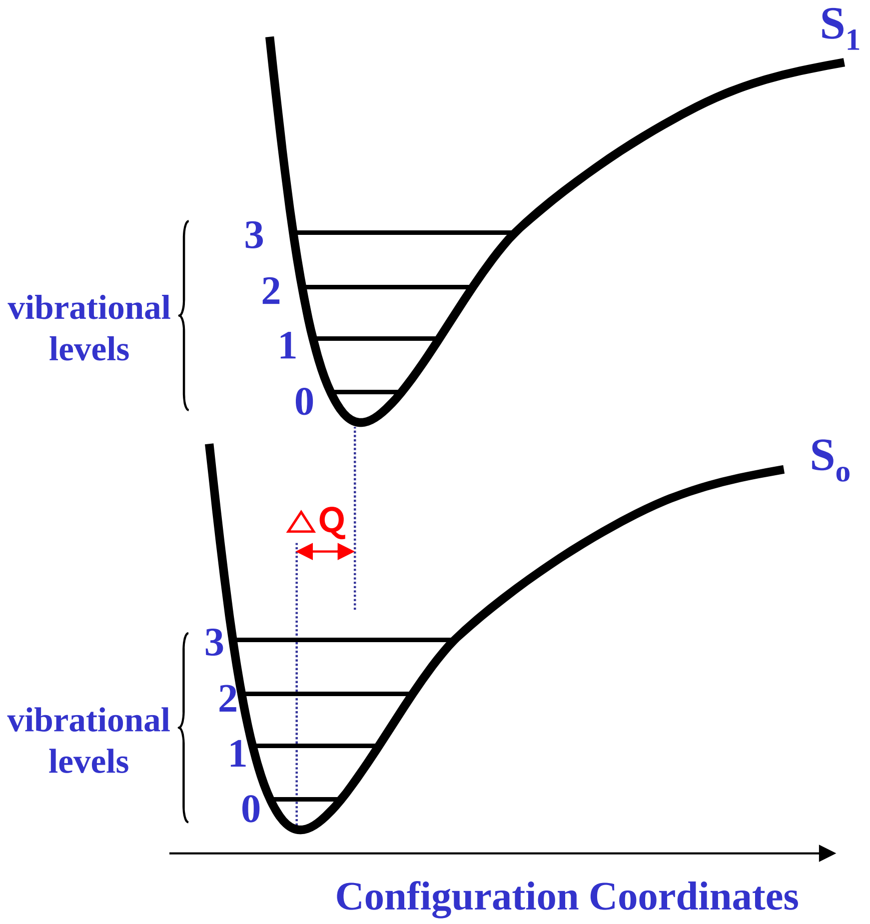
Vibronic intensity distribution :

$$I(n) = \frac{Z^n}{n!} e^{-Z} \quad : \text{Poisson distribution}$$

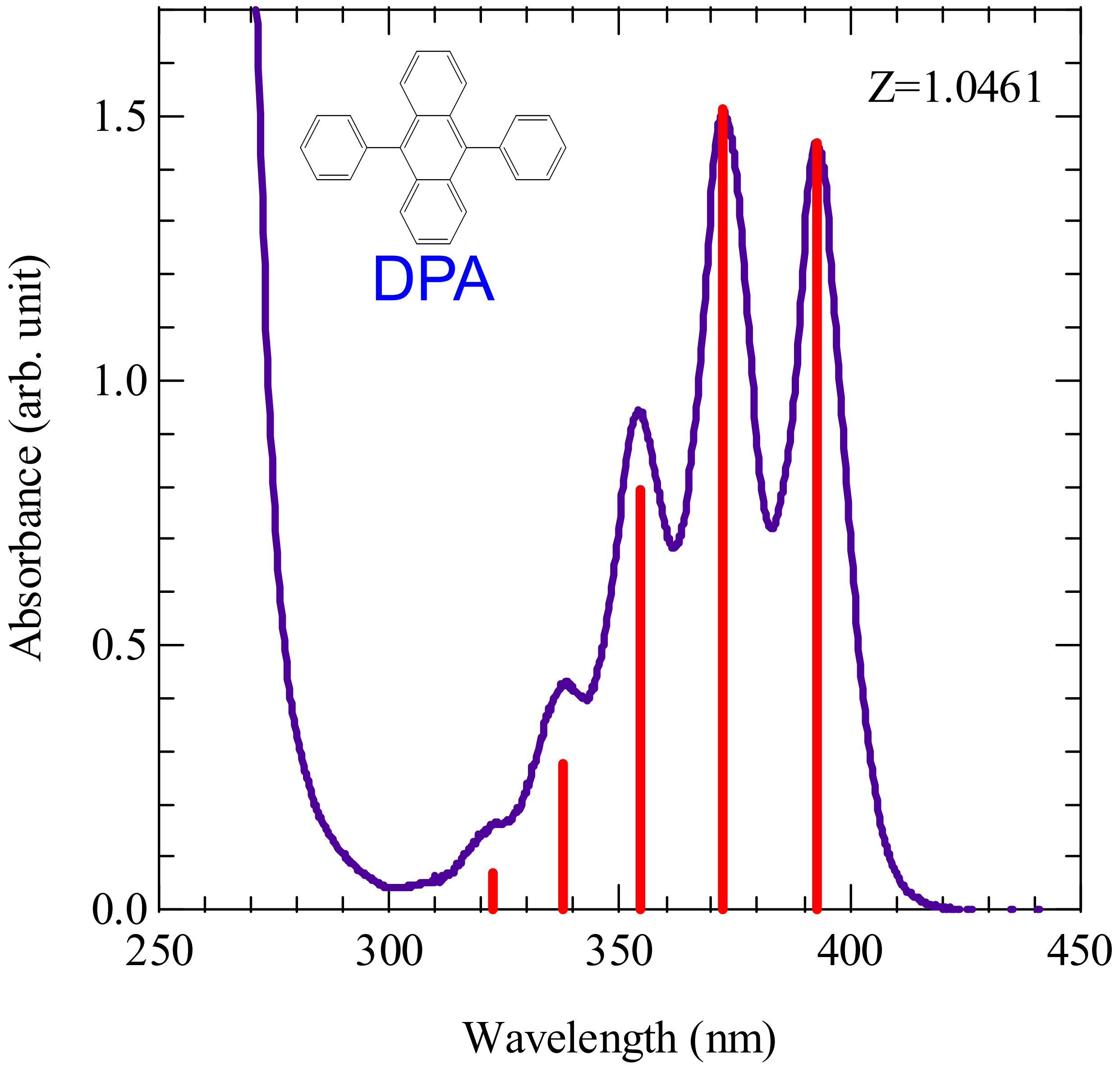
Huang – Rhys parameter :

$$Z = \frac{1}{2\hbar\omega} k(\Delta Q)^2 = \frac{M\omega}{2\hbar}(\Delta Q)^2 = \frac{E_d}{\hbar\omega} = n + \frac{1}{2}$$

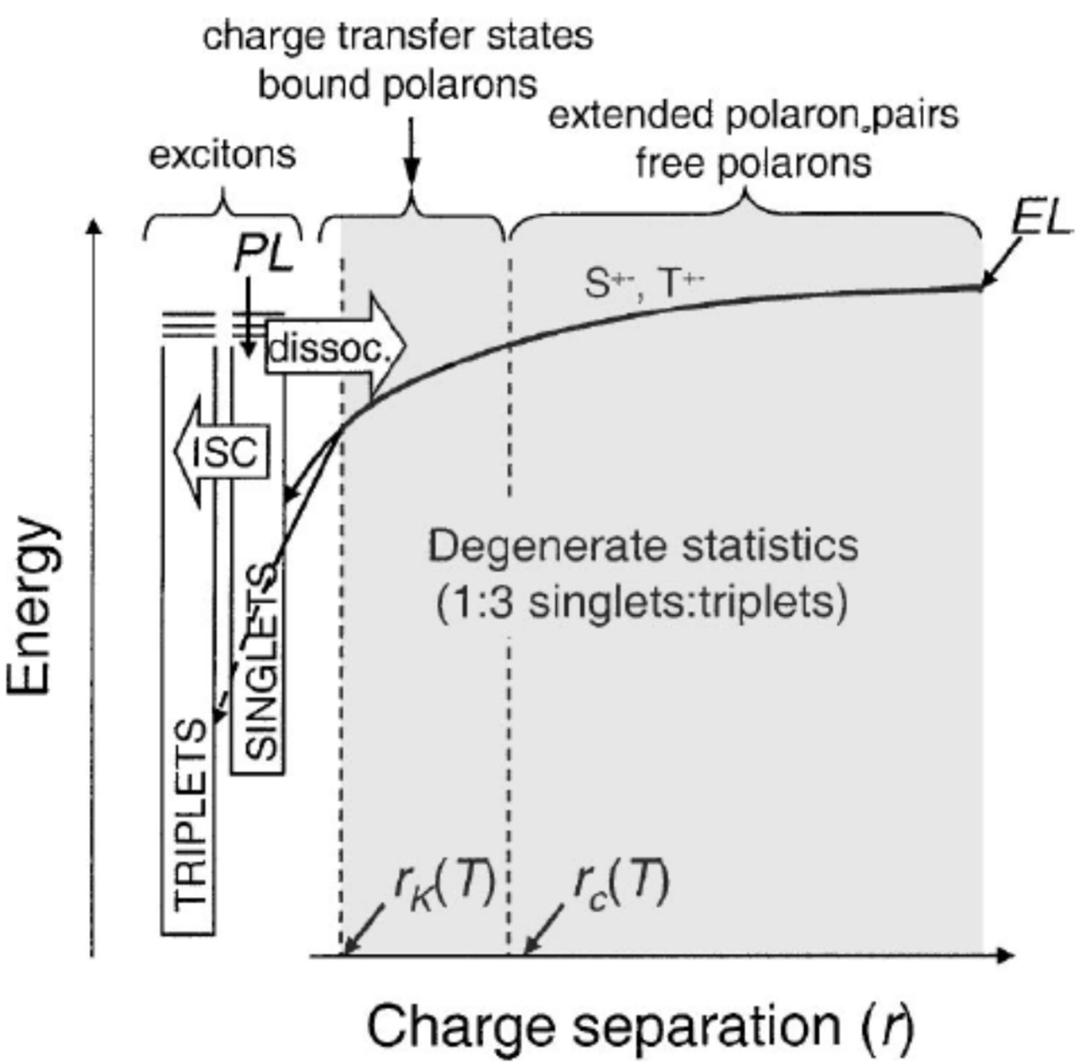


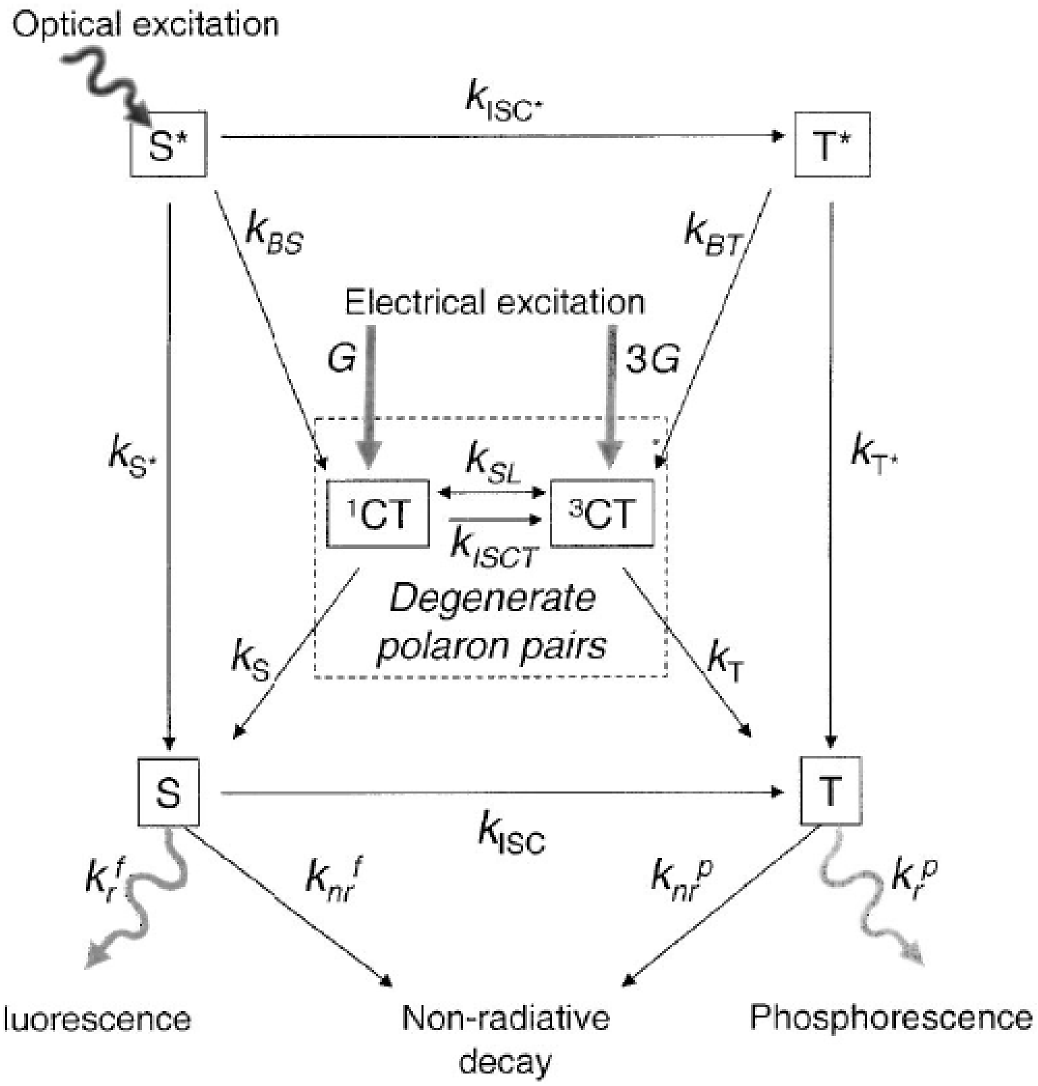


Franck-Condon intensity distribution: an example



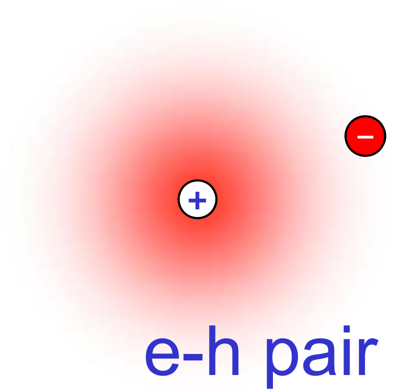
Exciton formation

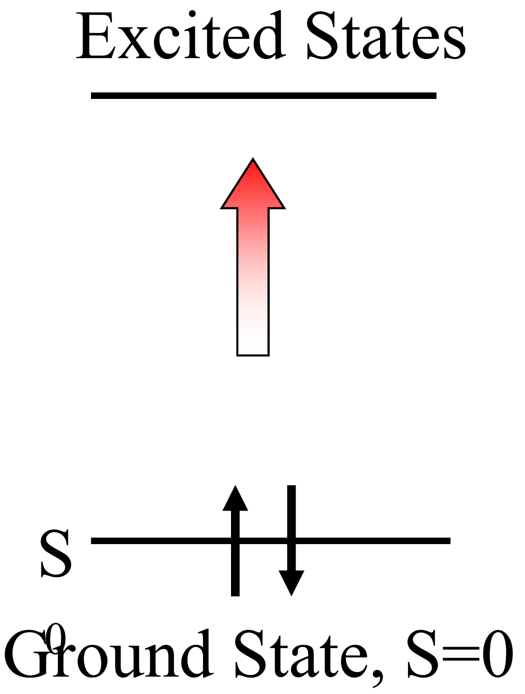




M. Segel, M. A. Baldo, R. J. Holmes, S. R. Forrest, Z. G. Soos, Phys. Rev. B 68, 075211 (2003)

Singlet & Triplet Excitons



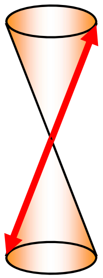

Excited States

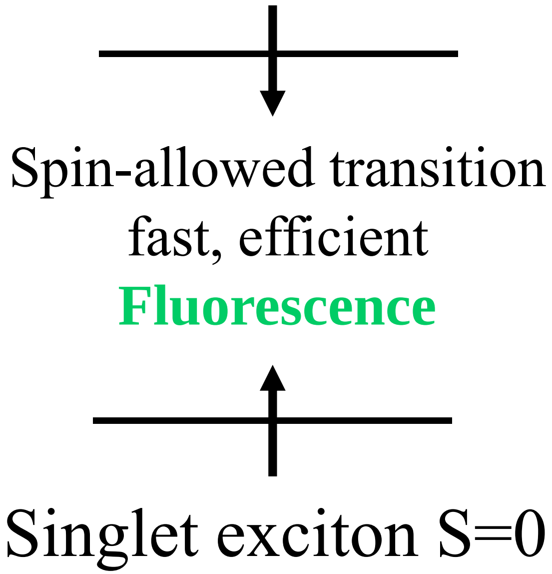
S_0

Ground State, S=0

Singlet exciton S=0

$$|\chi_1\chi_2\rangle = \frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right)$$




