Lecture 6:
Optical properties of organic semiconductors

Ref.
- M. Pope and C. E. Swenberg. Electronic Processes in Organic Crystals and Polymers, 2nd Ed. (Oxford, NY, 1999)

2009. 3. 26 & 31

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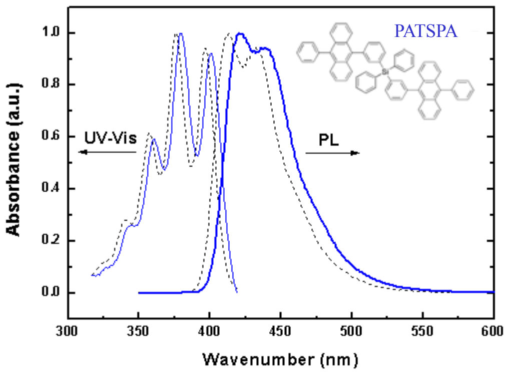
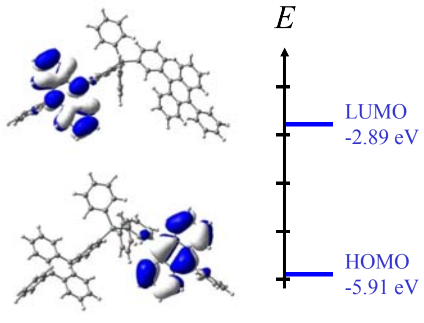
Absorption and PL of PATSPA

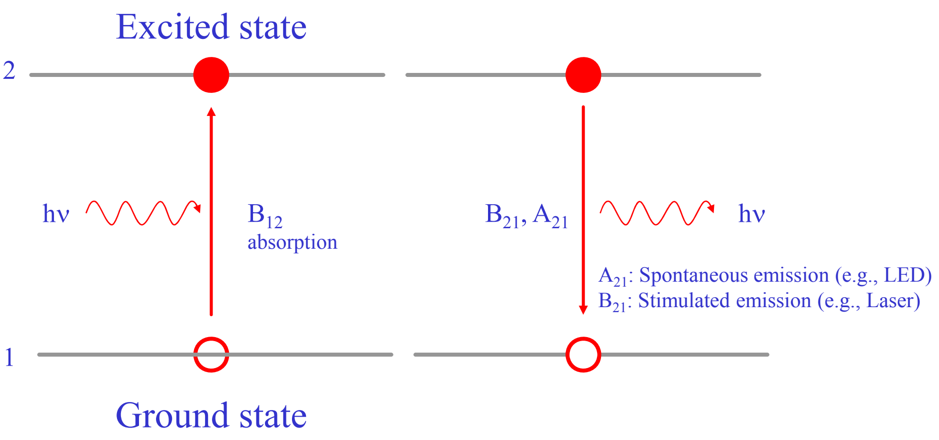




Bis[3-(10-phenylanthracen-9-yl)phenyl]diphenylsilane
PATSPA

Y.-Y. Lyu, J. H. Kwak, O. H. Kwon, S.-H. Lee, D. Y. Kim, C. H. Lee, and K. H. Char, Adv. Mater. **20** (2008).

Absorption and Emission of Light



Excited state

2

hν

B_{12}
absorption

B_{21}, A_{21}

hν

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

1

Ground state

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 $\boxed{\Delta l = \pm 1,\ \Delta \mathrm{S} = 0}$
- 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 $\boxed{\mathrm{H}_{\mathrm{SO}} = \frac{Ze^2}{2m^2c^2}\frac{1}{r^3}\vec{\mathrm{L}}\cdot\vec{\mathrm{S}} \propto \mathrm{Z}^4}$

(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

Consider a molecule with two energy levels 1 and 2.

The rate of transition B$_{12}$ induced by light of frequency ν

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

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

Transition rate for 1 → 2 (absorption): B$_{12}$ I(ν) N$_1$

Transition rate for 2 → 1 (emission): [B$_{21}$ I(ν) + 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.

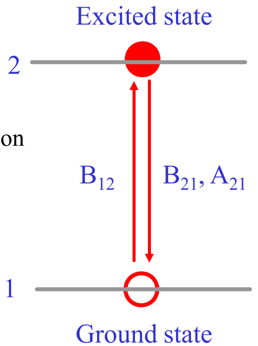
$$\frac{N_1}{N_2} = \frac{B_{21} I(\nu) + A_{21}}{B_{12} I(\nu)} = 1 + \frac{A_{21}}{B_{12} I(\nu)} \qquad (1)$$

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:

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

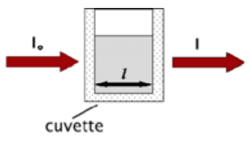
The stronger the absorption, the shorter the radiative lifetime. And the radiative lifetime decreases with increasing frequency (or decreasing wavelength).

