

# Week 4

Optical Properties 2

Excitons

Spin

Energy Transfer

Chapter 3.6, 3.7.1, 3.7.4, 3.8

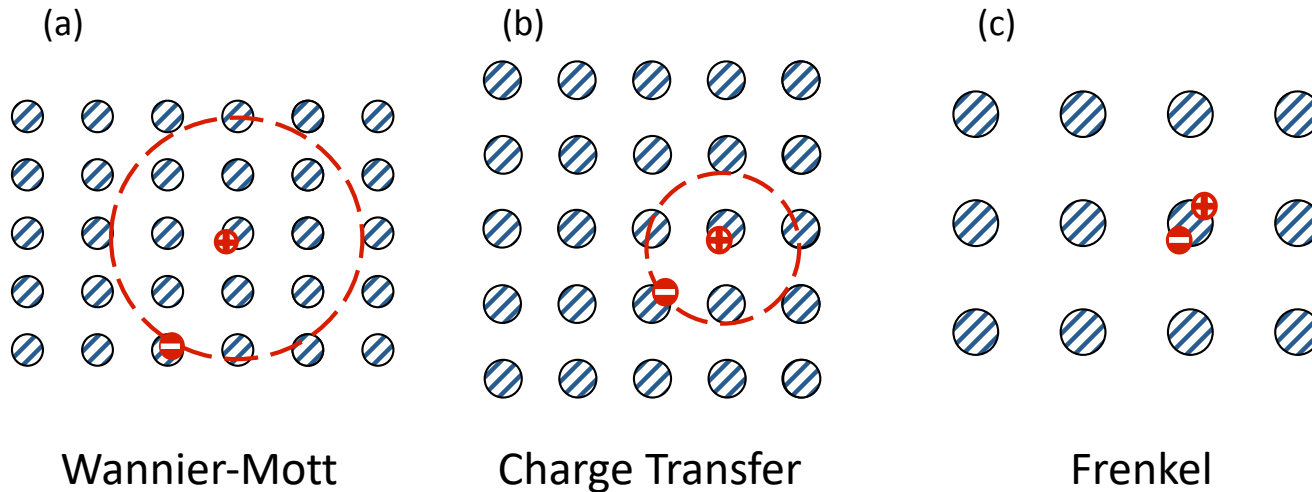


Organic Electronics  
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# Excitons & Spin

- Collective response of a solid to the excitation of a molecule
- Excited states that transport energy
  - But not charge, except for charged excitons (trions)
- The excited state transfers from molecule to molecule.
  - Energy migration is known as *exciton diffusion*.
- Migration can happen in gas, solution and especially solids.

# Three Types of Exciton



Bohr Model:

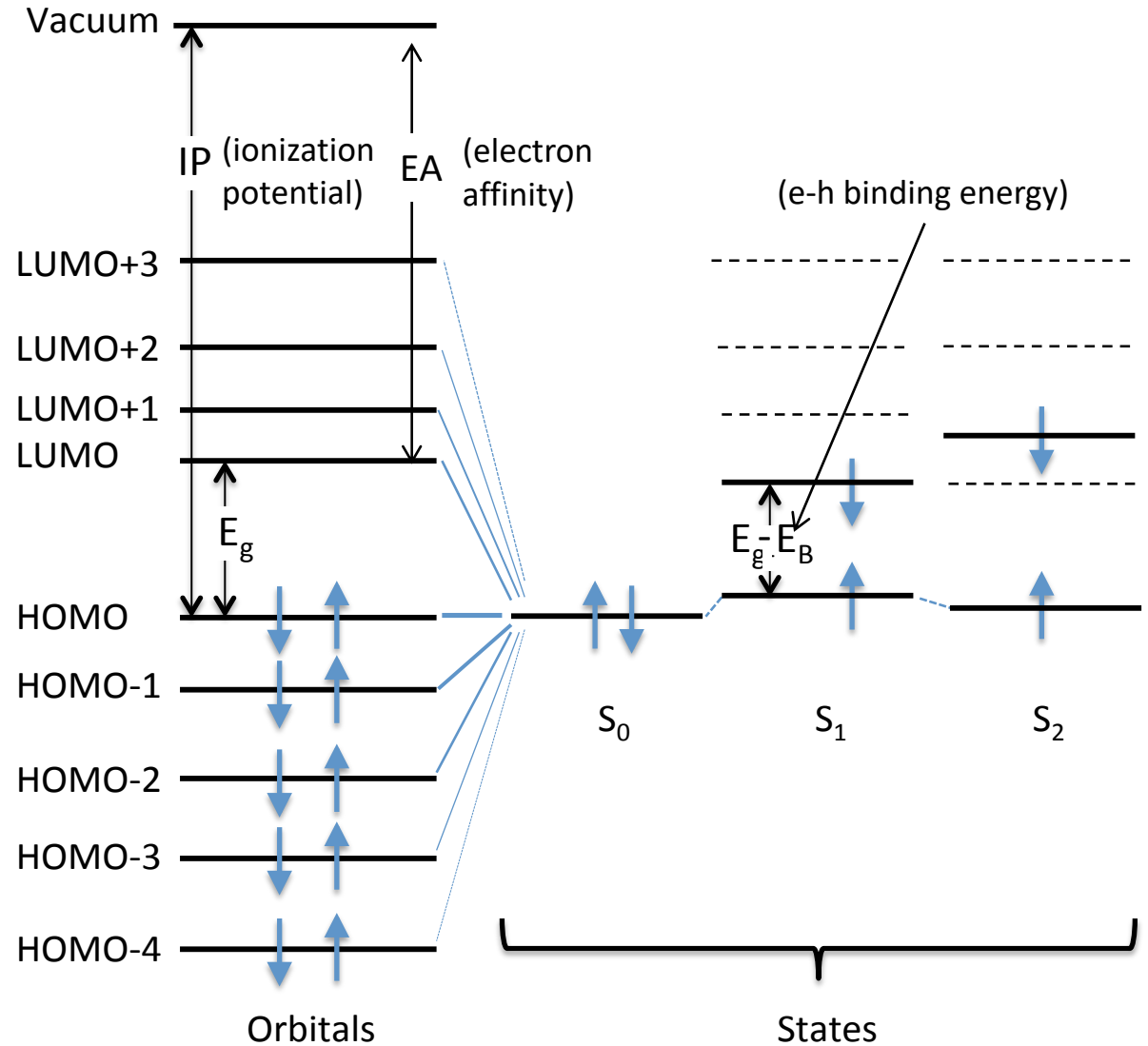
$$E_B = -\frac{q^2}{8\pi a_0 (\epsilon_r \epsilon_0)} \frac{1}{n^2}$$

$$a_0 = \frac{4\pi (\epsilon_0 \epsilon_r) \hbar^2}{m_r^* q^2}$$

Medium	$\epsilon_r$	$m_r^* / m_e$	$a_0$ (Å)	$E_B$ (eV)
Vacuum (H atom)	1	1	0.5	13.6
Anthracene <sup>(a)</sup>	2.4-4.1	1	1.2-2.1	0.8-2.4
PTCDA <sup>(b)</sup>	2.0-4.4	0.14-1	2.2-7.1	0.5-0.7
ZnS <sup>(c)</sup>	5.2	0.4	5.2	0.2
Si <sup>(c)</sup>	11.9	0.14	43	0.014
GaAs <sup>(c)</sup>	13.1	0.07	94	0.006