Spin-allowed transition
fast, efficient
Fluorescence

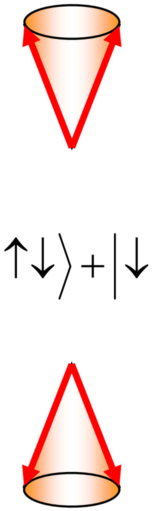
Singlet exciton S=0

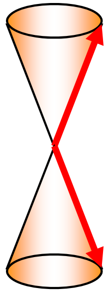
Triplet exciton S=1

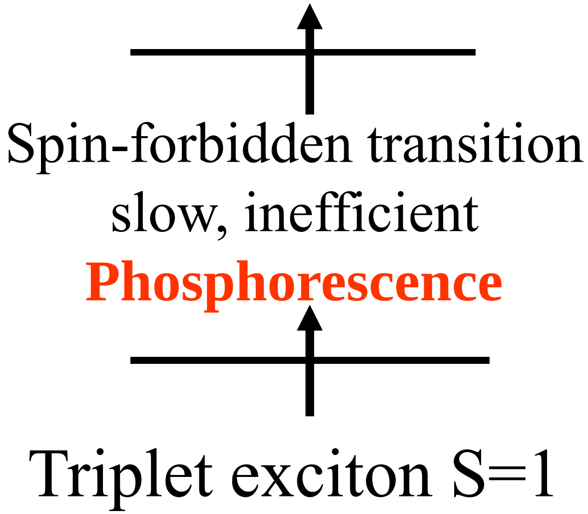
$$|\chi_1\chi_2\rangle = |\uparrow\uparrow\rangle$$

$$|\chi_1\chi_2\rangle = \frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle\right)$$

$$|\chi_1\chi_2\rangle = |\downarrow\downarrow\rangle$$






Spin-forbidden transition
slow, inefficient
Phosphorescence

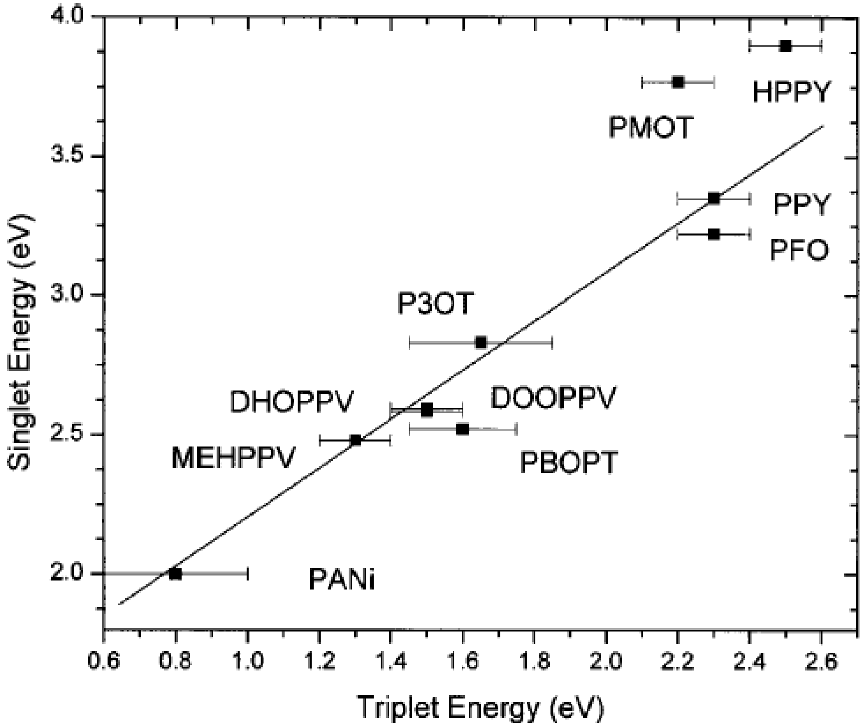
Triplet exciton S=1

Energy Difference between Singlet-Triplet Exciton Energy

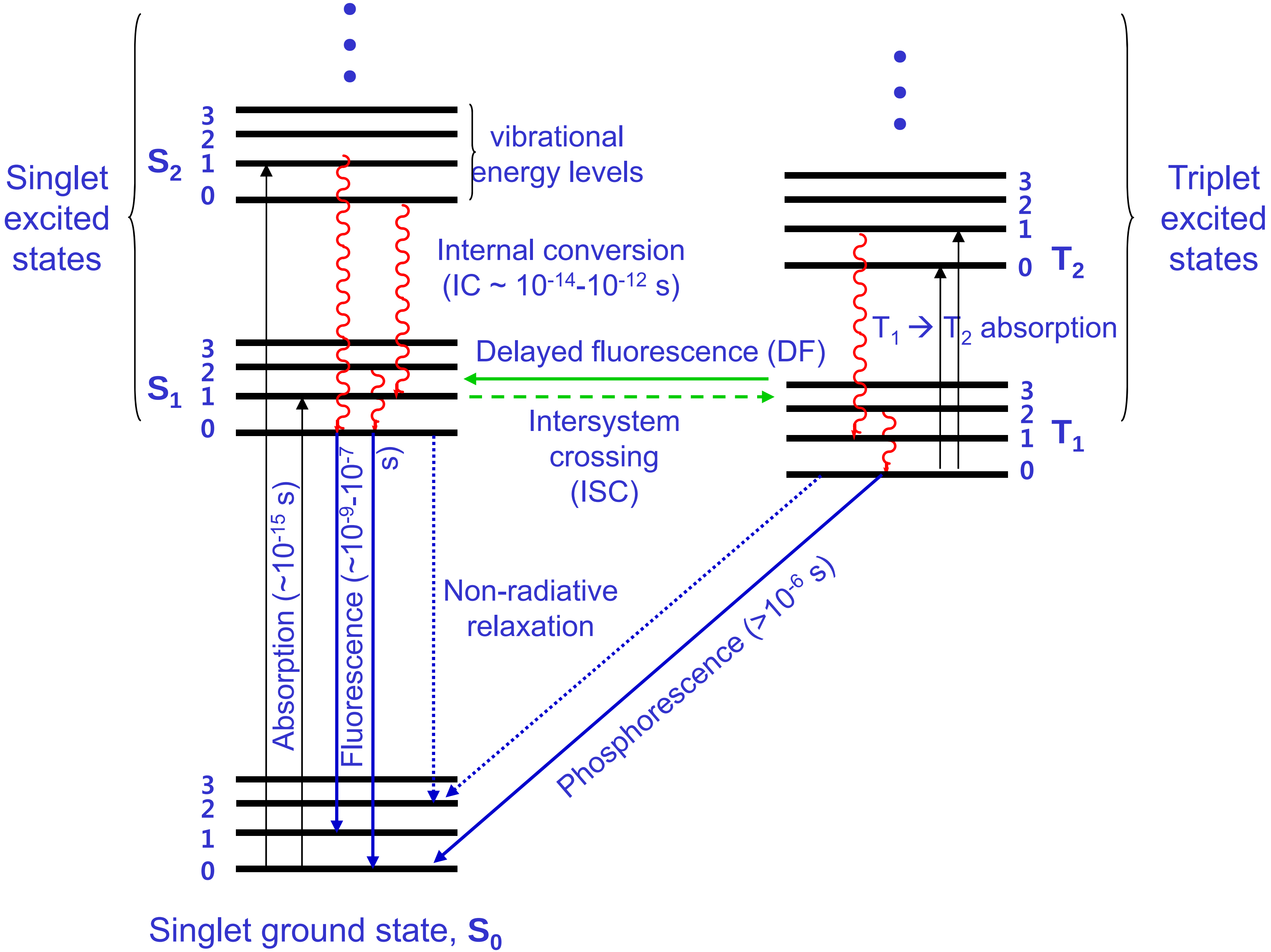
- Triplet state is at lower energy than the singlet state.
- Electrons in singlet state have the antisymmetric spins, thus can have the same position in space, resulting in a large electron-electron repulsion energy.
- Electrons in triplet state have the symmetric spins, thus cannot have the same position in space, reducing the electron-electron repulsion energy.
- The S - T splitting is proportional to orbital overlap and inversely proportional to orbital size.

anthracene: $S_1 - T_1 = 1.5$ eV
tetracene 1.3 eV
pentacene 1.1 eV

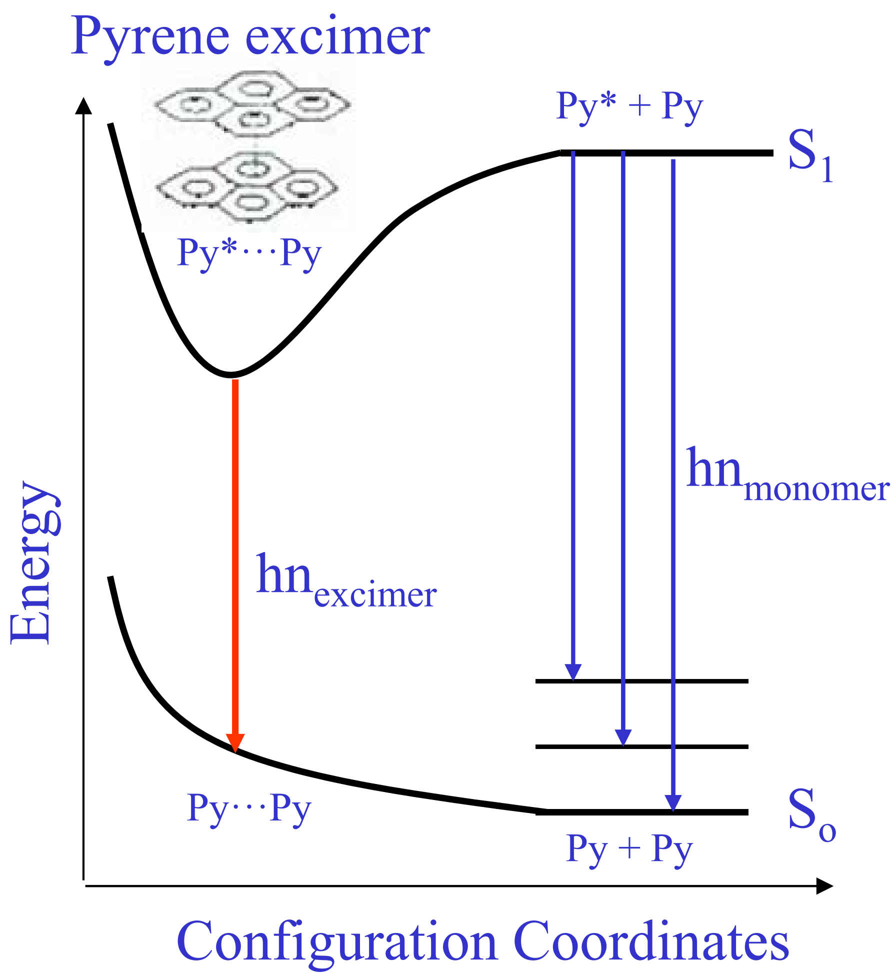
A. Monkman et al., Phys. Rev. Lett. **6**, 1358 (2001)

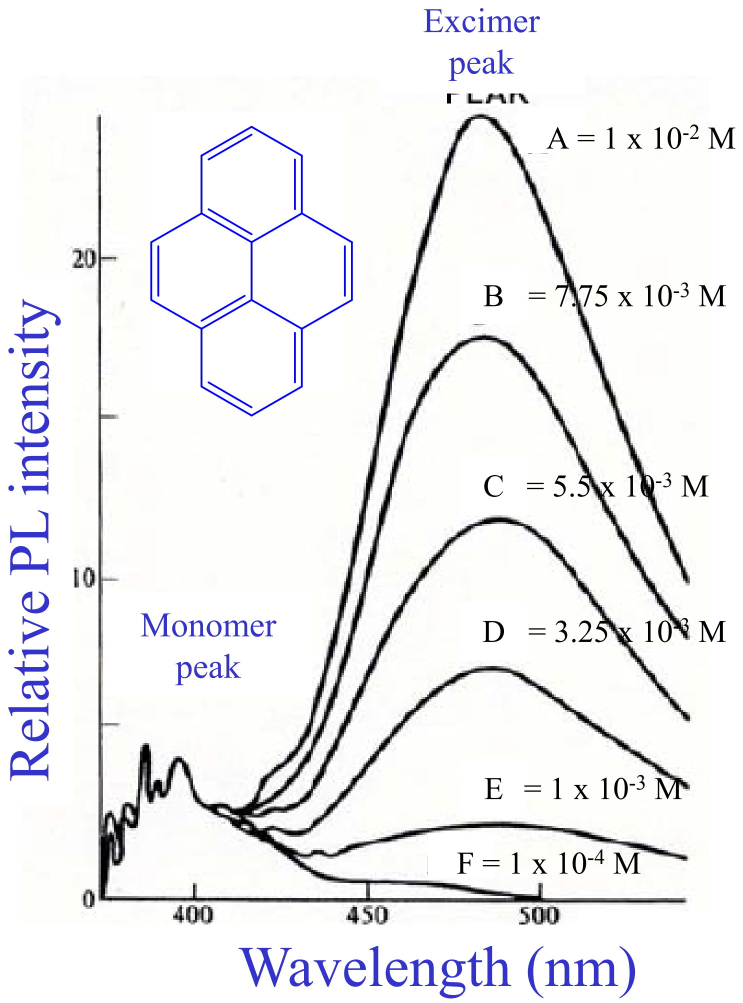


Jablonski Energy Diagram



Excimer or Exciplex





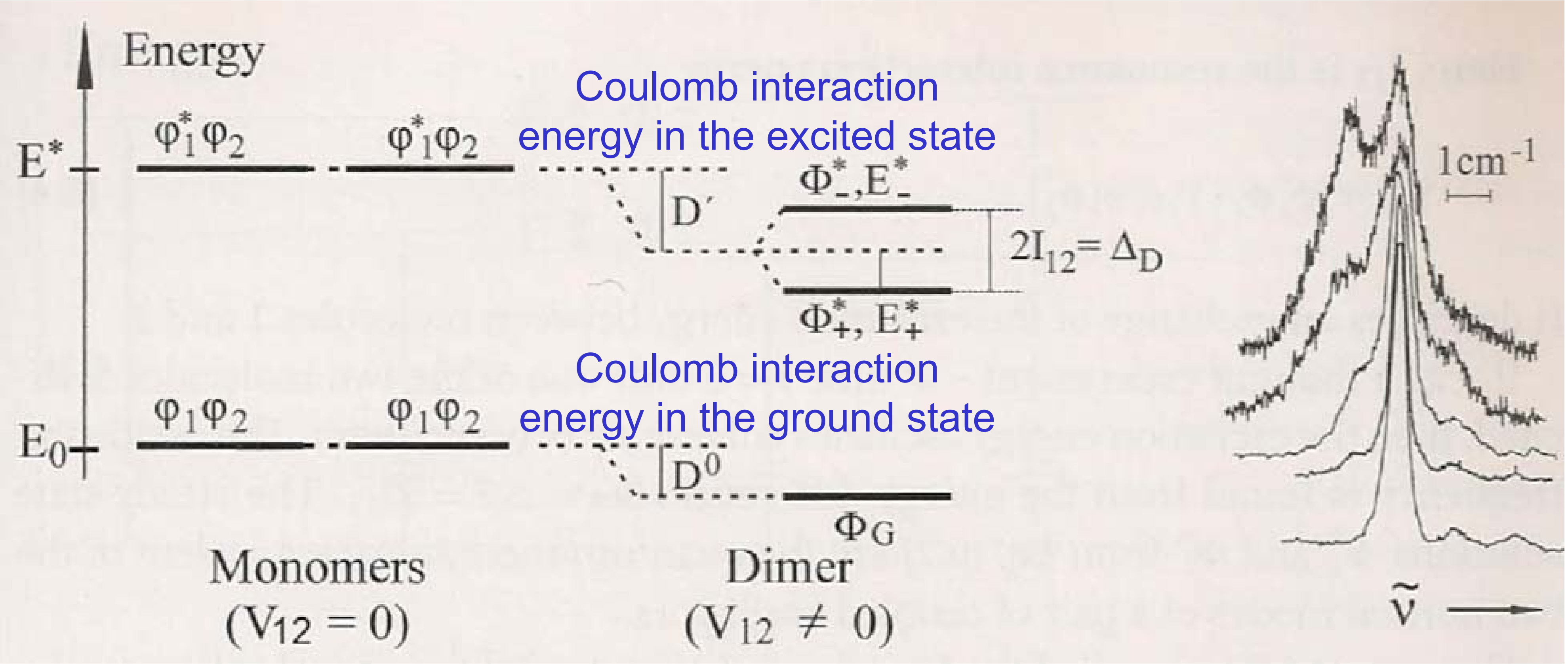
Excited state dimer; Repulsive ground state

Excimer: M+M*

Exciplex: D+A* or D*+A

- Red shift
- Broad peak with no vibronic structure

Davydov splitting



Coulomb interaction energy in the excited state

Coulomb interaction energy in the ground state

$$D' = <\phi_1^*\phi_2|V_{12}|\phi_1^*\phi_2> = <\phi_1\phi_2^*|V_{12}|\phi_1\phi_2^*> \ , \ D^o = <\phi_1\phi_2|V_{12}|\phi_1\phi_2>$$

$D = D' - D^0$ “**Solvent shift**” if one of the two molecules is a solvent molecule.