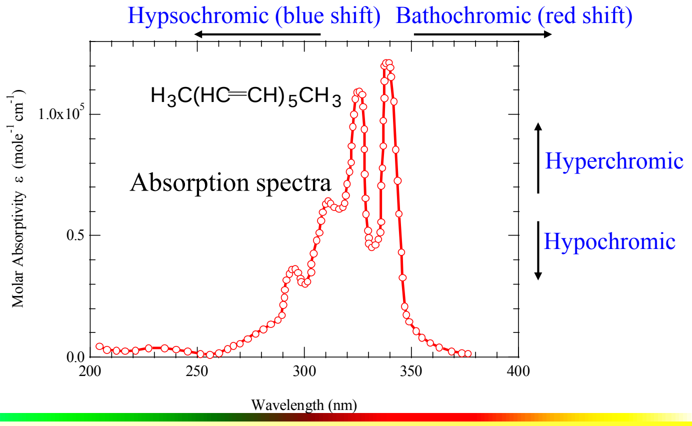
Absorption of Light

The Beer-Lambert Law: $\boxed{Absorbance \;\; = \log(\frac{I_o}{I}) = \varepsilon c l}$

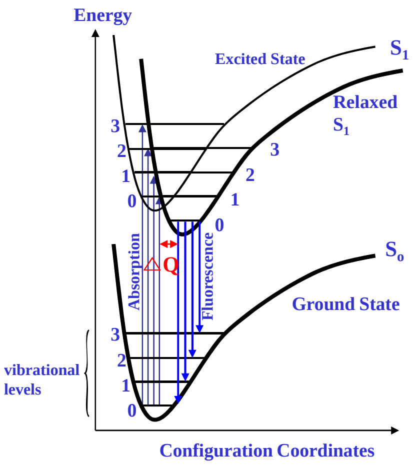
I_o and I are the intensities entering and leaving the sample, respectively. ε = the molar extinction coefficient or molar absorptivity, c = sample concentration in moles/liter, l = length of light path through the sample in cm.

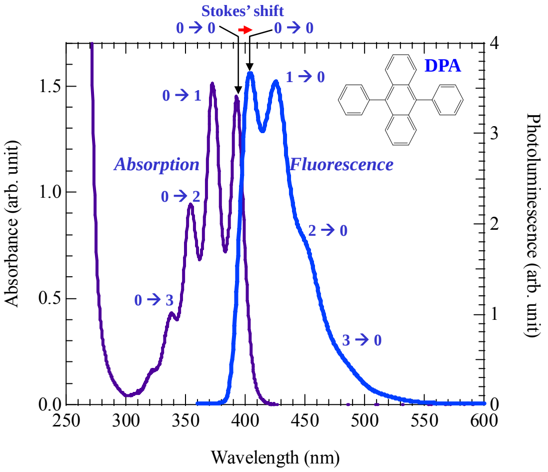
Molar Absorptivity, $\varepsilon = A / c\, l$, where A= absorbance (Optical Density)