# Important distinctions between electronic *orbitals* and electronic *states*

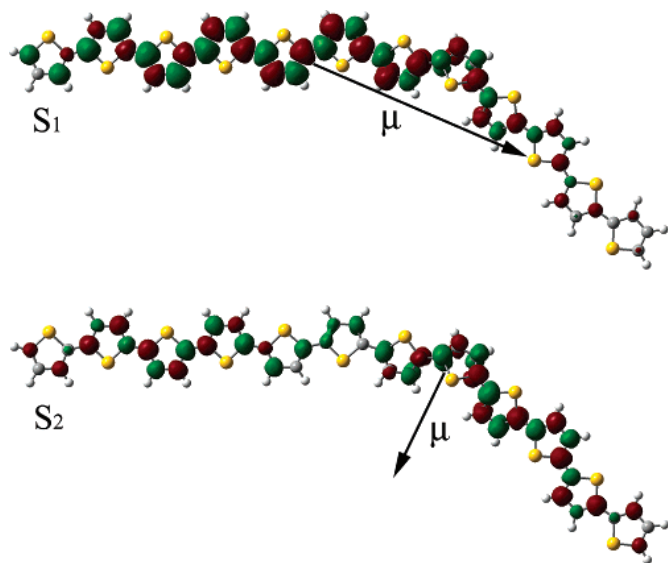
1. Orbital energies refer to single electrons
2. Orbital energies are referenced to the vacuum level: All HOMO and LUMO energies  $< 0$
3. State energies refer to collections of electrons: they are calculated from a linear combination of orbitals
4. State energies are referenced to each other (not vacuum)
5. States are formed after relaxation and include the electron-hole binding energy
6. States comprised of two or more electrons, and hence their spin multiplicity determines their character.
7. States and orbitals cannot co-exist meaningfully on the same diagram



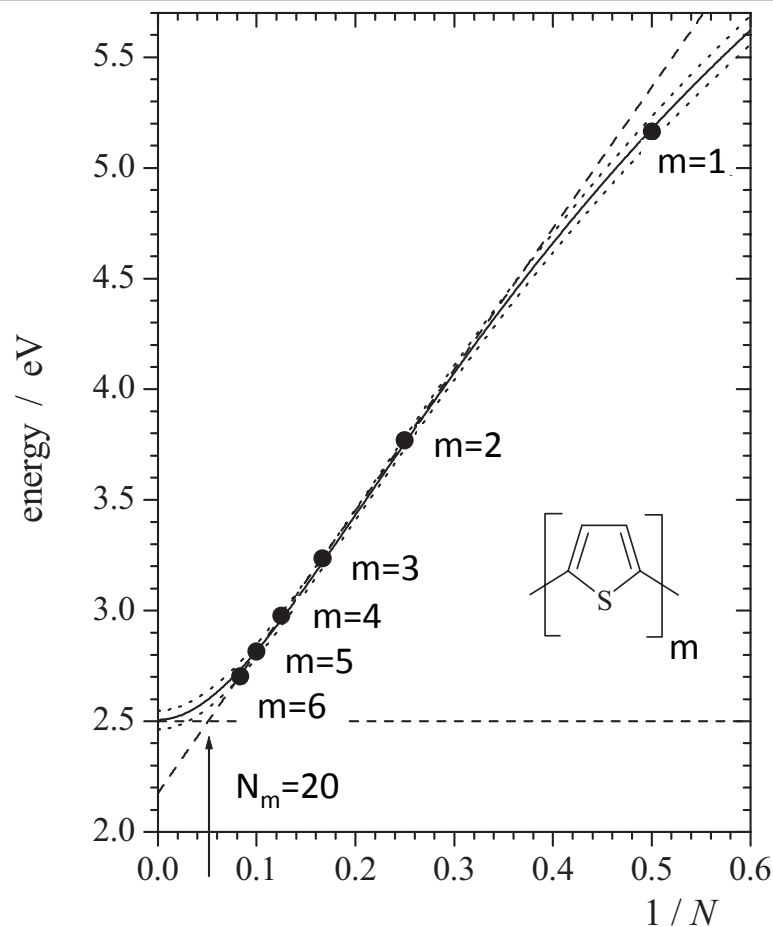
# How big is the excited state?

Low energy absorption cutoff of thiophene oligomers vs. no. of monomer segments,  $m$ .