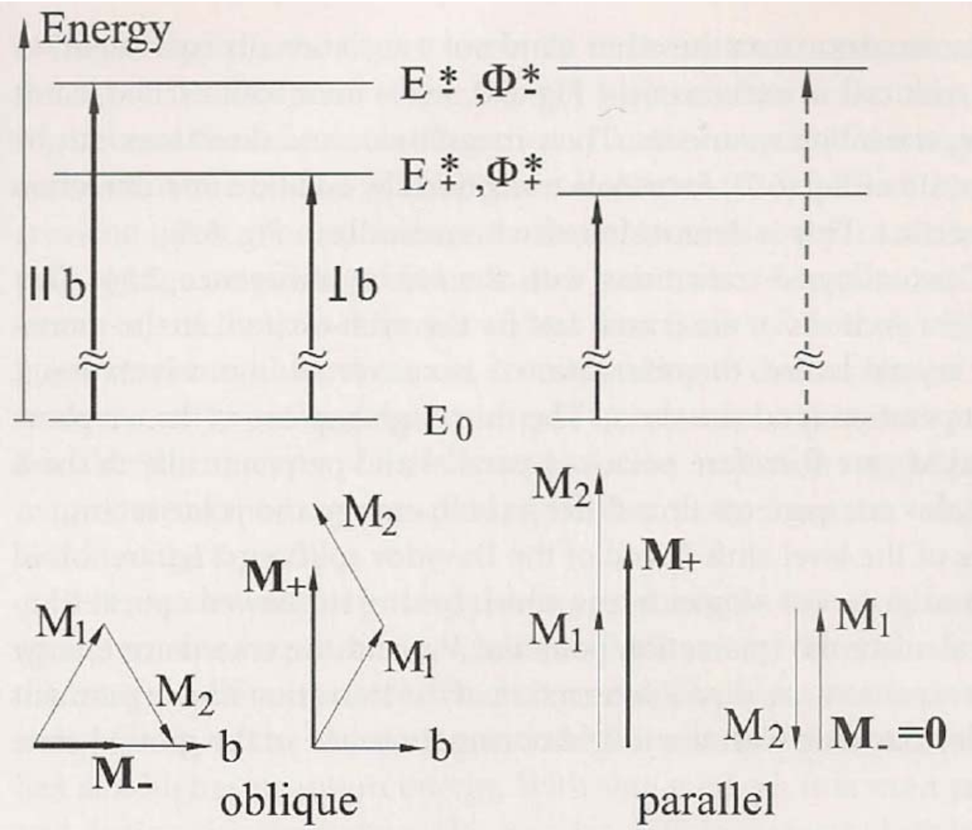
$E^*_{\pm} = E^* + E_0 + D' \pm I_{12}$ $\quad I_{12} = <\phi_1^*\phi_2|V_{12}|\phi_1\phi_2^*>$ Resonance interaction energy

$\Delta_D = 2I_{12}$ **Davydov splitting**

Polarization of the optical transition in Davydov components

$$M^1_{S_1\leftarrow S_0} =<\phi_1|e\vec{r}|\phi_1^*>,\ M^2_{S_1\leftarrow S_0} =<\phi_2|e\vec{r}|\phi_2^*>$$

$$\begin{aligned}M^{\pm}_{S_1\leftarrow S_0} &=<\Phi_G|e\vec{r}|\phi_\pm^*> \\ &=\frac{1}{\sqrt{2}}<\phi_1\phi_2|e\vec{r}|\phi_1\phi_2^* \pm \phi_1^*\phi_2> \\ &=\frac{1}{\sqrt{2}}[<\phi_1\phi_2|e\vec{r}|\phi_1\phi_2^*> \pm <\phi_1\phi_2|e\vec{r}|\phi_1^*\phi_2>] \\ &=\frac{1}{\sqrt{2}}[M^2_{S_1\leftarrow S_0} \pm M^1_{S_1\leftarrow S_0}]\end{aligned}$$



In the case of parallel orientation of two molecules, only one of the two optical transitions $S_1 \leftarrow S_0$ of the dimer is allowed.

$$M_+^{Dimer} = \frac{1}{\sqrt{2}} 2M^1_{S_1\leftarrow S_0} \quad \text{or} \quad \frac{1}{\sqrt{2}} 2M^2_{S_1\leftarrow S_0}$$

$$M_-^{Dimer} = 0$$

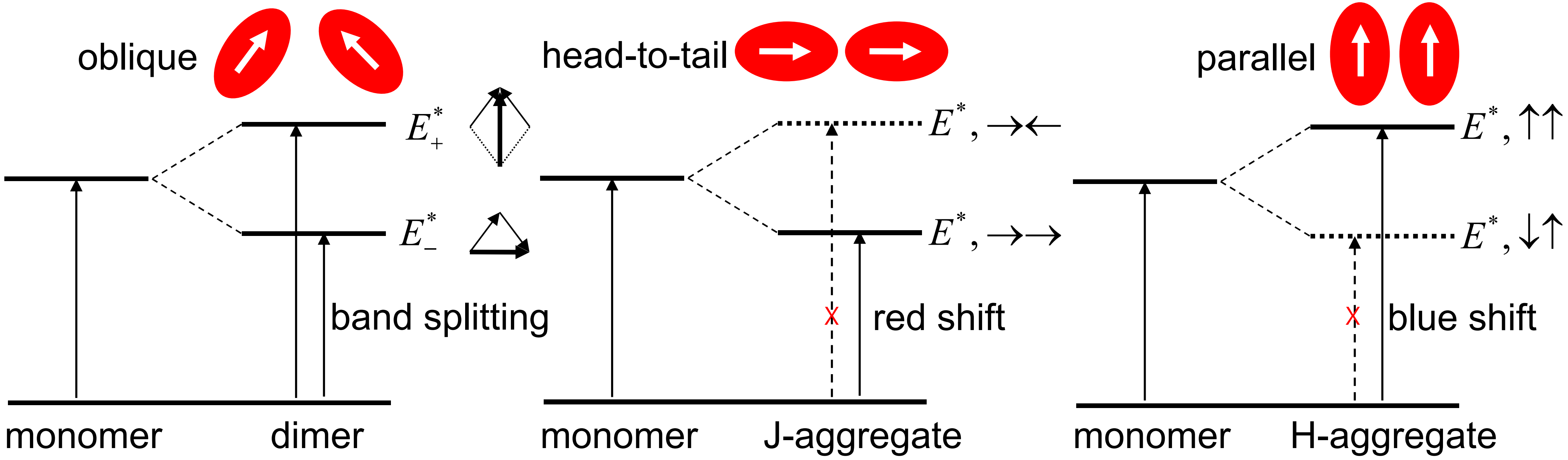
In the case of non-parallel orientation of two molecules, there are two allowed transitions.

Self-aggregation of dye molecules

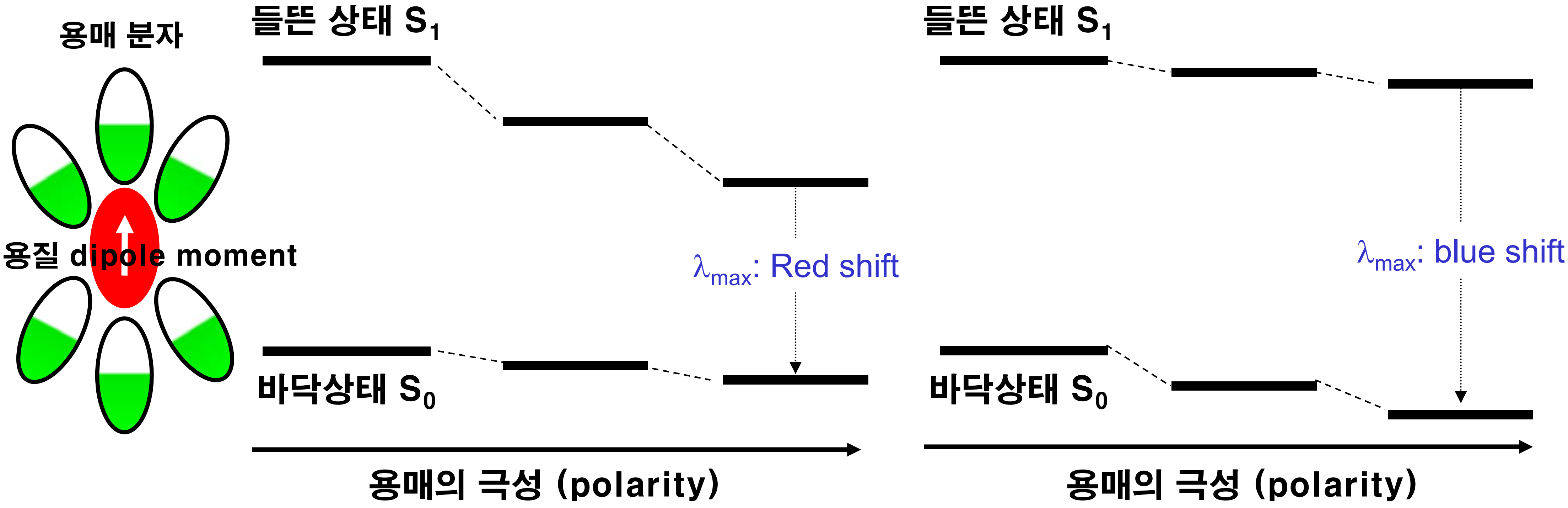
The self-association of dyes in solution or at the solid-liquid interface is a frequently encountered phenomenon owing to strong intermolecular van der Waals-like attractive forces between the molecules.

J-aggregate (J for Jelly, one of the first workers who investigated these shifts). Bathochromically shifted (red-shift): E. E. Jelly, *Nature* 1936, *138*, 1009.

H-aggregate (H for hypsochromic): Hypsochromically shifted (blue-shifted). L. G. S. Brooker, F. L. White, D. W. Heseltine, G. H. Keyes, S. G. Dent, E. J. VanLare, *J. Photogr. Sci.* 1953, *1*, 173.



Host – Dopant Interaction



용매 분자

용질 dipole moment

들뜬 상태 S_1

λ_{max}: Red shift

바닥상태 S_0

용매의 극성 (polarity)

$\mu_1 > \mu_0$

들뜬 상태 S_1

λ_{max}: blue shift

바닥상태 S_0

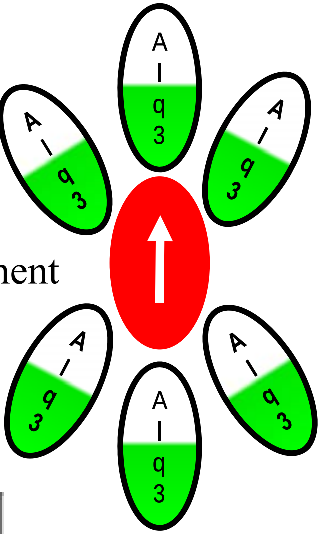
용매의 극성 (polarity)

$\mu_1 < \mu_0$

V. Bulovic, M.A. Baldo, and S. R. Forrest, *Excitons and Energy Transfer in Doped Luminescent Molecular Organic Materials*, in *Organic Electronic Materials*, edited by R. Farchioni and G. Grosso (Springer, Berlin, 2001).