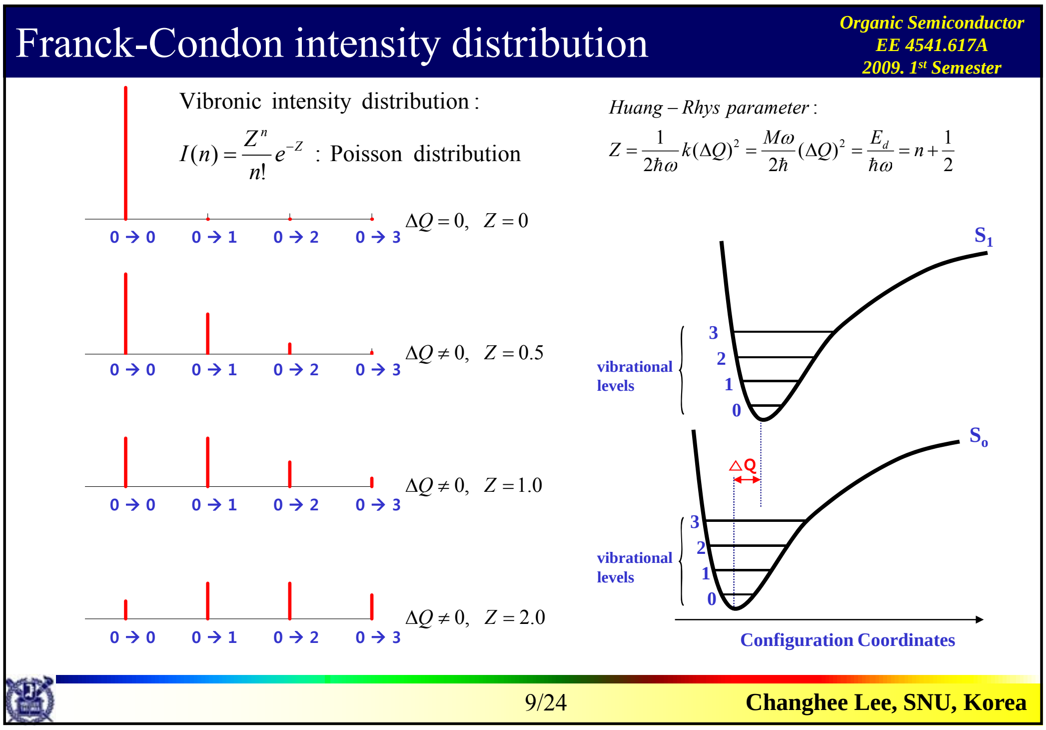
Absorption and PL of DPA





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

9,10-Diphenylanthracene dissolved in cyclohexane.



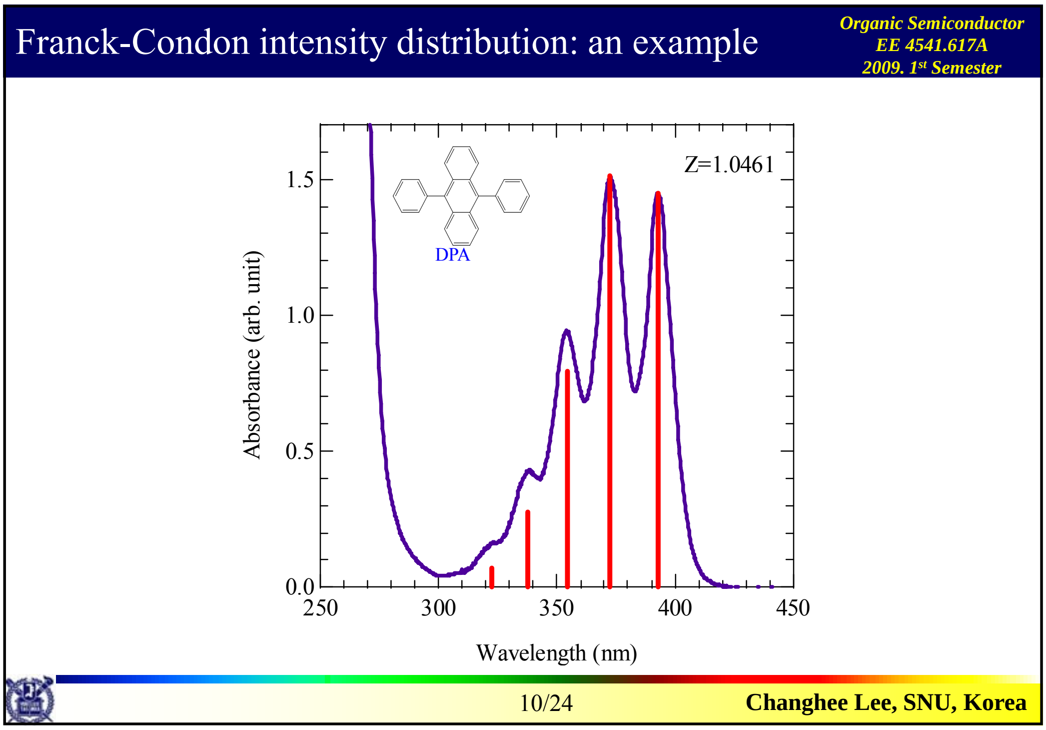
Franck-Condon intensity distribution

Vibronic intensity distribution:

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

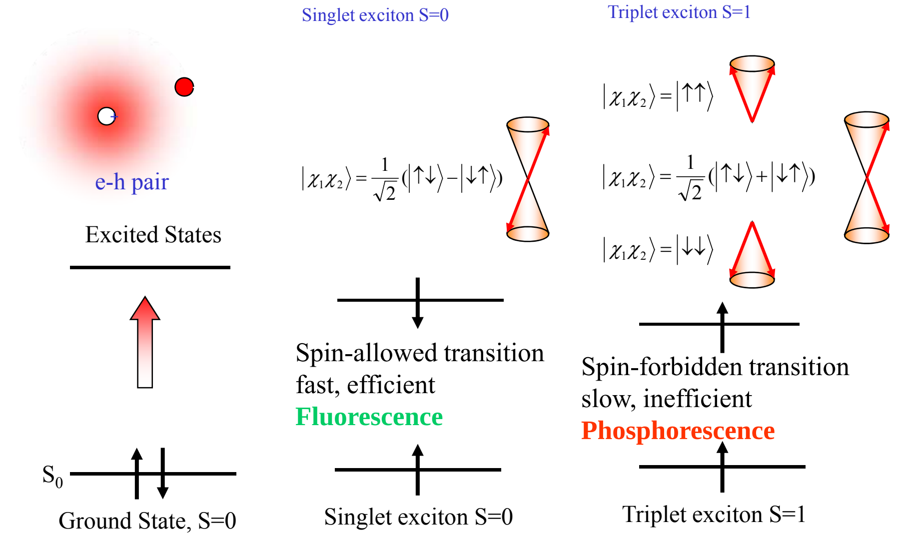
Huang – Rhys parameter:

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



Franck-Condon intensity distribution: an example

Singlet & Triplet Excitons



Singlet exciton S=0

Triplet exciton S=1

e-h pair

Excited States

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

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

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

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

Spin-allowed transition
fast, efficient
Fluorescence

Spin-forbidden transition
slow, inefficient
Phosphorescence

S_0

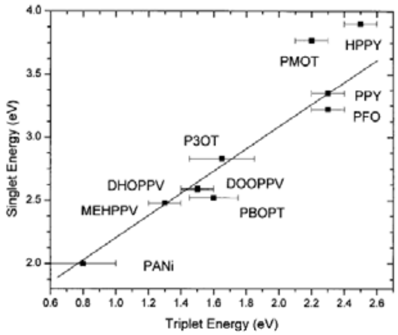
Ground State, S=0

Singlet exciton S=0

Triplet exciton S=1

Energy difference between Singlet-Triplet exciton energy

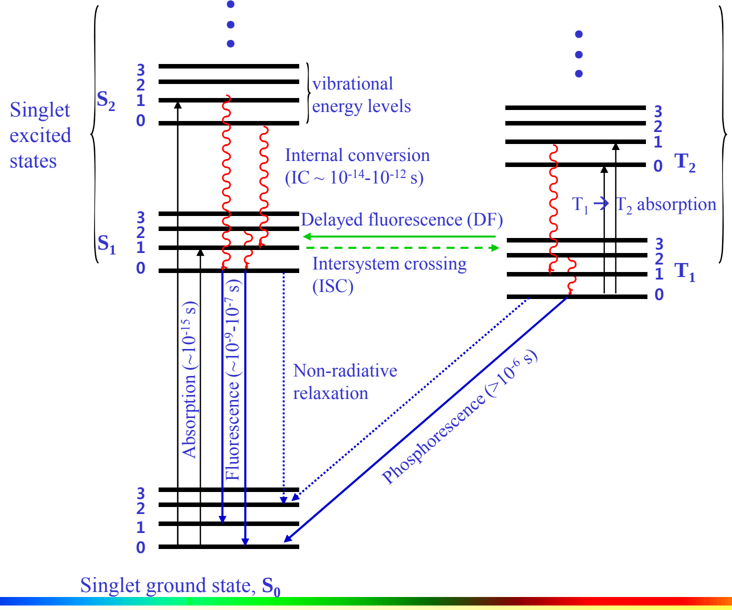
- Triplet state is at lower energy than the singlet state:
- Electrons in singlet state have the antisymmetric spins, thus can have the same position in space, resulting in a large electron-electron repulsion energy.
- Electrons in triplet state have the symmetric spins, thus cannot have the same position in space, reducing the electron-electron repulsion energy.
- The S - T splitting is inversely proportional to orbital size, because the electrons will on average be further apart
- The S - T splitting is proportional to orbital overlap, thus electrons promoted from substituent atomic orbitals to conjugated π-orbitals will have a small splitting.



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

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

Jablonski Energy Diagram



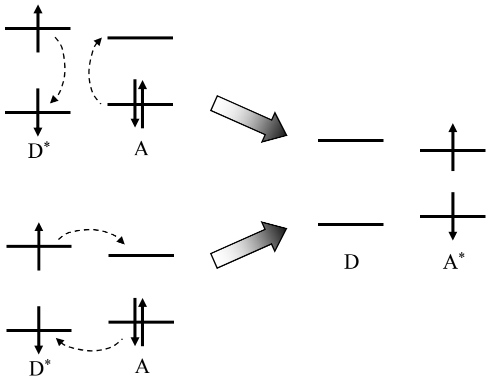
Energy Transfer Processes

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

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

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

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



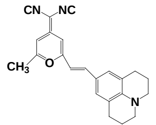
$$\text{Overlap integral}: J = \int \frac{\varepsilon_A(\tilde{\nu})\cdot F_D(\tilde{\nu})}{\tilde{\nu}^4} d\tilde{\nu}$$

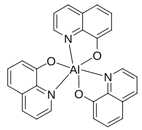
The Förster eq. is often written in the following form:

$$W_{DA} = k_r^D \left(\frac{R_0}{R}\right)^6 \qquad R_0^6 = 8.8\cdot10^{17}\cdot\frac{\kappa^2}{n^4}\cdot\int\frac{\varepsilon_A(\tilde{\nu})\cdot F_D(\tilde{\nu})}{\tilde{\nu}^4} d\tilde{\nu}$$