- $N$ =number of **double bonds** in the oligomer
- Result  $\Rightarrow$  excited state is  $< 6$  units
- Chain twists or kinks limit the extent of the electron charge distribution



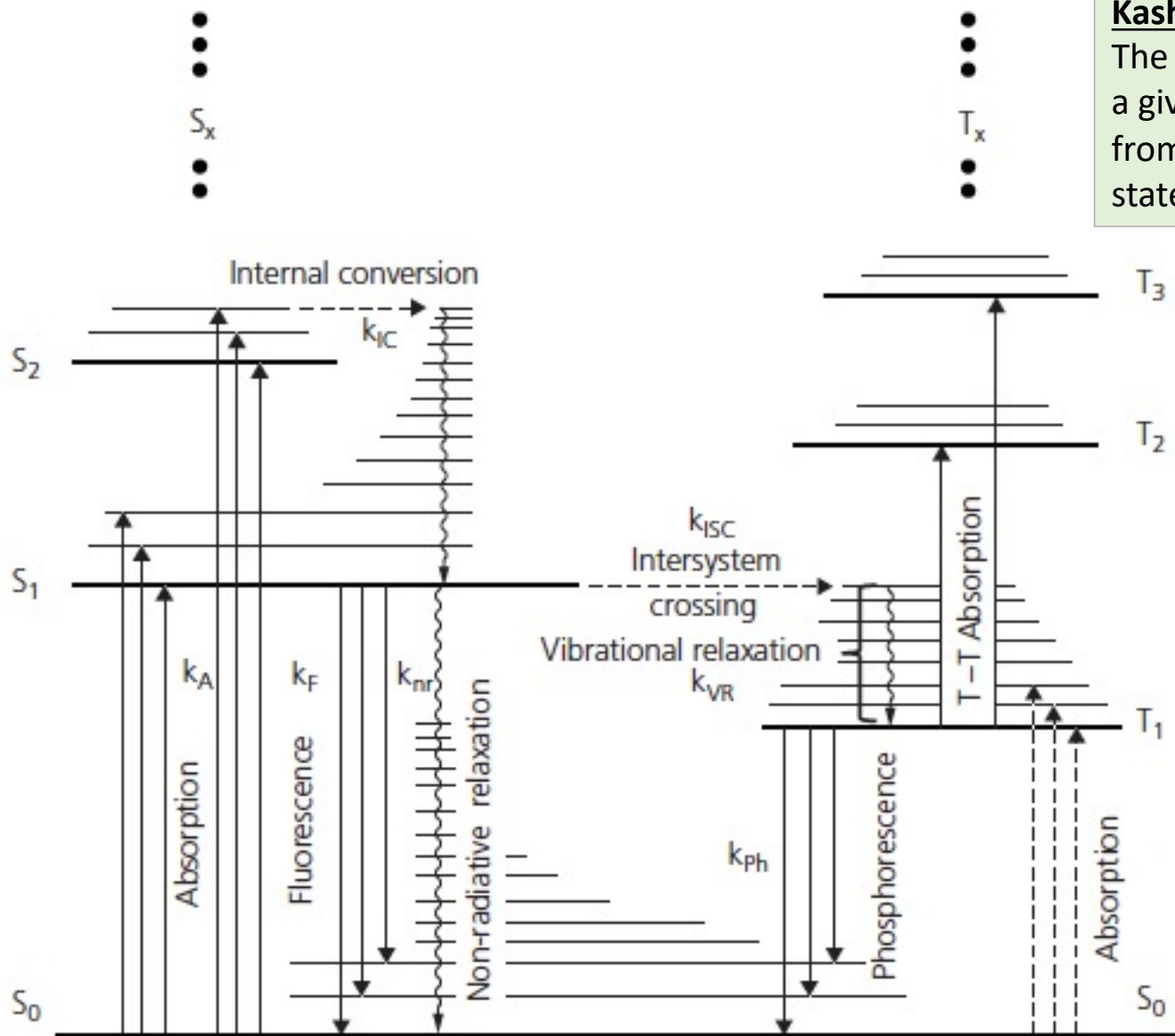
dodecithiophene



Gierschner, J., et al. 2007. *Adv. Mater.*, 19, 173.

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# Jablonski Diagrams: Life Histories of Excitons



## Kasha's rule

The radiative transition from a given spin manifold occurs from the lowest excited state.