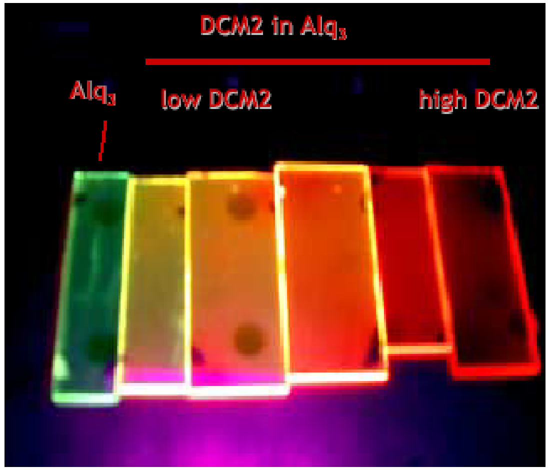
Host – Dopant Interaction

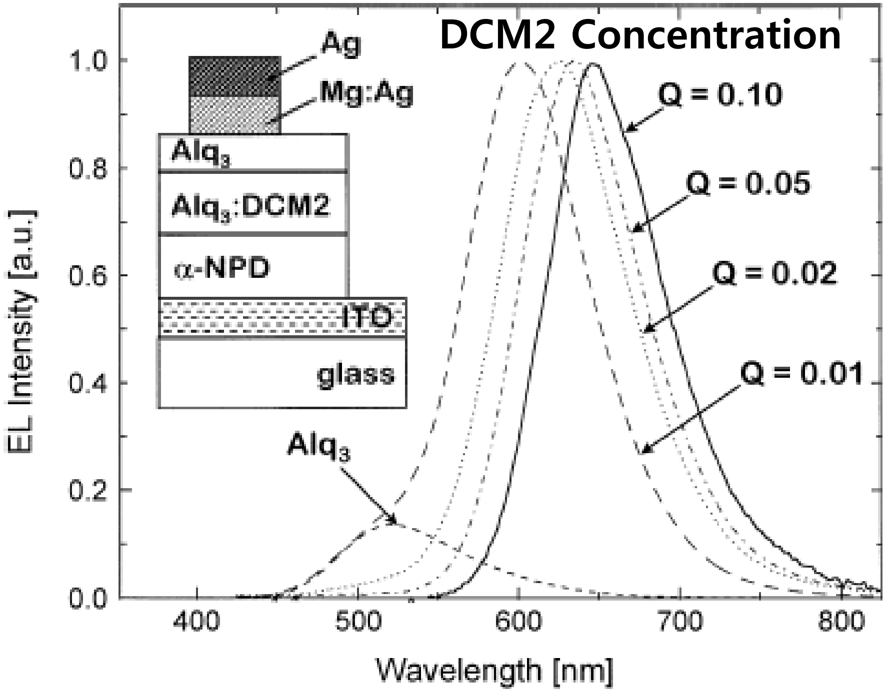
Solid state solvation effect

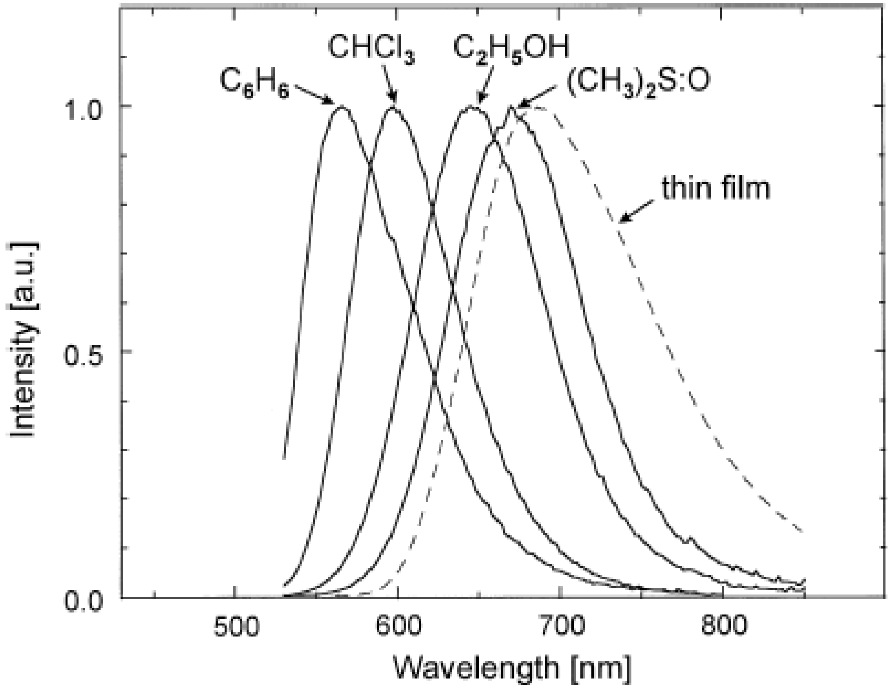


DCM2 dipole moment

Alq3 dipole moment

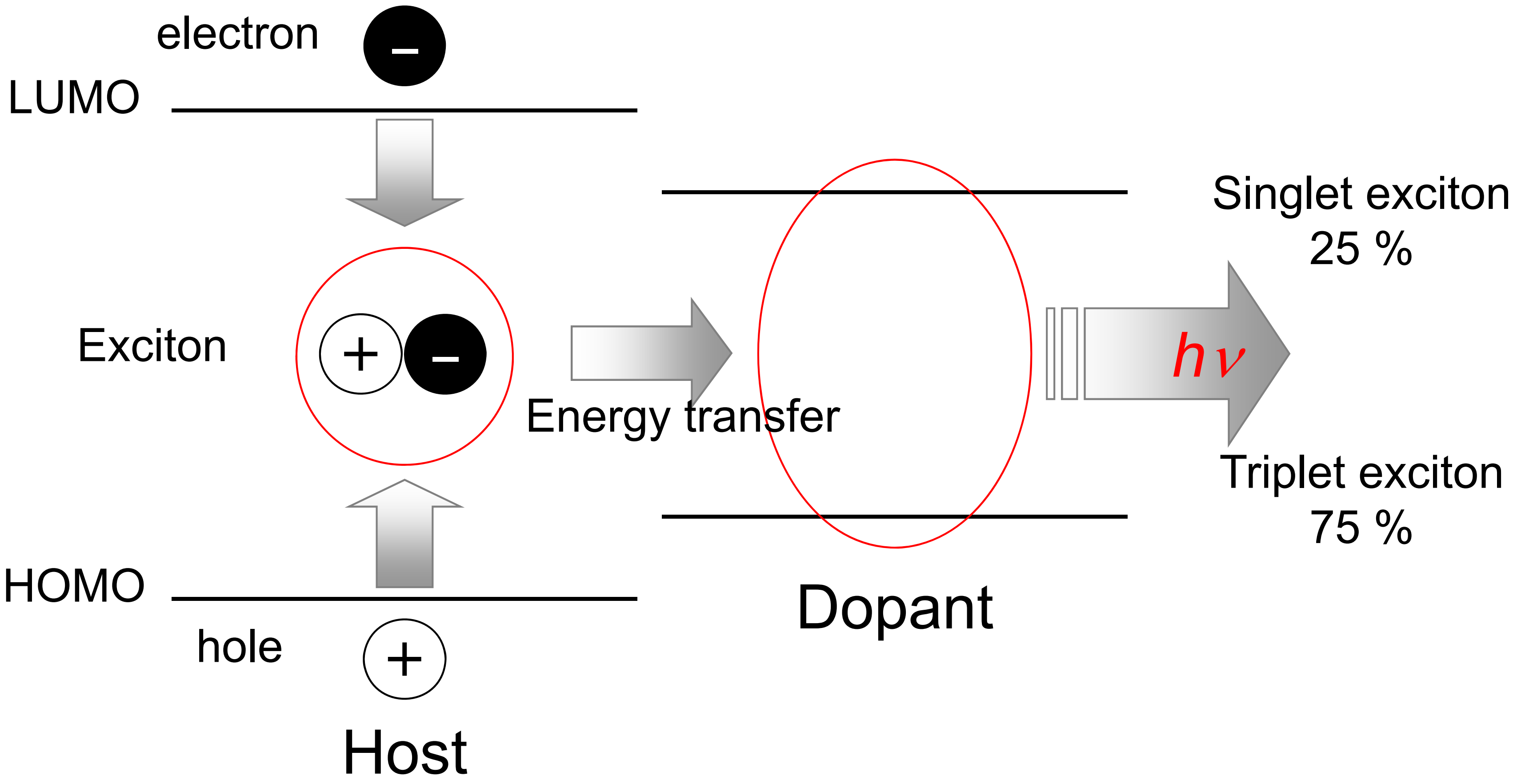






V. Bulovic, A. Shoustikov, M.A. Baldo, E. Bose, V.G. Kozlov, M. E. Thompson, S. R. Forrest, Chem. Phys. Lett. 287, 455 (1998).
V. Bulovic, R. Deshpande, M. E. Thompson, S. R. Forrest, Chem. Phys. Lett. **308**, 317 (1999).

Exciton Energy transfer



electron

LUMO

Exciton

Energy transfer

HOMO

hole

Host

Dopant

Singlet exciton
25 %

Triplet exciton
75 %

Exciton Energy transfer

Förster Transfer Process

Dipole-dipole interaction
(overlap of PL and Abs spectra)
long range ~30-100 Å

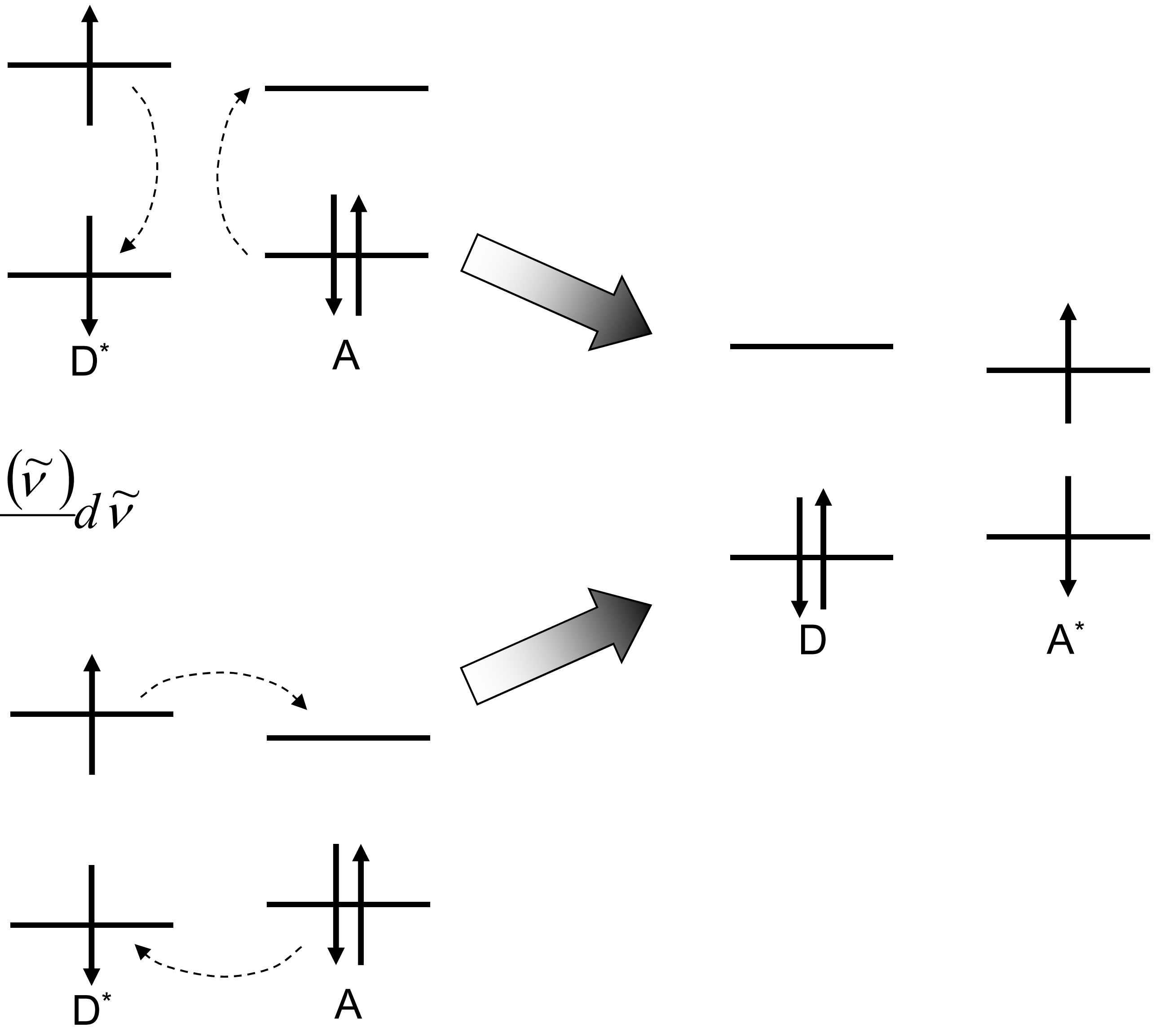
$$k_{D\rightarrow A} = \frac{K^2 J\, 8.8\times10^{-28}\ \mathrm{mol}}{n^4 \tau_o r^6}$$

$$\text{Overlap integral} : J = \int \frac{\varepsilon_A(\tilde{\nu})\cdot F_D(\tilde{\nu})}{\tilde{\nu}^4} d\tilde{\nu}$$

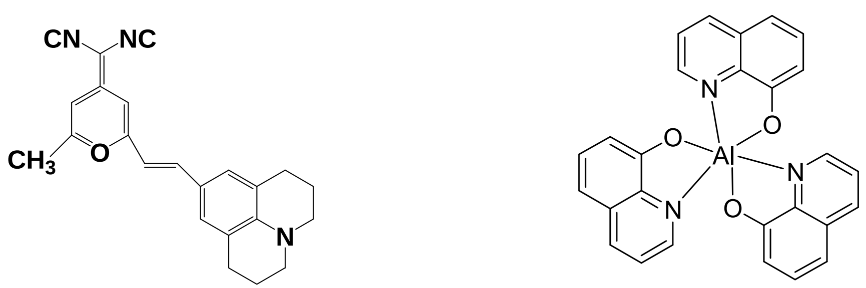
Dexter Transfer Process

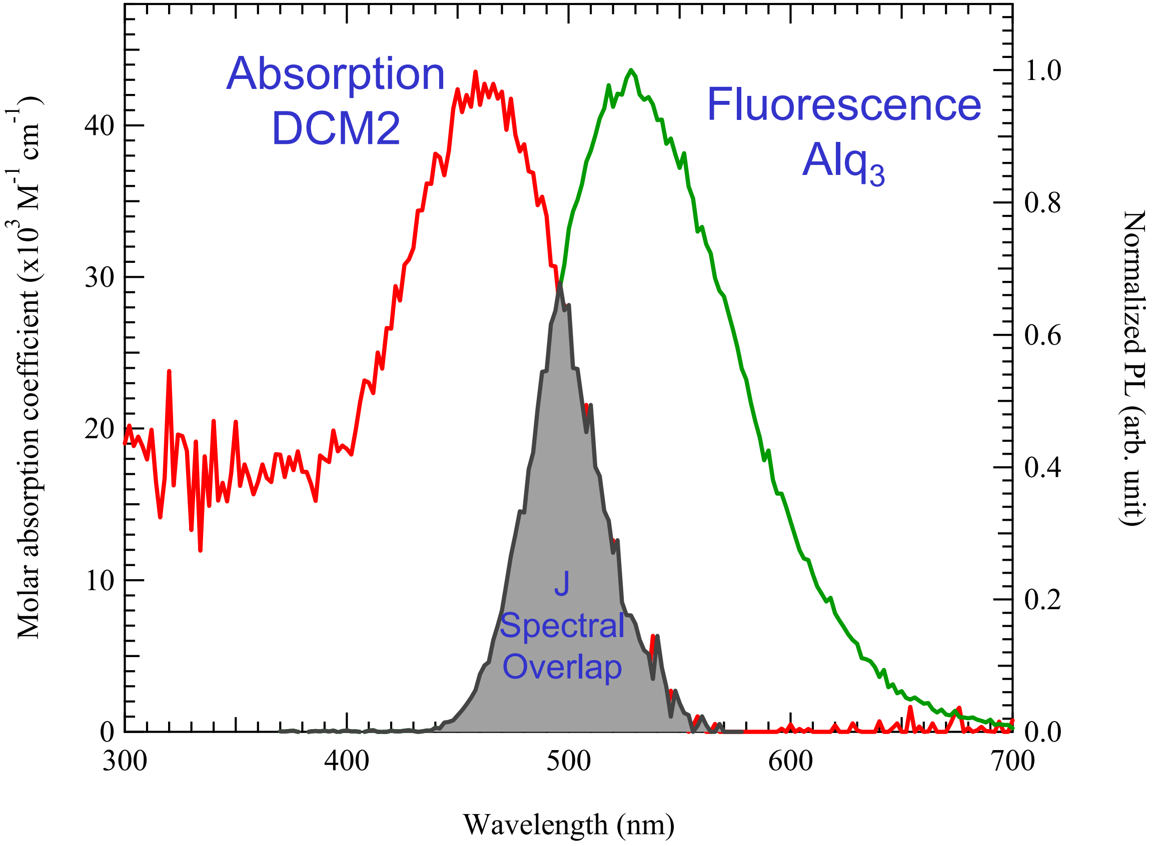
Electron exchange
(overlap of wavefunctions)
short range ~5-20 Å