For photosynthetic systems R is typically 1 nm, R_0 is typically 8 nm, $k_r^D \approx 5\cdot10^7 s^{-1} \rightarrow W_{DA} \approx 10^{13} s^{-1}$

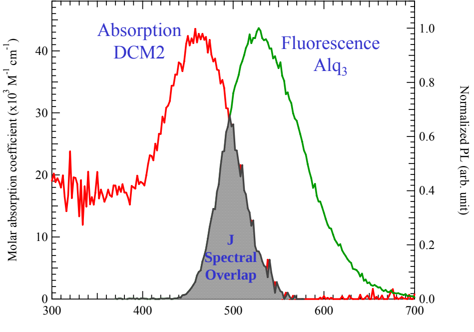
Calculation of Forster exciton energy transfer

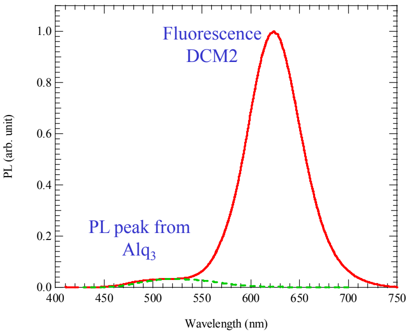




$$J = \frac{\int_0^\infty \lambda^4 F_d(\lambda)\varepsilon_a(\lambda)d\lambda}{\int_0^\infty F_d(\lambda)d\lambda}$$

$$R_0^6 = 8.79\times10^{-5}\left(\frac{\kappa^2 Q_d}{n^4}J\right)\mathring{A}^6;\quad R_o = 0.211\left(\frac{\kappa^2 Q_d}{n^4}J\right)^{1/6}\mathring{A}$$





Molar extinction coefficient of DCM: $\varepsilon_a(\lambda) \sim 4\times10^4\ M^{-1}\ cm^{-1}$ [J. Appl. Phys. 84 (8), 4096 (1998)]

Dipole orientation factor, $K^2=2/3$ for random orientation

Refractive index medium n=1.7

Fluorescent quantum efficiency of donor: QE~35% Alq3, [J. Appl. Phys. 84 (8), 4096 (1998)]

→ Forster radius R_0 =3.37 nm

Ref. "Topics in Fluorescence Spectroscopy, vol. 2, Principles, ed. By Joseph R. Lakowicz (Plenum, New York, 1991), pp.129-130.

Experimental results of Forster energy transfer in optically pumped organic semiconductor thin films

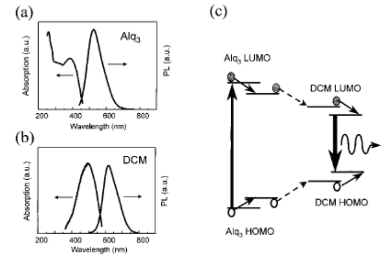


FIG. 2. (a),(b) Absorption and photoluminescence spectra of Alq_3 and DCM, respectively. (c) Energy level diagram of Alq_3:DCM illustrating the excitation of DCM molecules by means of nonradiative Förster energy transfer from Alq_3 (dashed arrows), and the Franck–Condon shift (solid arrows) in Alq_3 and DCM molecules.

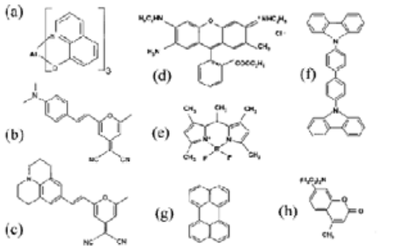


FIG. 1. Chemical structure formulas of (a) Alq_3, (b) DCM, (c) DCM2, (d) rhodamine 6G, (e) pyrromethane, (f) CBP, (g) perylene, (h) coumarin 47.

TABLE I. Characteristics of OSLs.

