

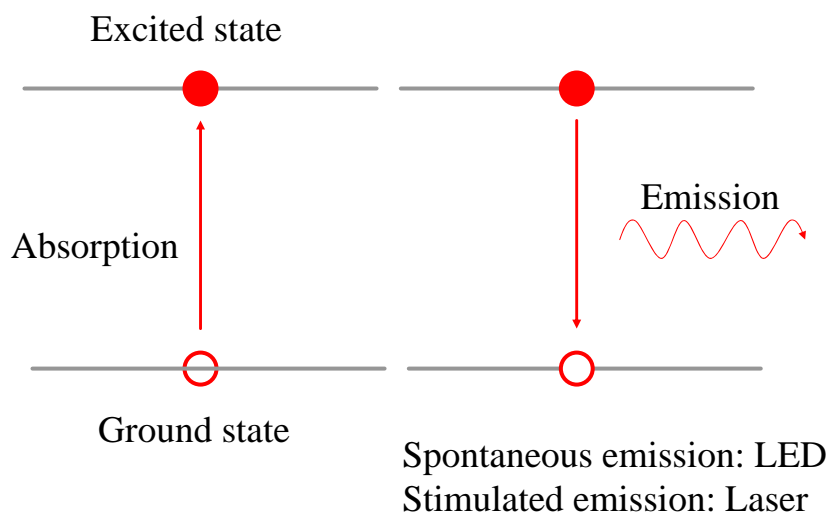
# 전자물리특강: 유기반도체의 광학적 특성

2007. 9. 17.

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## Absorption and Emission of Light



## Selection Rules for Electronic Transition

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### Fermi Golden Rule

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

Oscillator strength for the transition  $f \propto \left| \vec{\epsilon} \cdot \langle \psi_f | \vec{d} | \psi_i \rangle \right|^2$

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

• For the allowed transition  $\Delta l = \pm 1, \Delta S = 0$

• **Symmetry selection rule:** only  $g$  (even parity)  $\leftrightarrow$   $u$  (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

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

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

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

$$\tau = \frac{1}{\Gamma_{2p \rightarrow 1s}} \approx 1.6 \text{ ns}$$



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## Absorption and Emission of Light

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Consider a molecule with two energy levels 1 and 2.

The rate of transition  $B_{12}$  induced by light of frequency  $\nu$   $\Gamma_{1 \rightarrow 2} = B_{12} I(\omega_{fi})$

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

Transition rate for  $2 \rightarrow 1$  (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  $1 \leftrightarrow 2$  must be the same.

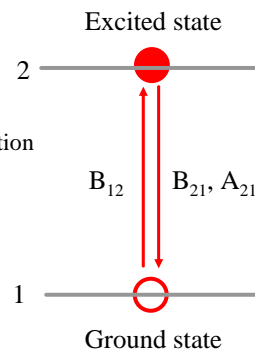
$$\frac{N_1}{N_2} = \frac{B_{21} I(\nu) + A_{21}}{B_{12} I(\nu)} = 1 + \frac{A_{21}}{B_{12} I(\nu)} \quad (1)$$

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

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

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

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



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# Absorption and Emission of Light

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

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

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

$$B_{12} = B_{21} \quad (5)$$

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

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

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

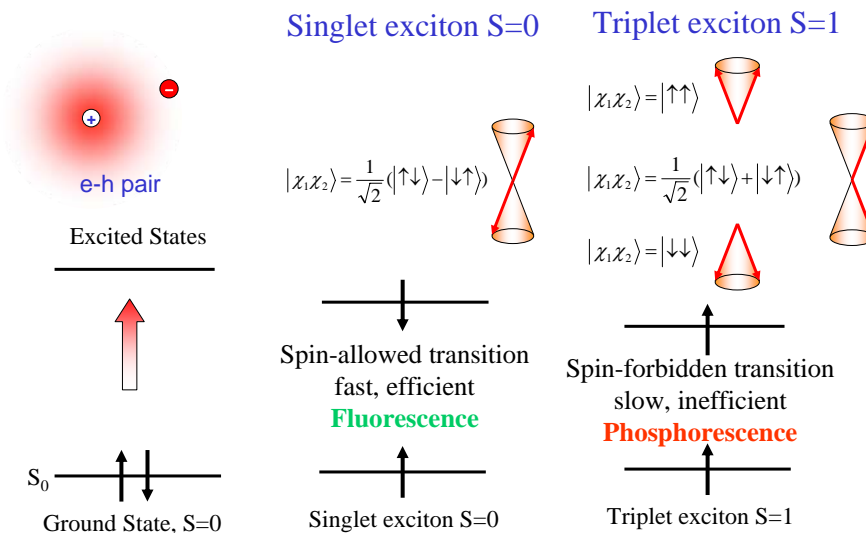
The radiative lifetime: 
$$\tau_r = \frac{1}{A_{21}} = \frac{c^3}{8\pi h \nu^3 B_{12}} = \frac{\lambda^3}{8\pi h B_{12}}$$