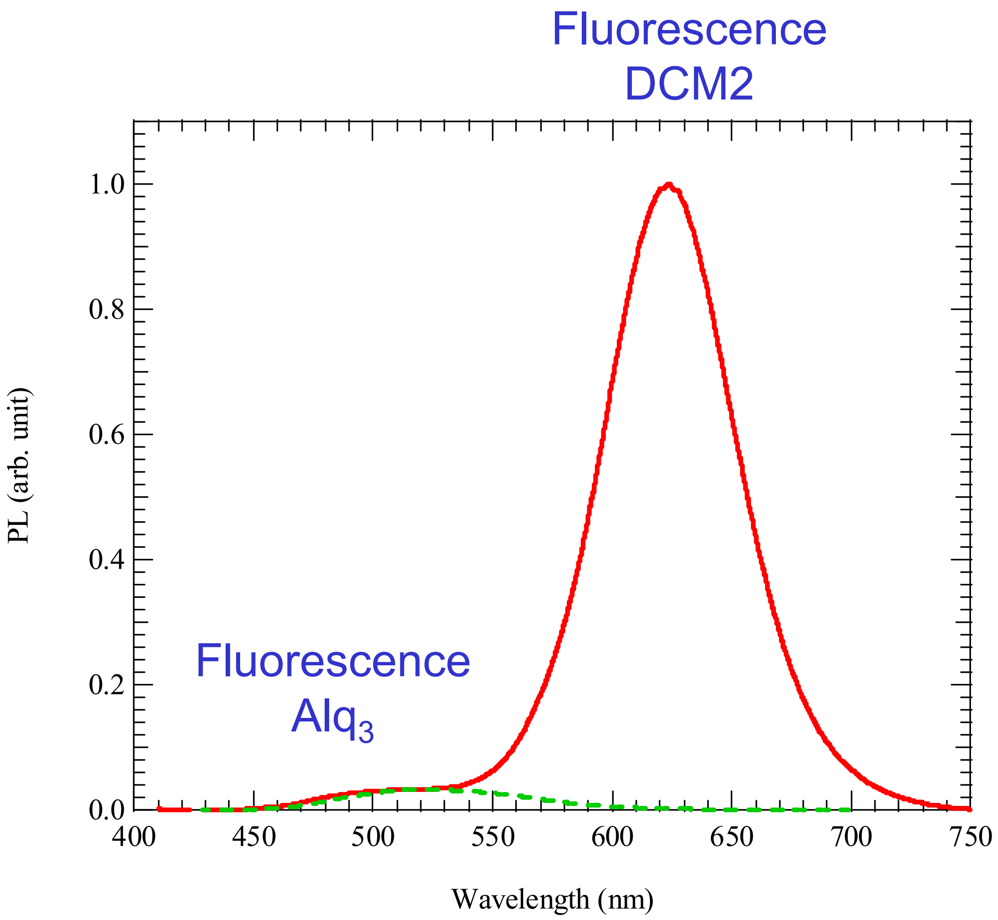
$$k_{ET} \propto \frac{h}{2\pi} P^2 J \exp\ (-2r/L)$$



Forster Exciton Energy transfer







Experimental results of Forster energy transfer

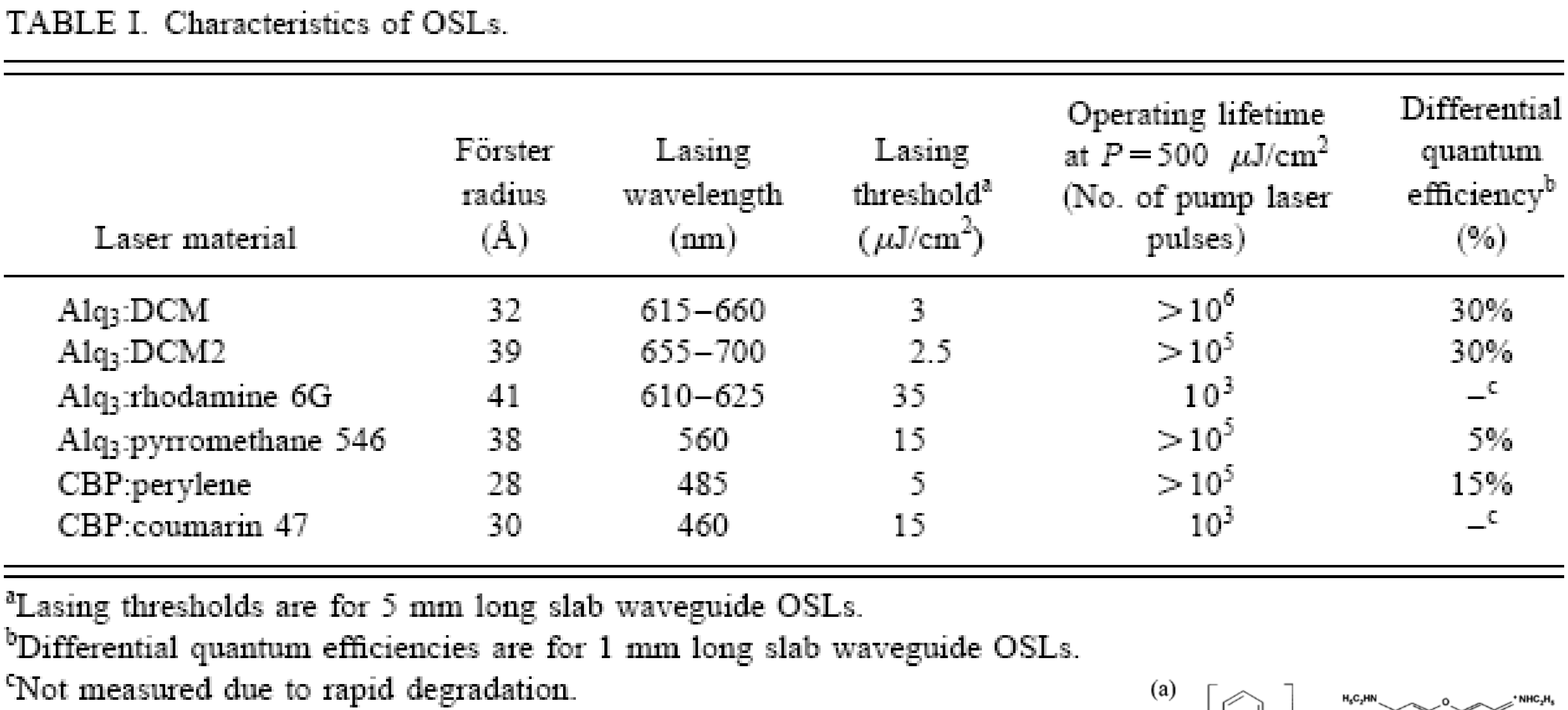


TABLE I. Characteristics of OSLs.

Laser material	Förster radius (Å)	Lasing wavelength (nm)	Lasing threshold[a] (μJ/cm^2)	Operating lifetime at $P=500$ μJ/cm^2 (No. of pump laser pulses)	Differential quantum efficiency[b] (%)
Alq$_3$:DCM	32	615–660	3	$>10^6$	30%
Alq$_3$:DCM2	39	655–700	2.5	$>10^5$	30%
Alq$_3$:rhodamine 6G	41	610–625	35	10^3	–[c]
Alq$_3$:pyrromethane 546	38	560	15	$>10^5$	5%
CBP:perylene	28	485	5	$>10^5$	15%
CBP:coumarin 47	30	460	15	10^3	–[c]

[a] Lasing thresholds are for 5 mm long slab waveguide OSLs.

[b] Differential quantum efficiencies are for 1 mm long slab waveguide OSLs.

[c] Not measured due to rapid degradation.

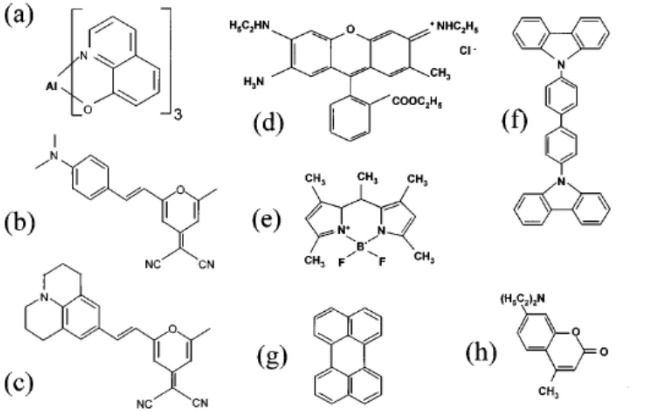
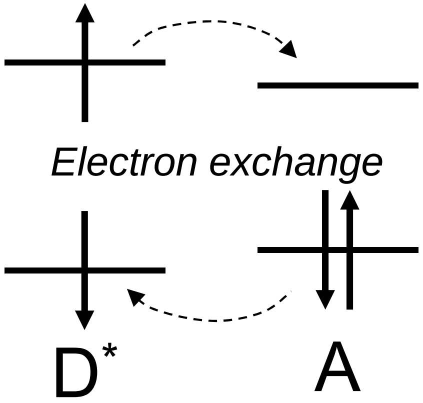


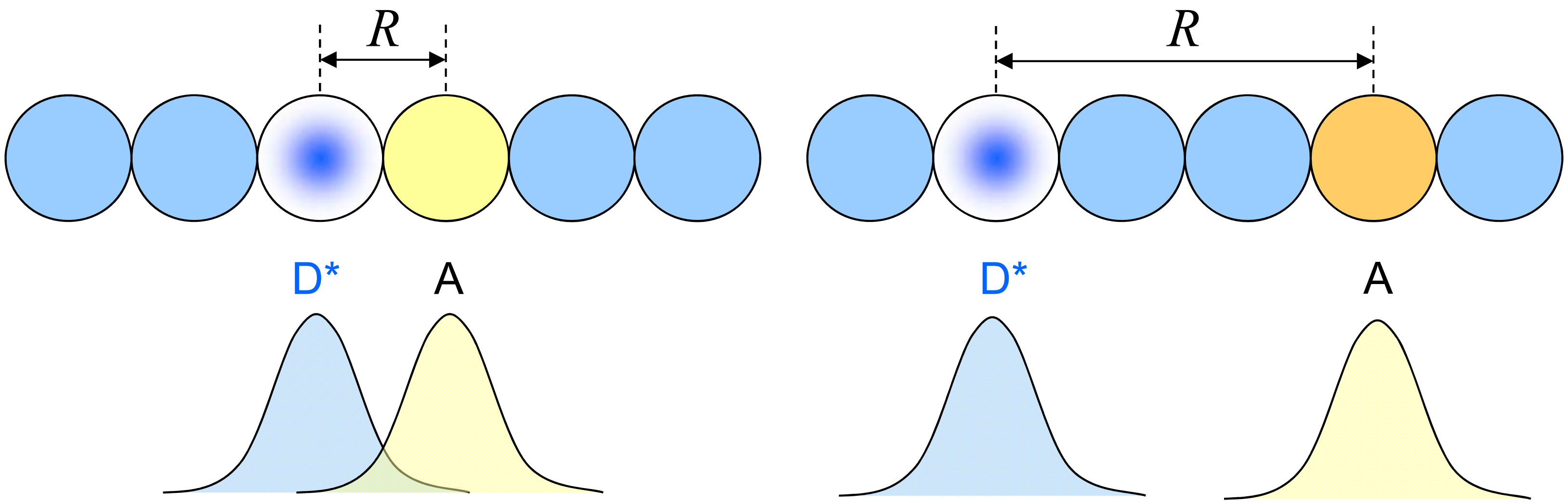
FIG. 1. Chemical structure formulas of (a) Alq$_3$, (b) DCM, (c) DCM2, (d) rhodamine 6G, (e) pyrromethane, (f) CBP, (g) perylene, (h) coumarin 47.

V. G. Kozlov, V. Bulovic, P. E. Burrows, M. Baldo, V. B. Khalfin, G. Parthasarathy,
S. R. Forrest, Y. You and M. E. Thompson, J. Appl. Phys. **84** (8), 4096 (1998)