# Oscillator Strength

The *oscillator strength* is the ratio of the emission or absorption rate of the molecule to that of a classical oscillator, which is defined by:

Recall this is simply  $|\mu_{if,e}|^2 FC_{if}$

$$f_{in,fm} = \frac{4\pi m_e c}{3q^2 \hbar} \langle \tilde{\nu}_{in,fm} \rangle \left| \langle \phi_{in} | H_{int} | \phi_{fm} \rangle \right|^2 = \frac{4\pi m_e c}{3q^2 \hbar} \langle \tilde{\nu}_{in,fm} \rangle |\mu_{in,fm}|^2$$

Ave. emission freq.

Einstein spontan. abs.

Normalized lineshape

It can be shown that the absorption cross section is:  $\sigma_0(\omega) = \hbar\omega B_{in,um} \gamma(\omega) / c$

This leads to more practical expressions for the oscillator strength:

$$f_{in,fm} = \frac{2m_e \epsilon_0 c}{\pi q^2 n_r} \int \sigma(\omega) d\omega = \frac{2303 m_e c^2}{N_A \pi q^2 n_r} \int \epsilon(\tilde{\nu}) d\tilde{\nu} = \frac{4.39 \times 10^{-9}}{n_r} \int \epsilon(\tilde{\nu}) d\tilde{\nu}$$

Decadic molar absorption  
Coefficient [l-cm<sup>-1</sup>-M<sup>-1</sup>]

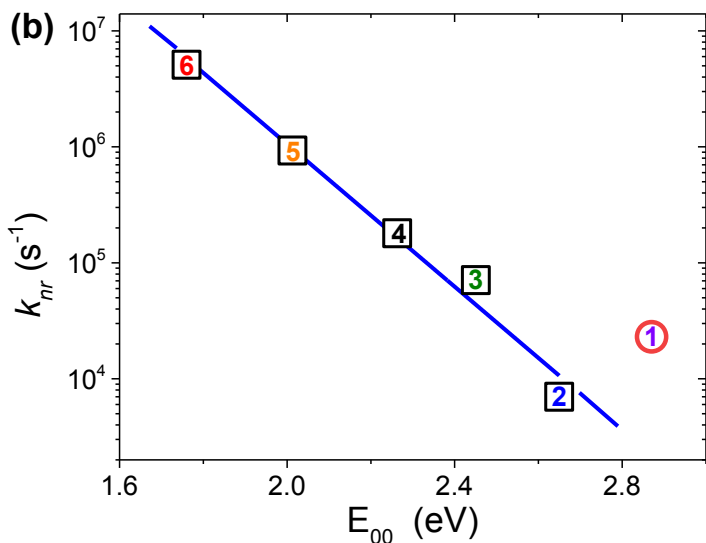
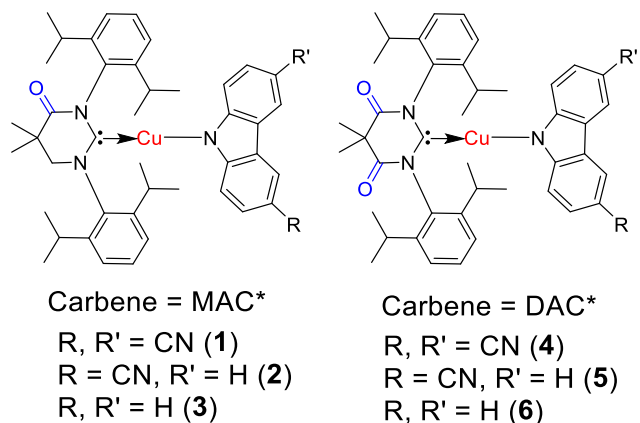
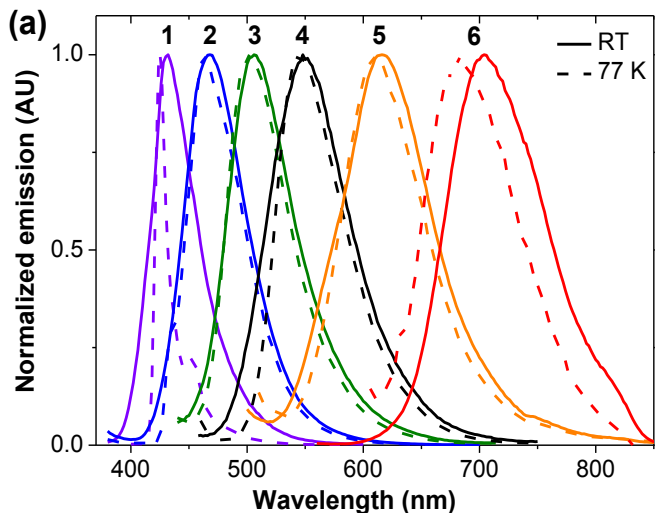
wavenumber =  $\nu/c$