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



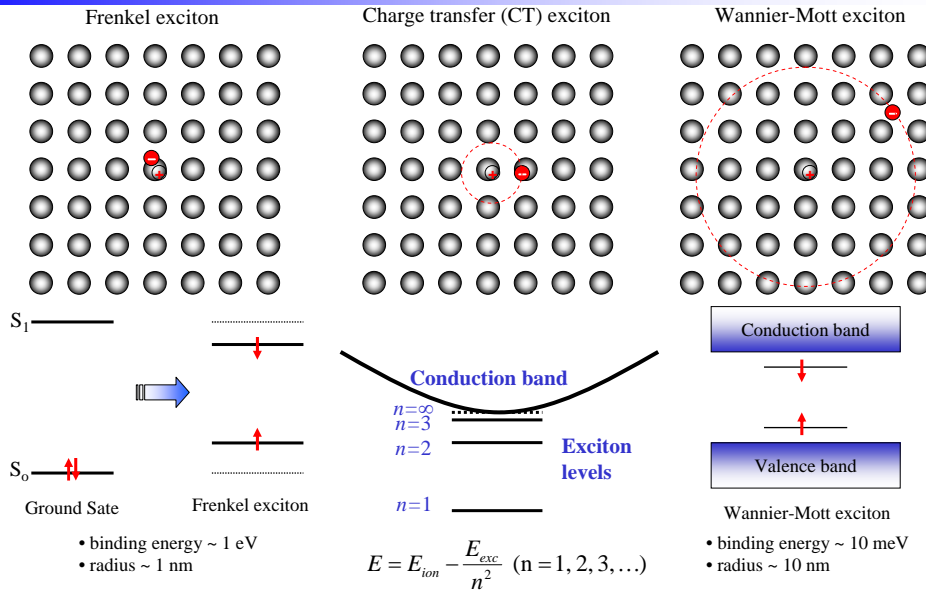
# Relaxation of Singlet & Triplet Excitons

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# Excitons

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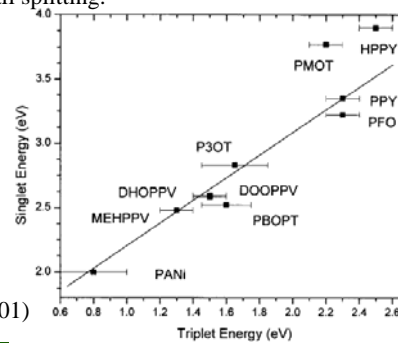
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# Energy Difference between Singlet-Triplet Exciton Energy

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- 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  $\pi$ -orbitals will have a small splitting.