Dexter Exciton Energy transfer



Dexter Transfer Process

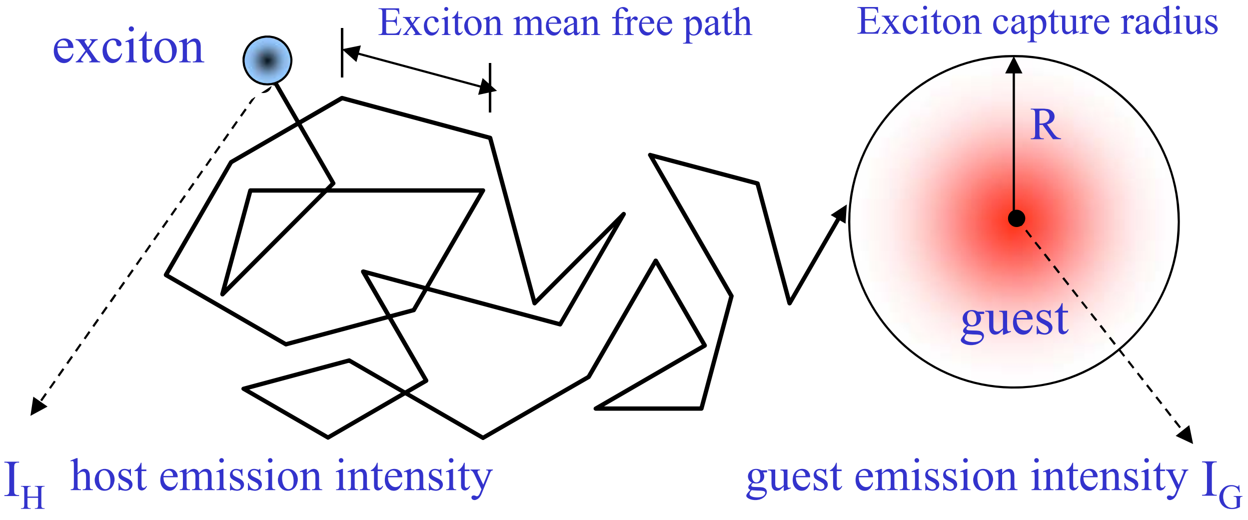


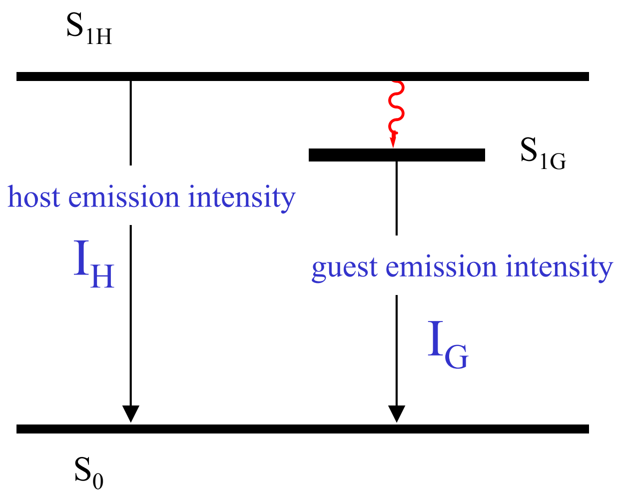
Wavefunction overlap ~ $e^{-2R/L}$

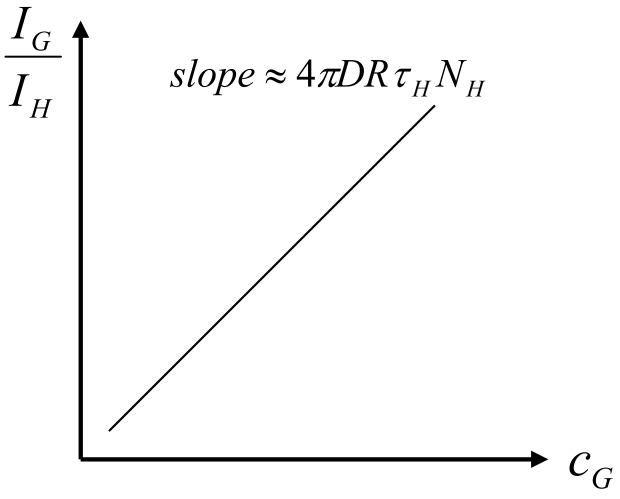
No overlap

N. J. Turro, *Modern Molecular Photochemistry*, (Benjamin/Cummings, 1978).

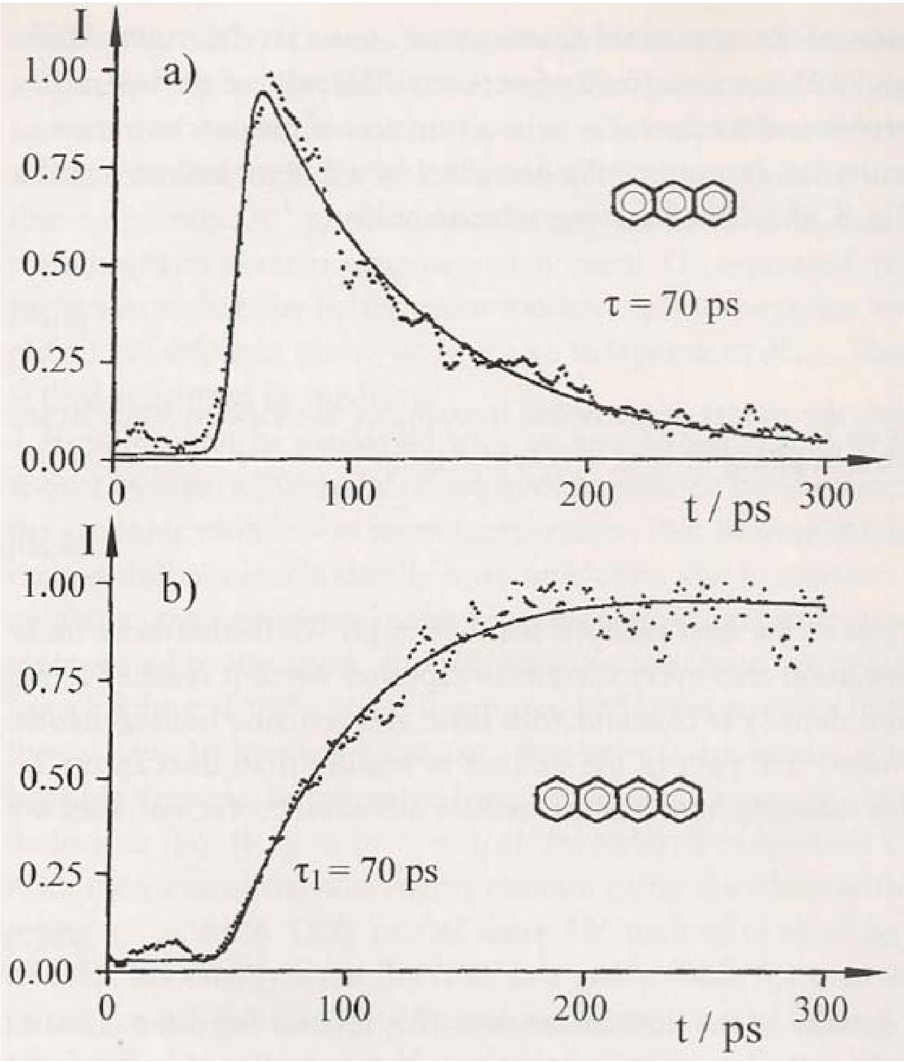
Exciton diffusion length



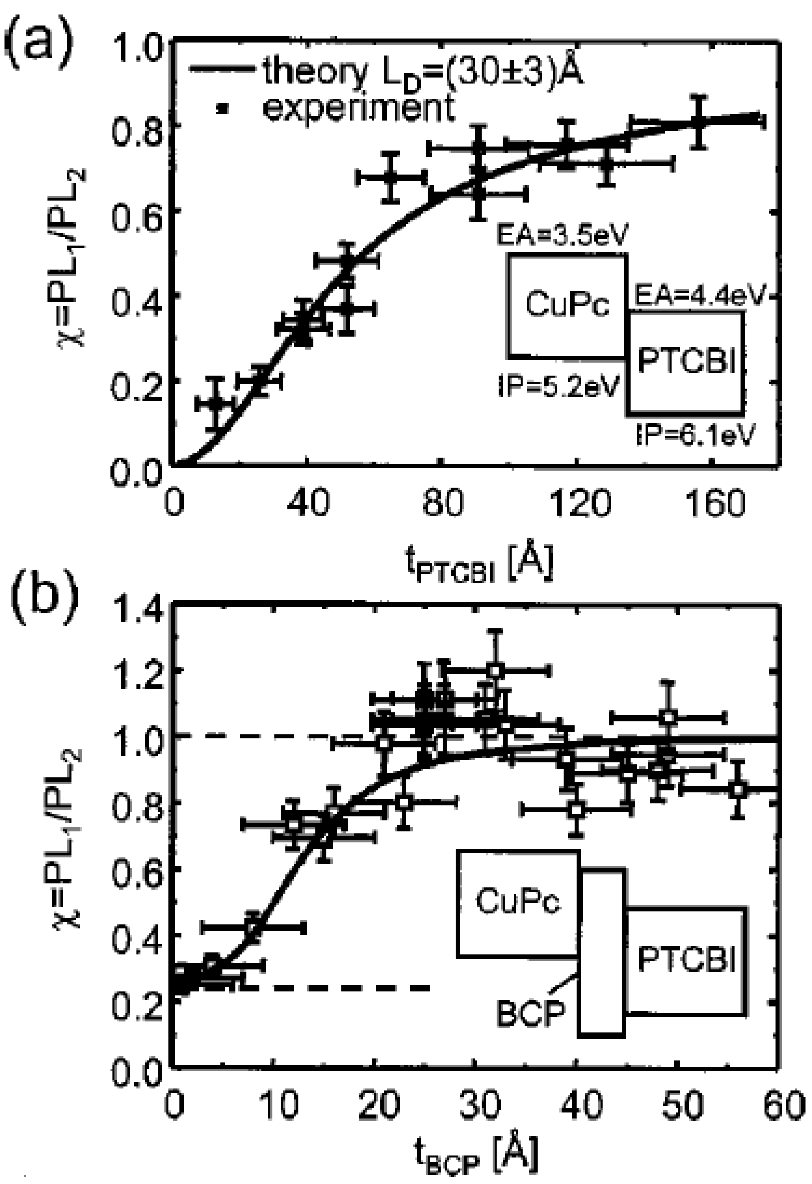




Sensitized fluorescence



Exciton diffusion lengths of organic semiconductor thin films



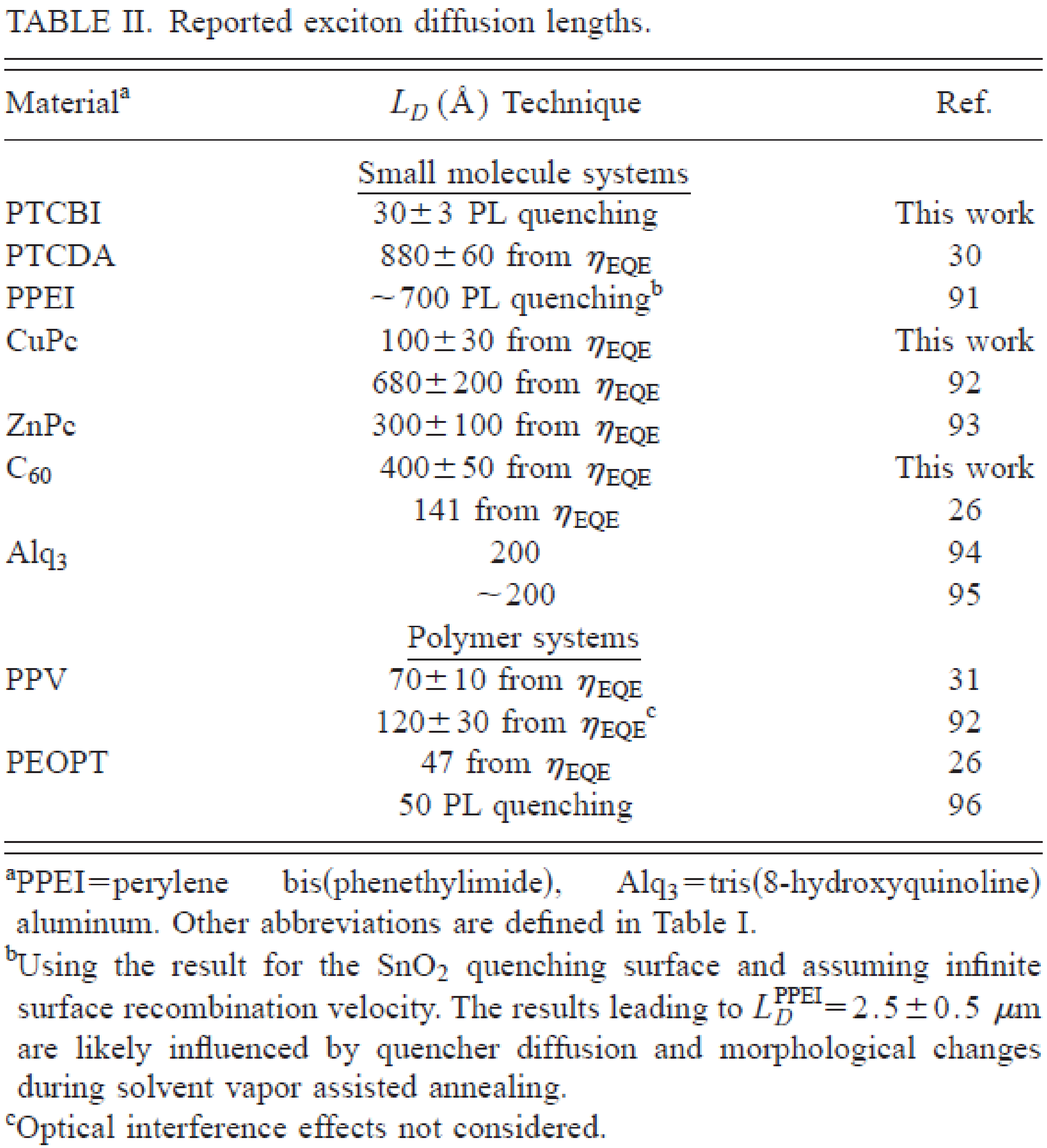


TABLE II. Reported exciton diffusion lengths.

Material[a]	L_D (Å)	Technique	Ref.
	Small molecule systems		
PTCBI	30±3	PL quenching	This work
PTCDA	880±60	from η_{EQE}	30
PPEI	~700	PL quenching[b]	91
CuPc	100±30	from η_{EQE}	This work
	680±200	from η_{EQE}	92
ZnPc	300±100	from η_{EQE}	93
C_{60}	400±50	from η_{EQE}	This work
	141	from η_{EQE}	26
Alq_3	200		94
	~200		95
	Polymer systems		
PPV	70±10	from η_{EQE}	31
	120±30	from η_{EQE}[c]	92
PEOPT	47	from η_{EQE}	26
	50	PL quenching	96

[a] PPEI=perylene bis(phenethylimide), Alq_3=tris(8-hydroxyquinoline) aluminum. Other abbreviations are defined in Table I.

[b] Using the result for the SnO_2 quenching surface and assuming infinite surface recombination velocity. The results leading to $L_D^{PPEI}=2.5\pm0.5$ μm are likely influenced by quencher diffusion and morphological changes during solvent vapor assisted annealing.

[c] Optical interference effects not considered.

Peter Peumans, Aharon Yakimov, and Stephen R. Forrest, J. Appl. Phys. **93**, 3693 (2003)

Exciton diffusion lengths of organic semiconductor thin films

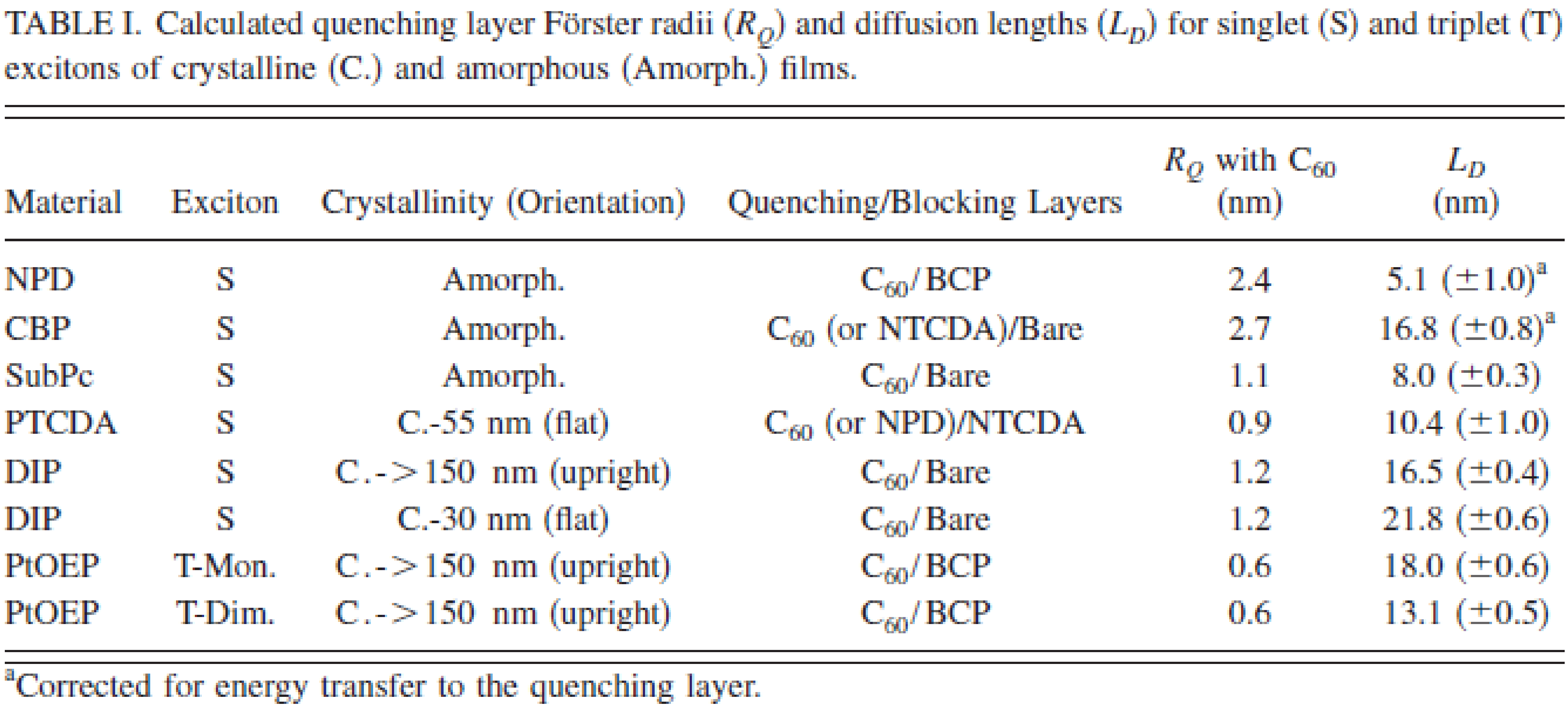


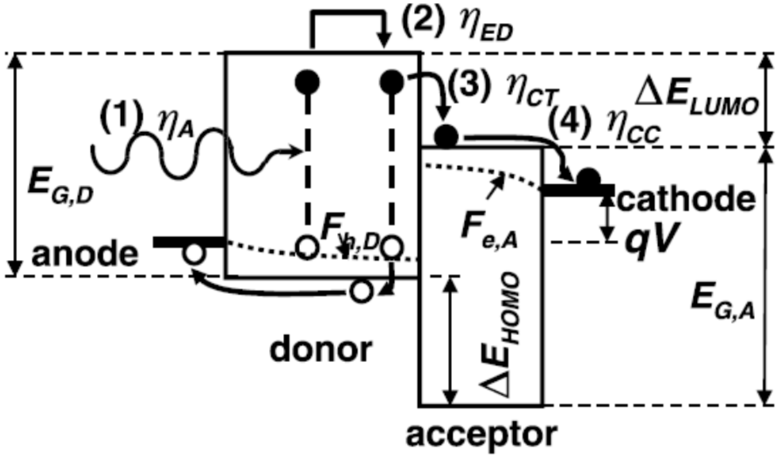
TABLE I. Calculated quenching layer Förster radii (R_Q) and diffusion lengths (L_D) for singlet (S) and triplet (T) excitons of crystalline (C.) and amorphous (Amorph.) films.