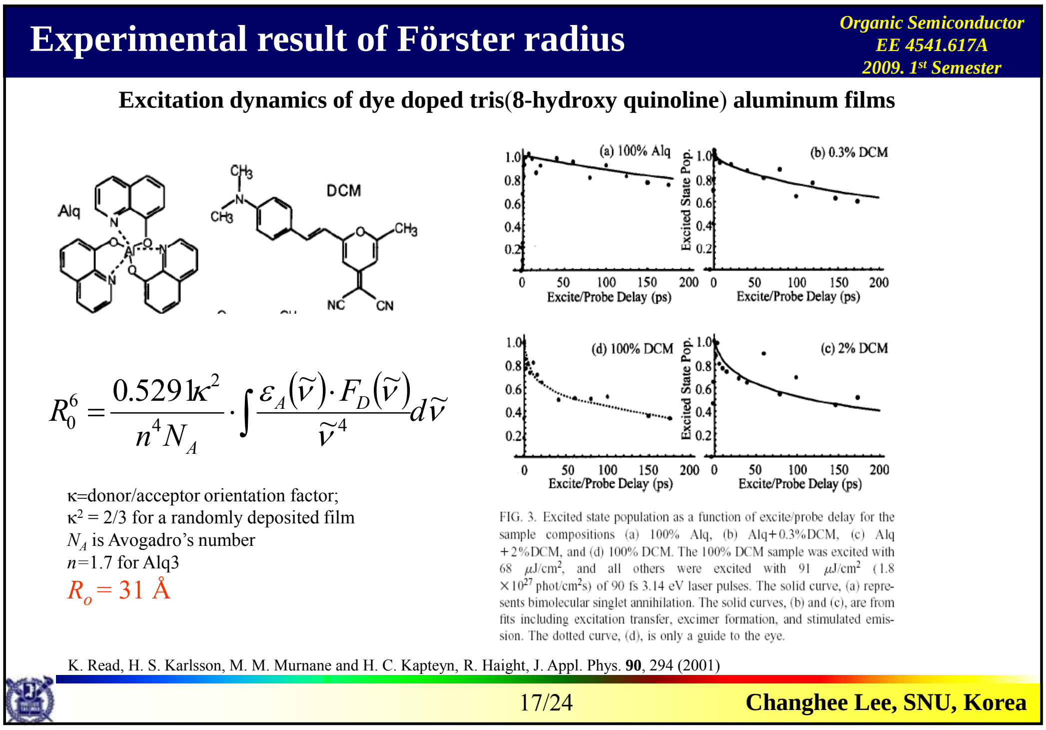
Laser material	Förster radius (Å)	Lasing wavelength (nm)	Lasing threshold[a] ($\mu J/cm^2$)	Operating lifetime at $P=500$ $\mu J/cm^2$ (No. of pump laser pulses)	Differential quantum efficiency[b] (%)
Alq_3:DCM	32	615–660	3	$>10^6$	30%
Alq_3:DCM2	39	655–700	2.5	$>10^5$	30%
Alq_3:rhodamine 6G	41	610–625	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.

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)



Experimental result of Förster radius

Organic Semiconductor
EE 4541.617A
2009. 1st Semester

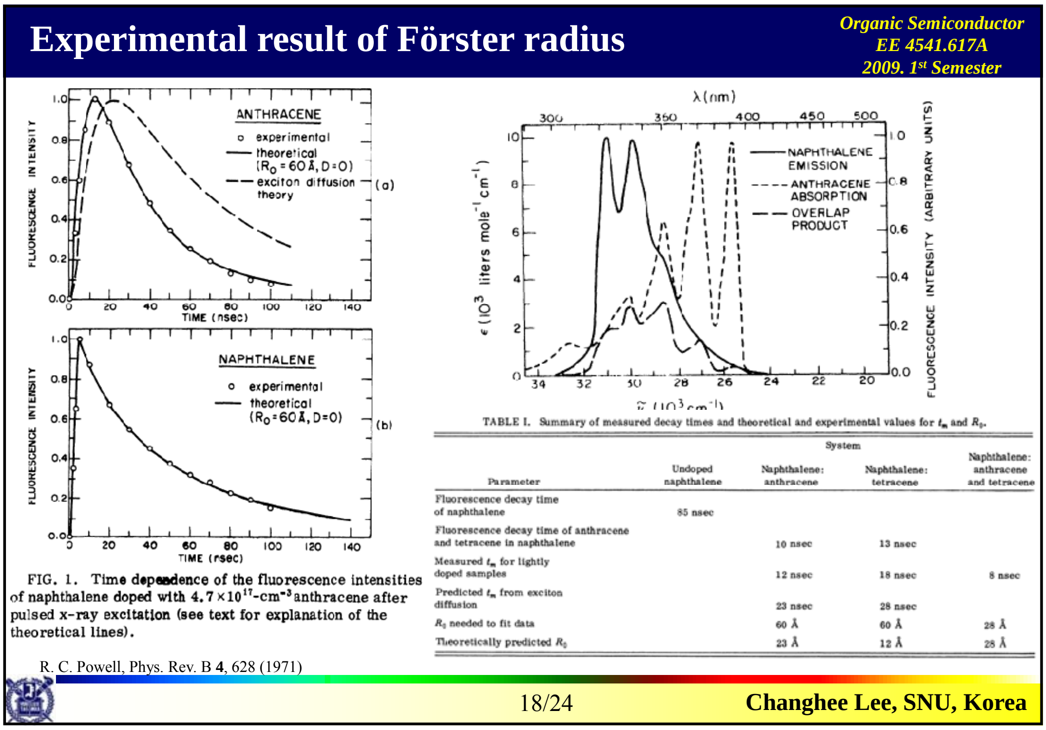
Excitation dynamics of dye doped tris(8-hydroxy quinoline) aluminum films

$$R_0^6 = \frac{0.5291\kappa^2}{n^4 N_A} \cdot \int \frac{\varepsilon_A(\tilde{\nu}) \cdot F_D(\tilde{\nu})}{\tilde{\nu}^4} d\tilde{\nu}$$