anthracene:	$S_1 - T_1 = 1.5 \text{ eV}$
tetracene	1.3 eV
pentacene	1.1 eV



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

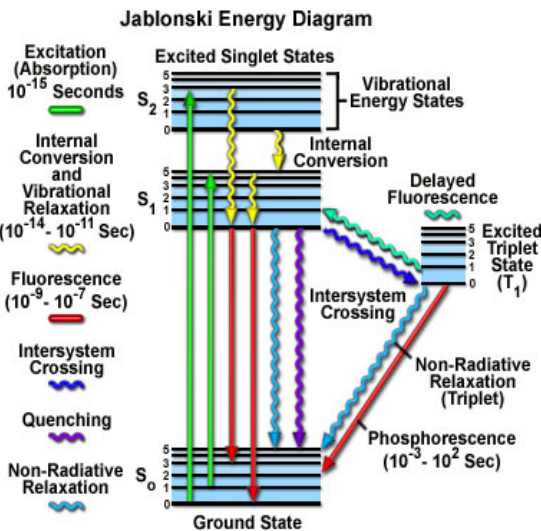


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# Jablonski Energy Diagram

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- Absorption occurs in the fs time regime ( $\sim 10^{-15}$  s)
- Excess energy can be transferred to the lattice (multi-phonon emission) in the ps time regime ( $10^{-14} \sim 10^{-11}$  s)  $\rightarrow$  internal conversion and vibrational relaxation
- Transition from the singlet states to the ground state is allowed.  $\rightarrow$  Fluorescence occurs in  $10^{-9} \sim 10^{-7}$  s
- Transition from the triplet states to the ground state is forbidden.  $\rightarrow$  Phosphorescence occurs in  $10^{-6} \sim 1$  s
- Intersystem crossing ( $S_1 \rightarrow T_1, T_1 \rightarrow S_0$ ) is possible when spin-orbit coupling is strong.

<http://microscopy.fsu.edu/primer/java/jablonski/jabintro/>

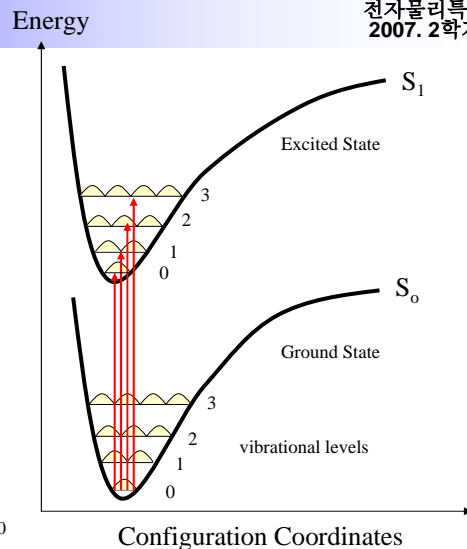
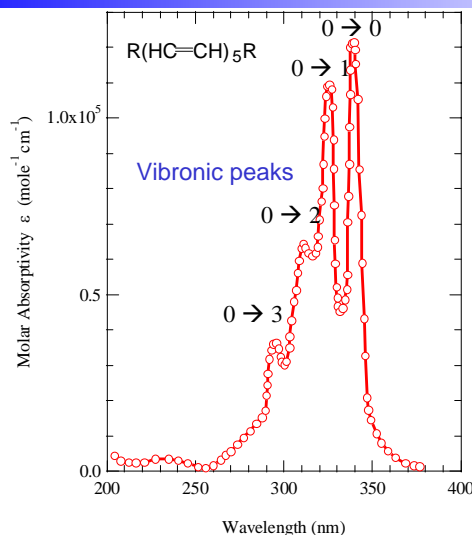


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# Franck-Condon principles

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If light of correct frequency is absorbed, the molecule can be excited to one of the many vibrational levels of the electronic excited states. The probability of excitation depends on the magnitude of the transition dipole between the initial and final states.

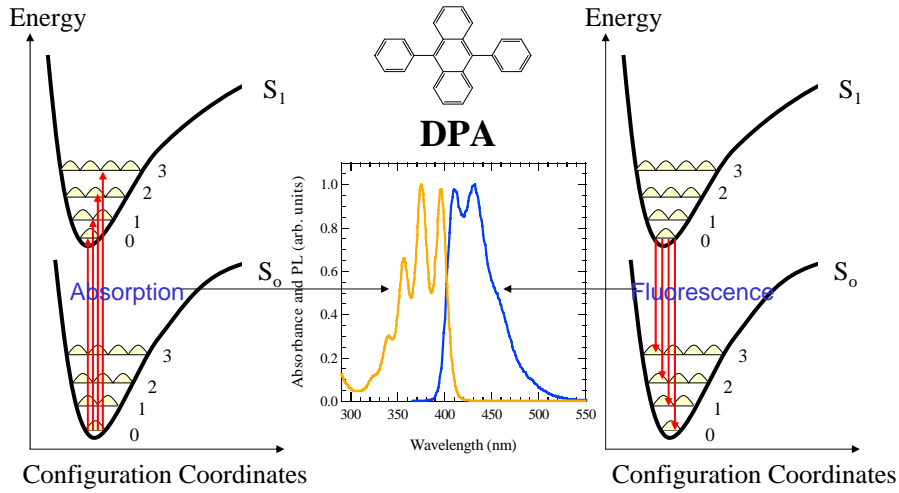


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# Absorption and PL Spectra of Organic Materials

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- Mirror symmetry between absorption and PL
- Stokes's shift: PL peak occurs at a longer wavelength than the absorption peak, because the excited state configuration can be different than the ground state.