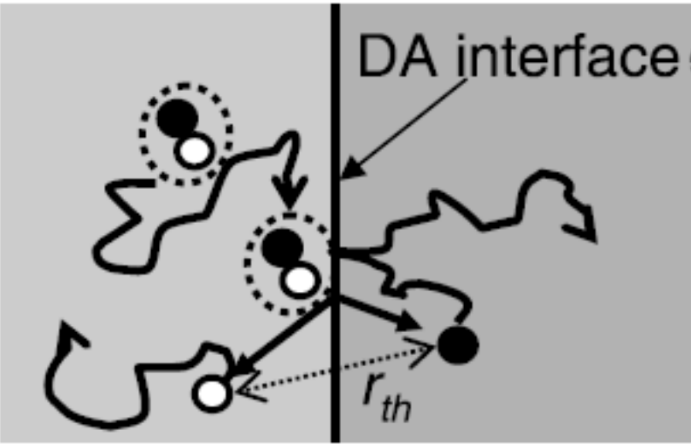
Material	Exciton	Crystallinity (Orientation)	Quenching/Blocking Layers	R_Q with C_{60} (nm)	L_D (nm)
NPD	S	Amorph.	C_{60}/ BCP	2.4	5.1 (±1.0)[a]
CBP	S	Amorph.	C_{60} (or NTCDA)/Bare	2.7	16.8 (±0.8)[a]
SubPc	S	Amorph.	C_{60}/ Bare	1.1	8.0 (±0.3)
PTCDA	S	C.-55 nm (flat)	C_{60} (or NPD)/NTCDA	0.9	10.4 (±1.0)
DIP	S	C.->150 nm (upright)	C_{60}/ Bare	1.2	16.5 (±0.4)
DIP	S	C.-30 nm (flat)	C_{60}/ Bare	1.2	21.8 (±0.6)
PtOEP	T-Mon.	C.->150 nm (upright)	C_{60}/ BCP	0.6	18.0 (±0.6)
PtOEP	T-Dim.	C.->150 nm (upright)	C_{60}/ BCP	0.6	13.1 (±0.5)

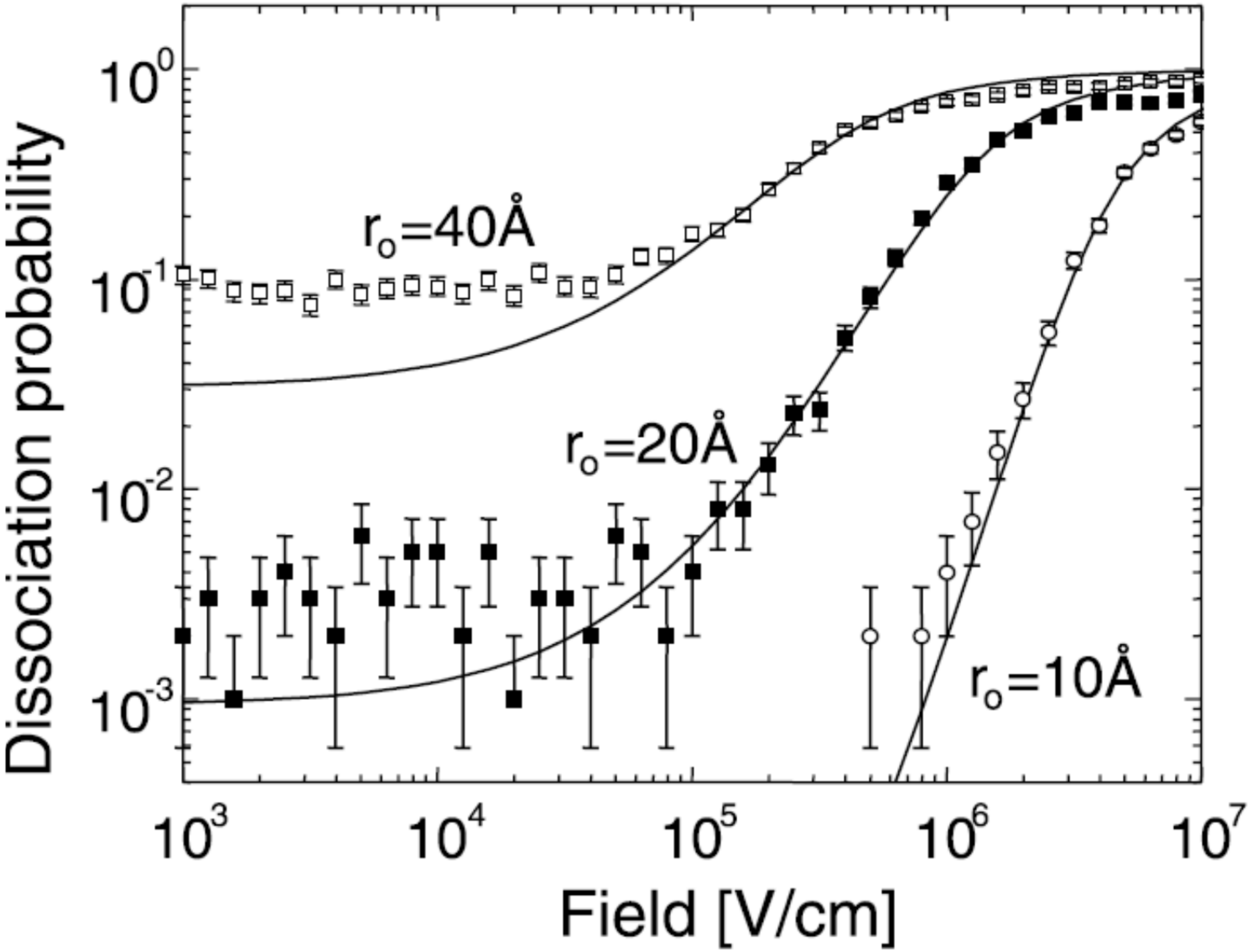
[a] Corrected for energy transfer to the quenching layer.

Richard R. Lunt, Noel C. Giebink, Anna A. Belak, Jay B. Benziger, and Stephen R. Forrest, J. Appl. Phys. **105**, 053711 (2009)

Probability of exciton dissociation at D/A heterojunction







P. Peumans and S. R. Forrest, Chem. Phys. Lett., 398, 27 (2004).

Delayed fluorescence by triplet excitons

Annihilation of two triplet excitons

$$\begin{aligned} T_1 + T_1 \quad &\rightarrow \quad S_0 + T_n \quad \rightarrow \quad T_1 \quad \text{triplet quenching} \\ &\rightarrow \quad S_0 + S_n \quad \rightarrow \quad S_1 \quad \text{delayed fluorescence} \end{aligned}$$

Strong excitation	Weak excitation
$I_P \propto \sqrt{\alpha I_E}$	$I_P \propto \alpha I_E$
$I_{DF} \propto \alpha I_E$	$I_{DF} \propto (\alpha I_E)^2$

Intensity of the delayed fluorescence: $I_{DF} = k_r [S_1] = \Phi_F \frac{1}{2} f \gamma_{tot} [T_1]^2$

where kr is the rate constant for the radiative decay of the singlet states, $[S_1]$ is the density of the S_1 states, F_F is the quantum efficiency of the fluorescence, f is the fraction of the triplet-triplet annihilations that leads to a singlet exciton, γ_{tot} is the total bimolecular annihilation (fusion) rate constant, and the factor of 1/2 occurs since the disappearance of the two triplets results in only one singlet.

M. Colle, C. Garditz, M. Braun, J. Appl. Phys. Lett. 96, 6133 (2004)

Delayed fluorescence by triplet excitons

The time evolution of the concentration of the triplet state $[T_1]$ after the excitation light was turned off (t=0) is given by

$$\frac{d[T_1]}{dt} = -k_T[T_1] - \gamma_{tot}[T_1]^2$$

At very high triplet concentrations,

$$\frac{d[T_1]}{dt} \approx -\gamma_{tot}[T_1]^2 \quad \Rightarrow \quad [T_1]^{-1} \approx \gamma_{tot} t. \quad \therefore\ I_{DF}(t) \propto [T_1]^2 \propto \frac{1}{t^2}.$$

After some time or by using a less-intense excitation light, the second term can be neglected due to the small triplet concentration ($k_T[T_1]>>g_{tot}[T_1]^2$). The decay time of the DF intensity is half of the correlated triplet lifetime tT.

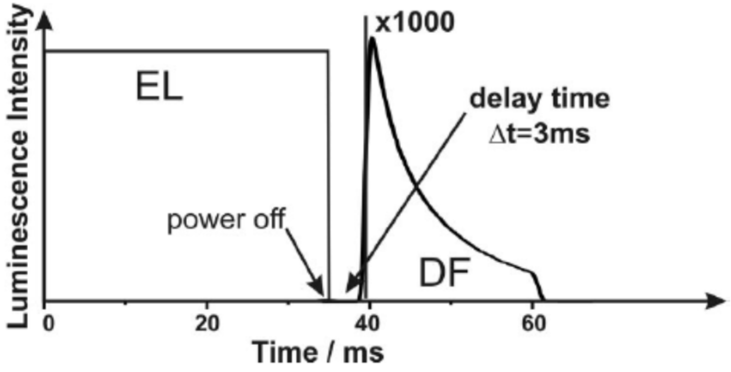
$$\frac{d[T_1]}{dt} \approx -k_T[T_1] \quad \Rightarrow \quad [T_1] \approx e^{-k_T t} = e^{-\frac{t}{\tau_T}}$$

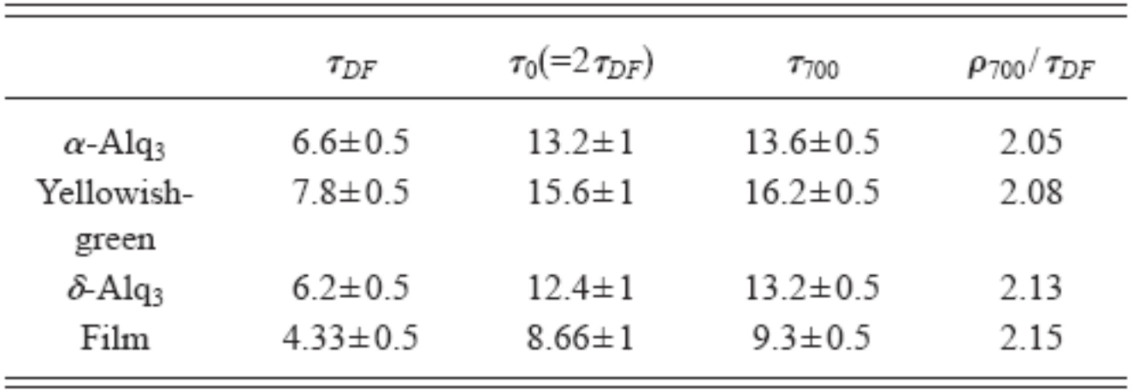
$$\therefore\ I_{DF}(t) \propto [T_1]^2 \propto e^{-\frac{2t}{\tau_T}} = e^{-\frac{t}{\tau_{DF}}}.$$

$$\boxed{\tau_{DF} = \frac{\tau_T}{2}}$$

M. Colle, C. Garditz, M. Braun, J. Appl. Phys. Lett. 96, 6133 (2004)

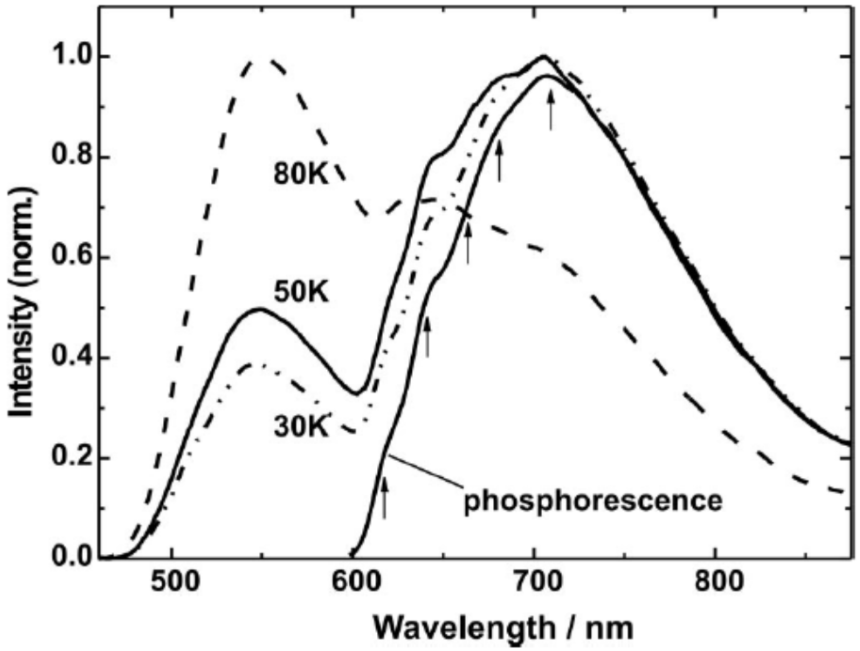
Delayed Fluorescence in Alq3



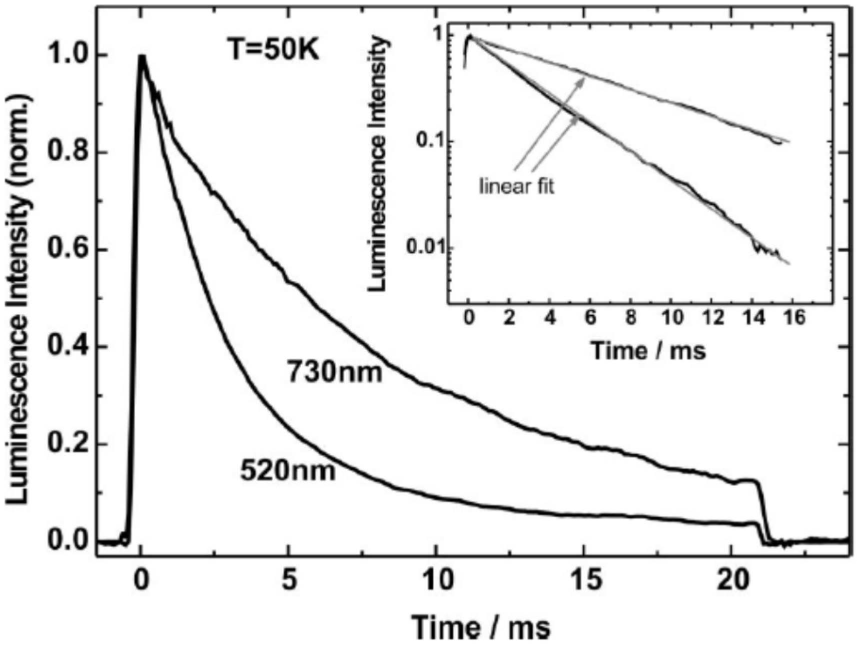


	τ_{DF}	$\tau_0(=2\tau_{DF})$	τ_{700}	ρ_{700}/τ_{DF}
α-Alq$_3$	6.6±0.5	13.2±1	13.6±0.5	2.05
Yellowish-green	7.8±0.5	15.6±1	16.2±0.5	2.08
δ-Alq$_3$	6.2±0.5	12.4±1	13.2±0.5	2.13
Film	4.33±0.5	8.66±1	9.3±0.5	2.15

M. Colle, C. Garditz, M. Braun, J. Appl. Phys. Lett. 96, 6133 (2004)



Delayed EL spectra of Alq3 taken after the end of the voltage pulse (D*t*=3 ms) at 30, 50, and 80 K.



Transient intensity of the delayed luminescence detected at 520 and 730 nm, measured at a temperature of 50 K.