κ=donor/acceptor orientation factor;
$\kappa^2 = 2/3$ for a randomly deposited film
N_A is Avogadro's number
n=1.7 for Alq3
R_o = 31 Å

FIG. 3. Excited state population as a function of excite/probe delay for the sample compositions (a) 100% Alq, (b) Alq+0.3%DCM, (c) Alq +2%DCM, and (d) 100% DCM. The 100% DCM sample was excited with 68 μJ/cm², and all others were excited with 91 μJ/cm² (1.8×10^{27} phot/cm²s) of 90 fs 3.14 eV laser pulses. The solid curve, (a) represents bimolecular singlet annihilation. The solid curves, (b) and (c), are from fits including excitation transfer, excimer formation, and stimulated emission. The dotted curve, (d), is only a guide to the eye.

K. Read, H. S. Karlsson, M. M. Murnane and H. C. Kapteyn, R. Haight, J. Appl. Phys. **90**, 294 (2001)



Experimental result of Förster radius

Organic Semiconductor
EE 4541.617A
2009. 1st Semester

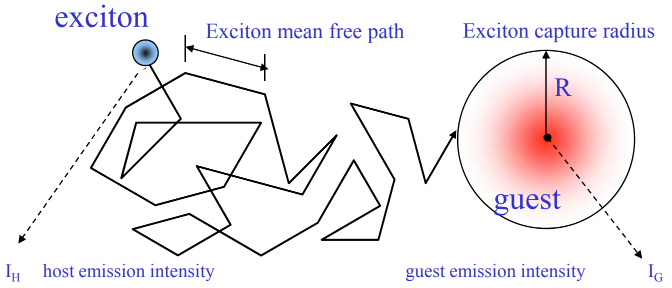
FIG. 1. Time dependence of the fluorescence intensities of naphthalene doped with 4.7×10^{17}-cm^{-3} anthracene after pulsed x-ray excitation (see text for explanation of the theoretical lines).

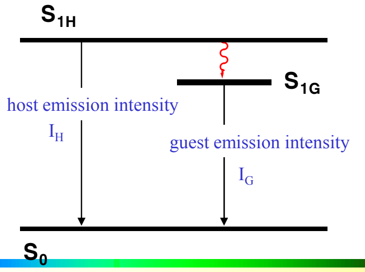
TABLE I. Summary of measured decay times and theoretical and experimental values for t_m and R_0.

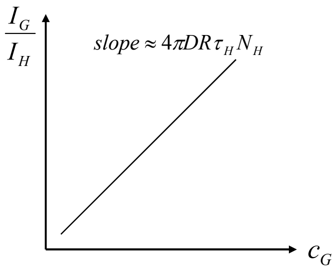
	System			
Parameter	Undoped naphthalene	Naphthalene: anthracene	Naphthalene: tetracene	Naphthalene: anthracene and tetracene
Fluorescence decay time of naphthalene	85 nsec			
Fluorescence decay time of anthracene and tetracene in naphthalene		10 nsec	13 nsec	
Measured t_m for lightly doped samples		12 nsec	18 nsec	8 nsec
Predicted t_m from exciton diffusion		23 nsec	28 nsec	
R_0 needed to fit data		60 Å	60 Å	28 Å
Theoretically predicted R_0		23 Å	12 Å	28 Å