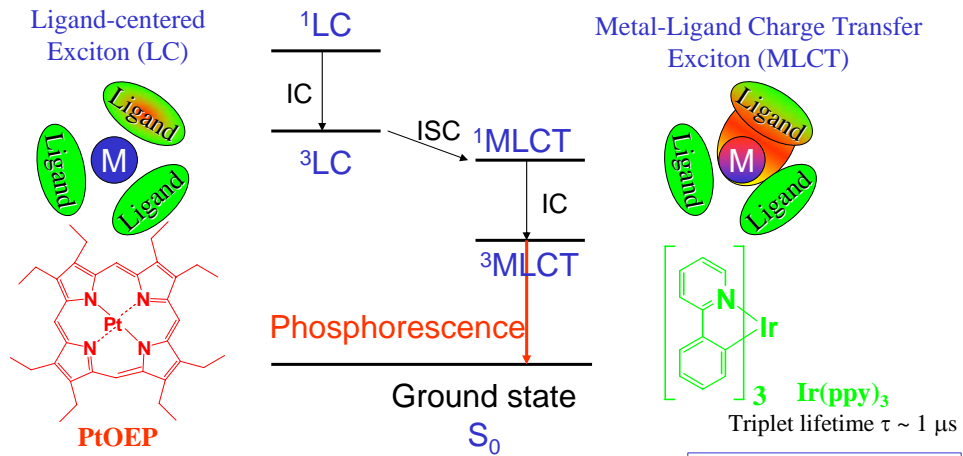


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# Organic Phosphorescent Dyes

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- The emissive state is a mixture of a LC exciton and a MLCT exciton
- The MLCT state has stronger singlet - triplet mixing, due to the overlap with the heavy metal atom.
- For strong spin-orbit coupling, the IC and ISC rates are very fast.

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



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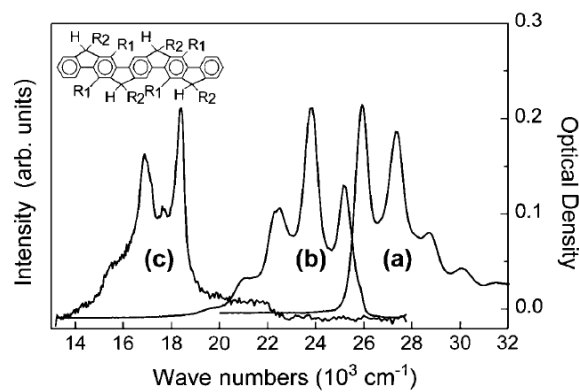
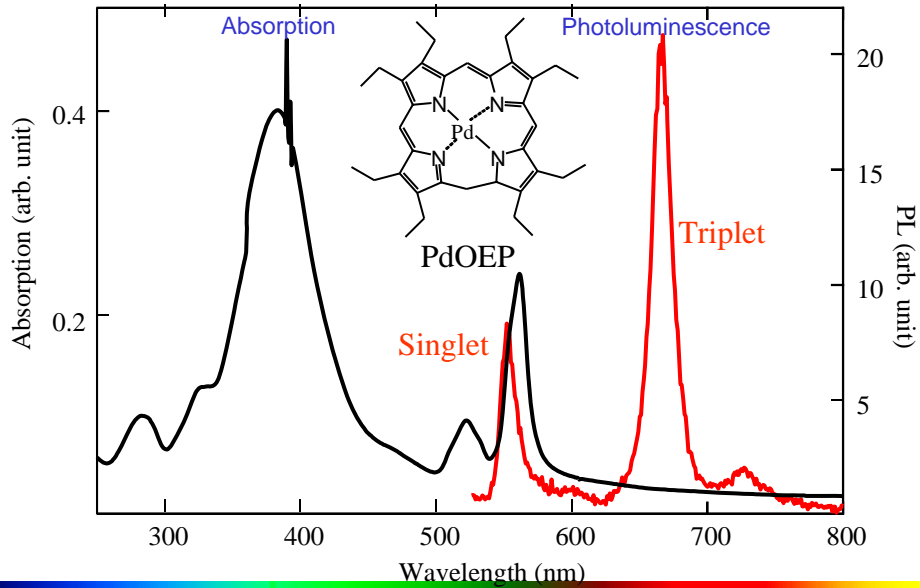


FIG. 3. Spectra of LDPP [ $R_1 = n\text{-C}_6\text{H}_{13}$  and  $R_2 = 1,4\text{-(C}_6\text{H}_4\text{)-C}_4\text{H}_9$ ] in MTHF solution (a) absorption spectrum (295 K), (b) delayed fluorescence spectrum (integration time 100 ns, delay 30 ns) at 77 K, and (c) phosphorescence spectrum (integration time 10 ms, delay 3 ms) at 77 K. The excitation energy was  $\nu_{\text{exc}} = 25\,975\text{ cm}^{-1}$ .