M. Colle and C. Garditz, Appl. Phys. Lett. 84, 3160 (2004)

Singlet-triplet and singlet-singlet annihilation

Singlet-triplet annihilation $S_1 + T_1 \xrightarrow{\gamma_{ST}} T_n + S_0$

$$\rightarrow T_1 + heat$$

Singlet-singlet annihilation $S_1 + S_1 \xrightarrow{\gamma_{SS}} S_n^* + S_0$

$$\rightarrow S_1 + S_0$$

$$\rightarrow e^- + h^+$$

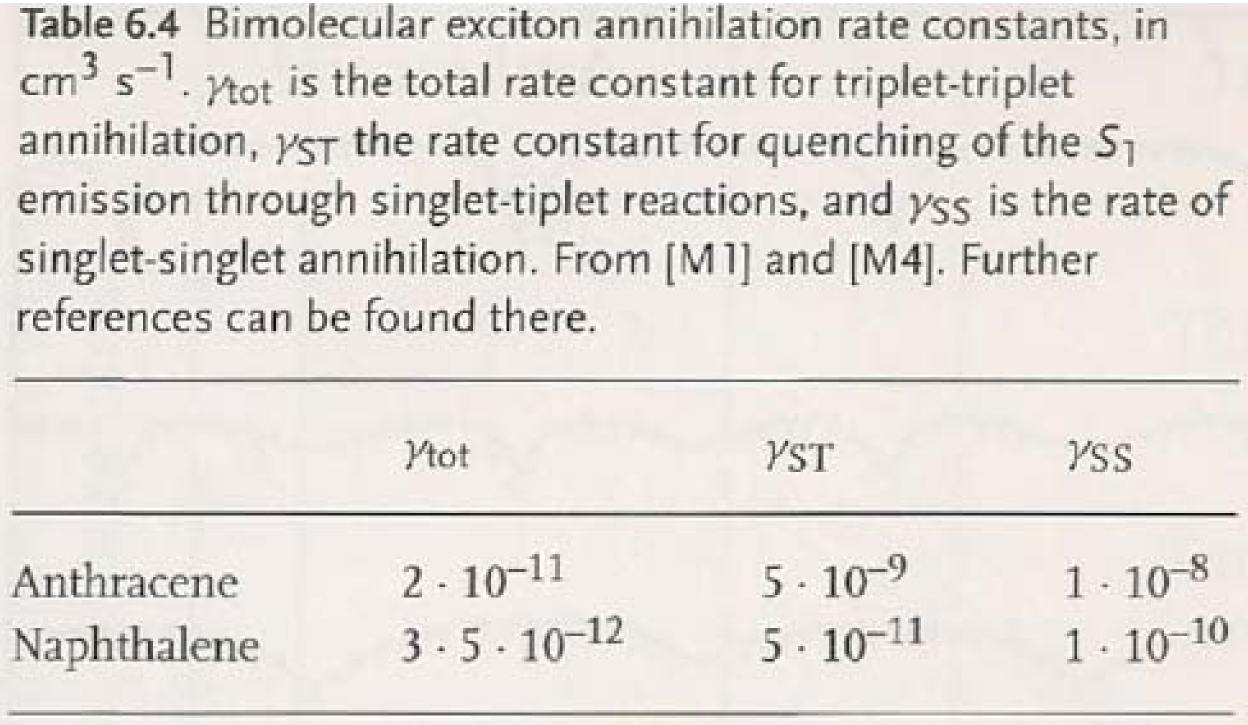


Table 6.4 Bimolecular exciton annihilation rate constants, in cm^3 s^{-1}. γ_{tot} is the total rate constant for triplet-triplet annihilation, γ_{ST} the rate constant for quenching of the S_1 emission through singlet-tiplet reactions, and γ_{SS} is the rate of singlet-singlet annihilation. From [M1] and [M4]. Further references can be found there.

	γ_{tot}	γ_{ST}	γ_{SS}
Anthracene	$2 \cdot 10^{-11}$	$5 \cdot 10^{-9}$	$1 \cdot 10^{-8}$
Naphthalene	$3 \cdot 5 \cdot 10^{-12}$	$5 \cdot 10^{-11}$	$1 \cdot 10^{-10}$

Triplet – Triplet (T – T) Annihilation

$$T_1 + T_1 \xrightarrow{k_T} T_1 + S_0$$

Rate equation for the triplet-triplet annihilation $\dfrac{dn_T}{dt} = -\dfrac{n_T}{\tau} - k_T n_T{}^2 + \dfrac{J}{qd}$

1) transient $t > 0, J(t) = 0$

trial solution $n_T(t) = \dfrac{1}{Ae^{\frac{t}{\tau}} + B}$ $\qquad \dfrac{-\dfrac{A}{\tau}e^{\frac{t}{\tau}}}{(Ae^{\frac{t}{\tau}} + B)^2} = -\dfrac{\dfrac{1}{\tau}}{(Ae^{\frac{t}{\tau}} + B)} - \dfrac{k_T}{(Ae^{\frac{t}{\tau}} + B)^2}$

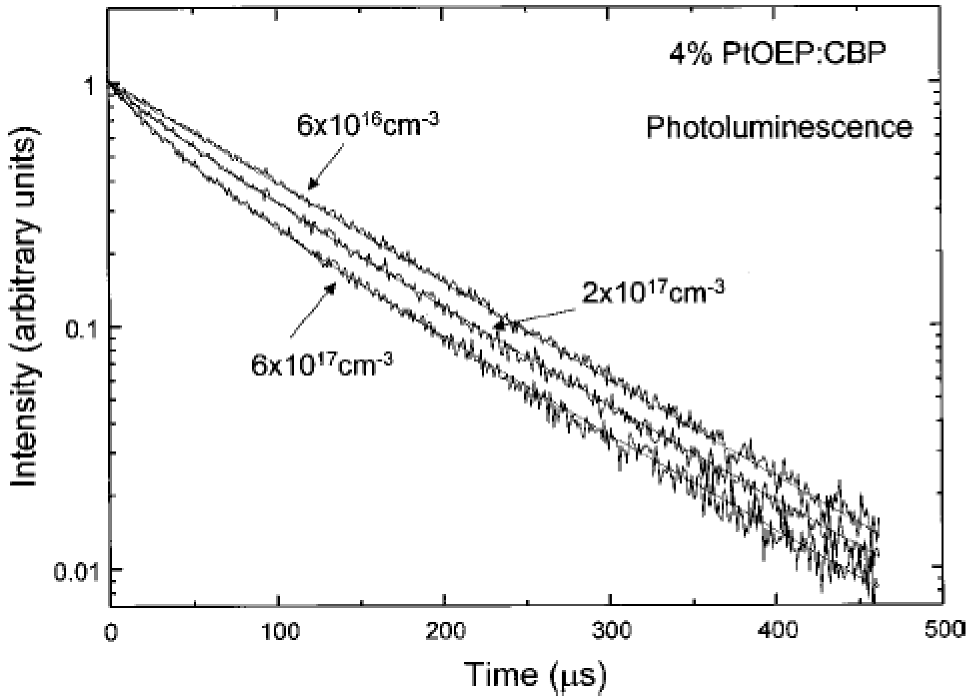
$$-\frac{A}{\tau}e^{\frac{t}{\tau}} = -\frac{1}{\tau}(Ae^{\frac{t}{\tau}} + B) - k_T \qquad \therefore B = -k_T\tau$$

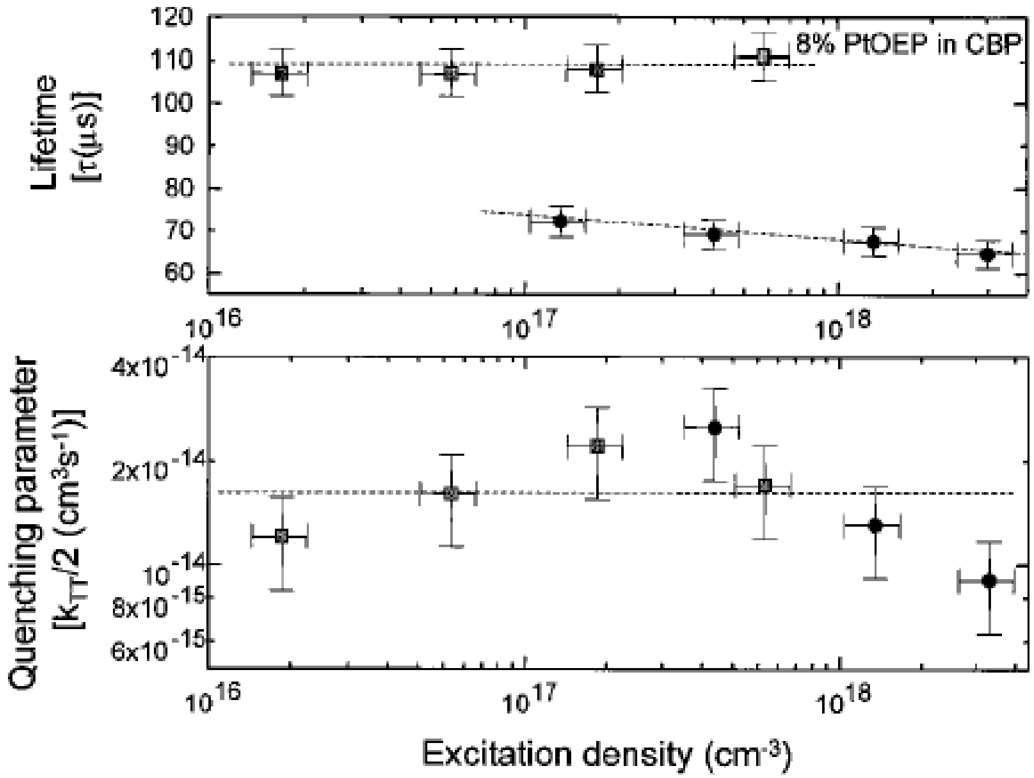
$$t = 0 \;\; ; \;\; n_T(0) = \frac{1}{A+B} \qquad \therefore A = \frac{1}{n_T(0)} - B = \frac{1}{n_T(0)} + k_T\tau$$

$$\boxed{\therefore \quad n_T(t) = \frac{n_T(0)}{[1 + k_T\tau n_T(0)]e^{\frac{t}{\tau}} - k_T\tau n_T(0)}}$$

T – T Annihilation: Transient Solution

Light emission intensity $L(t) = \frac{n_T(t)}{\tau} = \frac{L(0)}{(1+K\tau)e^{\frac{t}{\tau}} - K\tau}$ $\quad (let \;\; k_T n_T(0) = K)$





M. A. Baldo, C. Adachi, and S. R. Forrest, Phys. Rev. B **62**,10967 (2000)

T – T Annihilation: Steady-state solution

$$\frac{dn_T}{dt} = 0 \qquad k_T n_T^{\,2} + \frac{n_T}{\tau} - \frac{J}{gd} = 0$$

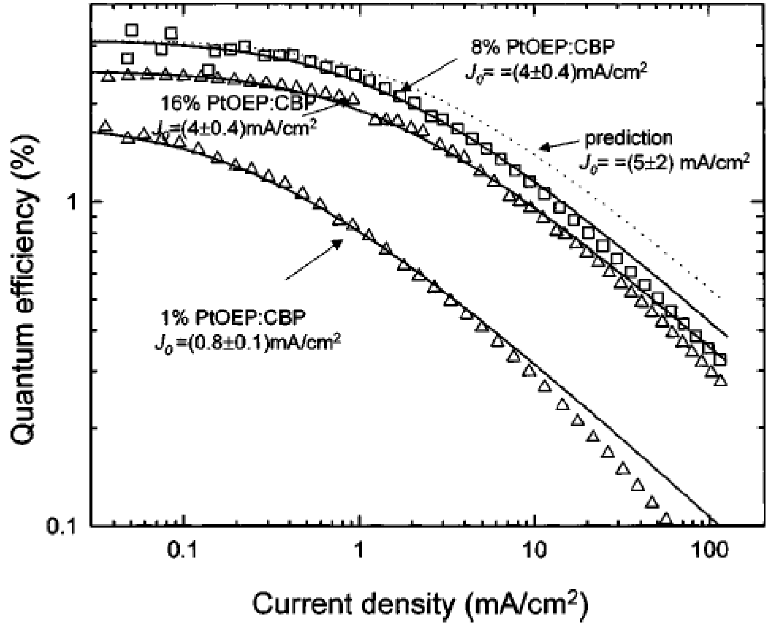
$$n_T = \frac{-\frac{1}{\tau} + \sqrt{(\frac{1}{\tau})^2 + \frac{4Jk_T}{qd}}}{2k_T} = \frac{1}{2k_T\tau}\left[-1+\sqrt{1+\frac{4Jk_T\tau^2}{qd}}\right] = \frac{1}{2k_T\tau}\left[-1+\sqrt{1+\frac{8J}{J_T}}\right] \qquad (\because \frac{k_T\tau^2}{2qd} = J_T^{\,-1})$$

Light emission intensity $L = \frac{n_T}{\tau}$ QE : $\eta = \frac{L}{J} = \frac{n_T}{J\tau}$

η_0 : $k_T = 0$ (without T-T annihilation) $\frac{n_T}{\tau} = \frac{J}{gd}$

$$\therefore \eta_0 = \frac{L}{J} = \frac{\frac{n_T}{\tau}}{J} = \frac{1}{qd}$$

$$\frac{\eta}{\eta_0} = \frac{qd}{2k_T\tau^2 J}\left[-1+\sqrt{1+\frac{8J}{J_T}}\right] = \frac{J_T}{4J}\left[-1+\sqrt{1+\frac{8J}{J_T}}\right]$$

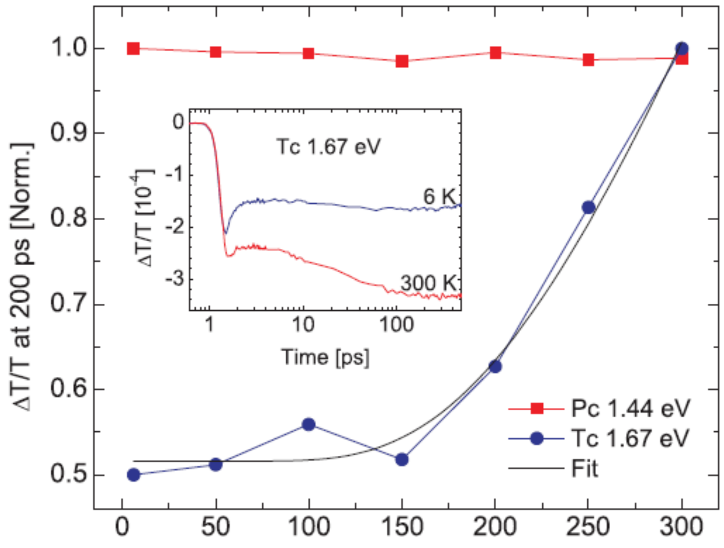


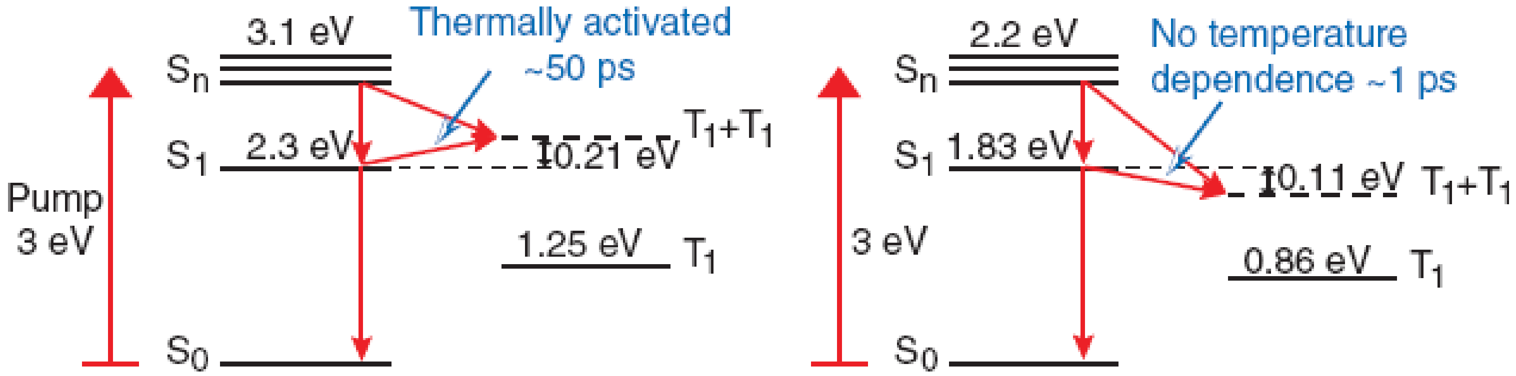
M. A. Baldo, C. Adachi, and S. R. Forrest, Phys. Rev. B **62**,10967 (200

Exciton fission

$$S_1 \rightarrow T_1 + T_1$$

$$S_1 + \Delta E \rightarrow T_1 + T_1$$





In the polyacene series of organic crystals, the energy level of the lowest triplet exciton $E(T_1)$ decreases faster than the lowest singlet-exciton energy $E(S_1)$ with increasing molecular size. The energy difference $E(S_1) - 2\,E(T_1)$ is -1.3 eV in naphthalene (Nph), -0.55 eV in anthracene (Ac), -0.21 eV in Tc, and 0.11 eV in Pc [C. Jundt et al., Chem. Phys. Lett. 241, 84 (1995).]. In Pc, the excitonic fission process from the lowest singlet exciton to a pair of the lowest triplet excitons $S \rightarrow 2T_1$ is energetically allowed, while in Tc this same process is only possible by thermal activation. This process is strongly suppressed in Nph and Ac.

V. K. Thorsmølle, R. D. Averitt, J. Demsar, D. L. Smith, S. Tretiak, R. L. Martin, X. Chi, B. K. Crone, A. P. Ramirez, and A. J. Taylor, Phys. Rev. Lett. **102**, 017401 (2009)