R. C. Powell, Phys. Rev. B **4**, 628 (1971)

Exciton diffusion

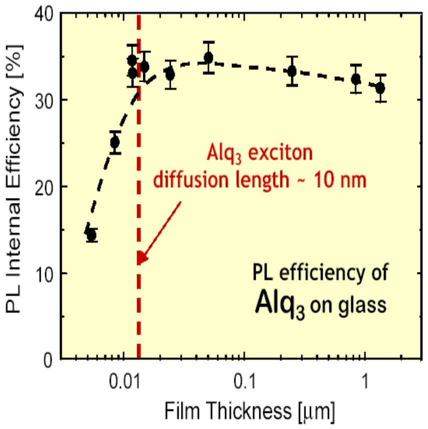




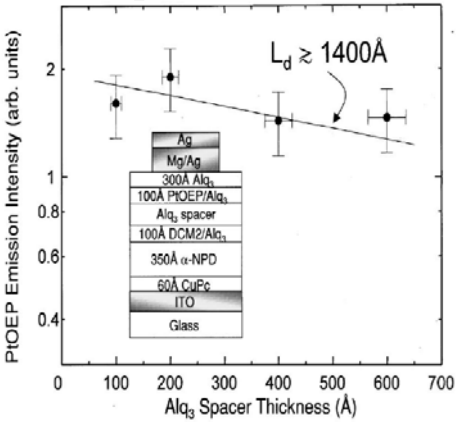


Diffusion Length of Excitons

Singlet Exciton



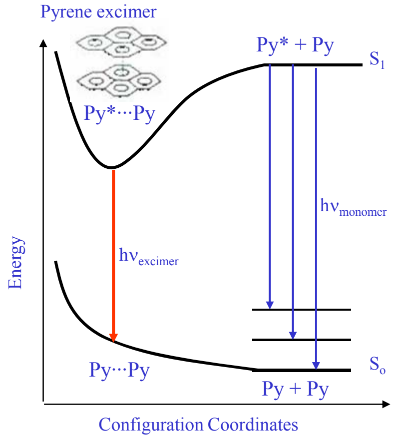
Triplet Exciton

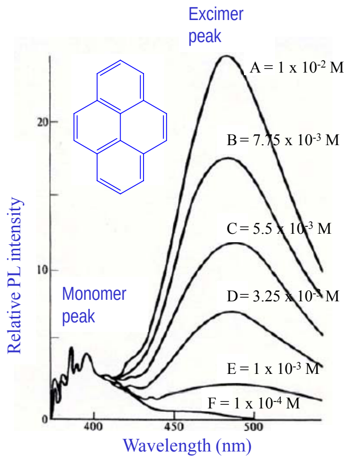


Long L_d for triplet exciton requires an exciton blocking layer

M.A. Baldo, D.F. OBrien, Y. You, A. Shoustikov, S. Sibley, M.E. Thompson, S.R. Forrest, Nature 395 (1998) 151.
D.F. OBrien, M.A. Baldo, M.E. Thompson, S.R. Forrest, Appl. Phys. Lett. 74 (1999) 442.

Excimer or Exciplex



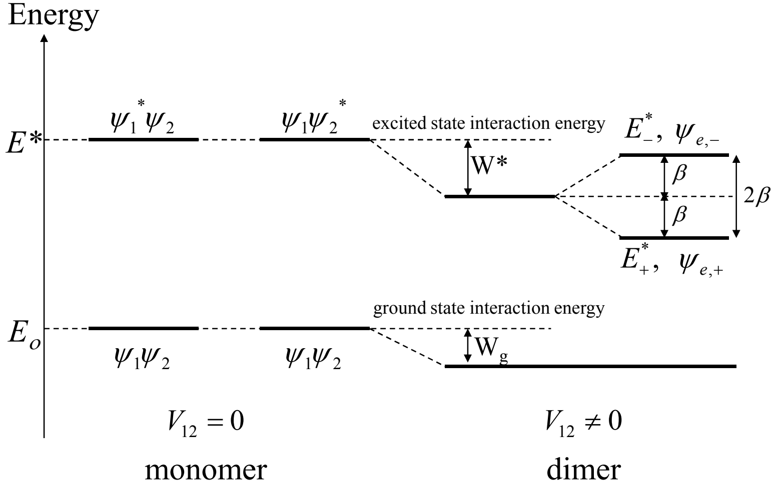


Excited state dimer; Repulsive ground state

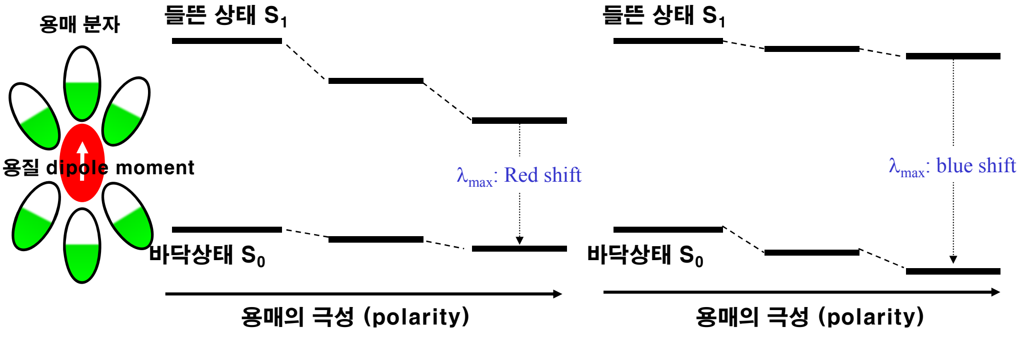
Excimer: M+M*
Exciplex: D+A* or D*+A

- Red shift
- Broad peak with no vibronic structure

Davidov splitting



Host – Dopant Interaction



$\mu_1 > \mu_0$ $\mu_1 < \mu_0$

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).

Self-aggregation of 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.