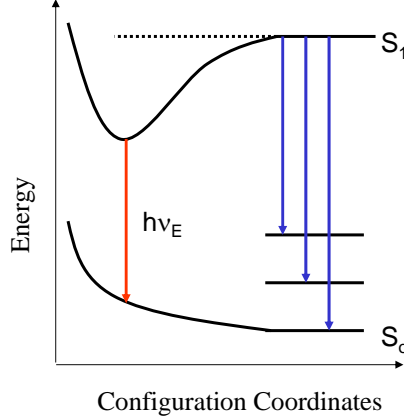
Yu.V. Romanovskii, A. Gerhard, B. Schweitzer, U. Scherf, R. I. Personov, and H. Bässler, Phys. Rev. Lett. **84**, 1027 (2000)



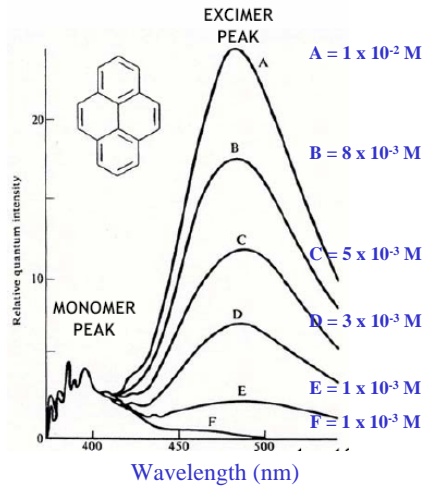
# Excimer or Exciplex

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## Potential Energy Curve



Excited state dimer; Repulsive ground state  
Excimer:  $M+M^*$   
Exciplex:  $D+A^*$  or  $D^*+A$



Excimer emission:  
• Red shift (large Stokes' shift)  
• Broad, unstructured and inefficient

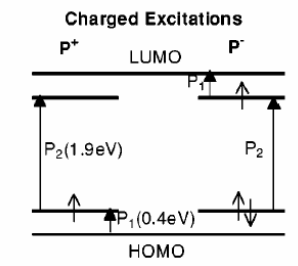
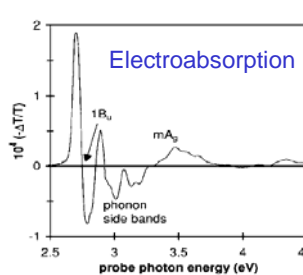
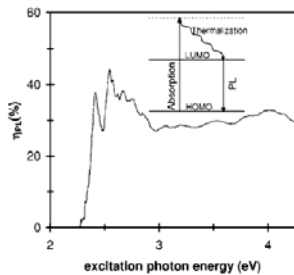
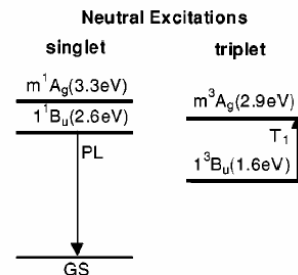
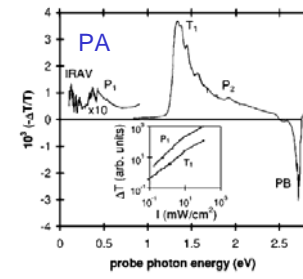
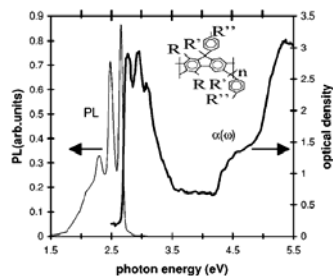


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# Excitons and polarons in Conjugated Polymers

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M. Wohlgenannt, et al., Photogeneration and recombination processes of neutral and charged excitations in films of a ladder-type poly(para-phenylene). Phys. Rev. B 60, 5321 (1999)



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