Absorption coeff't relationships:  $\alpha(\nu) = \ln 10 \epsilon(\nu) C = 2.303 \epsilon(\nu) C$

C=concentration [M/l]

# Energy Gap Law

- The larger the energy gap, the lower the probability for non-radiative recombination.
  - ⇒ As the energy gap of a molecular species decreases, radiative transitions have a higher probability for non-radiative decay.



$$k_{if} = A \exp(-\gamma E_g / \hbar \omega_p)$$

$$\gamma = \log \left( \frac{E_g}{\Omega E_p} \right) - 1$$

$\Omega$  = number of modes contributing to the maximum phonon energy,  
 = ½ the Stokes shift.



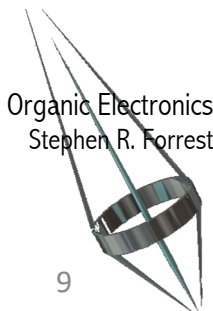


# Dimers

- Interaction of an isolated pair of molecules
- First step in building up a solid: smallest possible aggregate unit
- Chemical dimer: the pair forms a bond
- Physical dimer: the pair is attracted by a bonding force, typically van der Waals
- New energy levels appear that do not exist in the individual molecules
- Treatment much like that of a H<sub>2</sub> molecule.
  - Ground state:  $\psi_G(\mathbf{r}_1, \mathbf{r}_2) = \psi(\mathbf{r}_1)\psi_2(\mathbf{r}_2)$ :  $\psi(\mathbf{r}_{1,2})$  = ground state of individual molecules comprising the pair.
  - These identical molecules have identical energies:  $E_1 = E_2 = E_0$
  - When interacting to form a dimer, the ground state energy is perturbed:

$$E_I = \langle \psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) | H_{\text{int}} | \psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) \rangle$$

- With (for vdW interactions):  $H_{\text{int}} = -\frac{A_{12}}{r_{12}^6}$



# Normal Modes of a Dimer

Excited state 'oscillates' between the two molecules forming two normal modes:

$$\psi'_{\pm} = \frac{1}{\sqrt{2}}(\psi'_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) \pm \psi_1(\mathbf{r}_1)\psi'_2(\mathbf{r}_2))$$



Two energies associated with these normal modes:

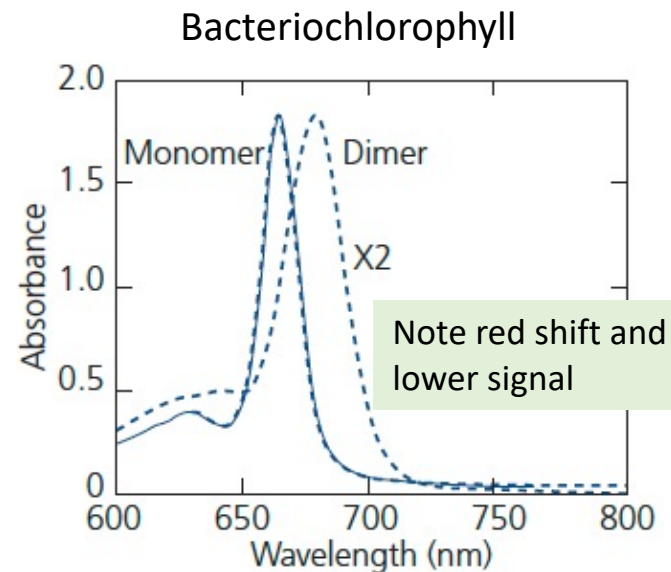
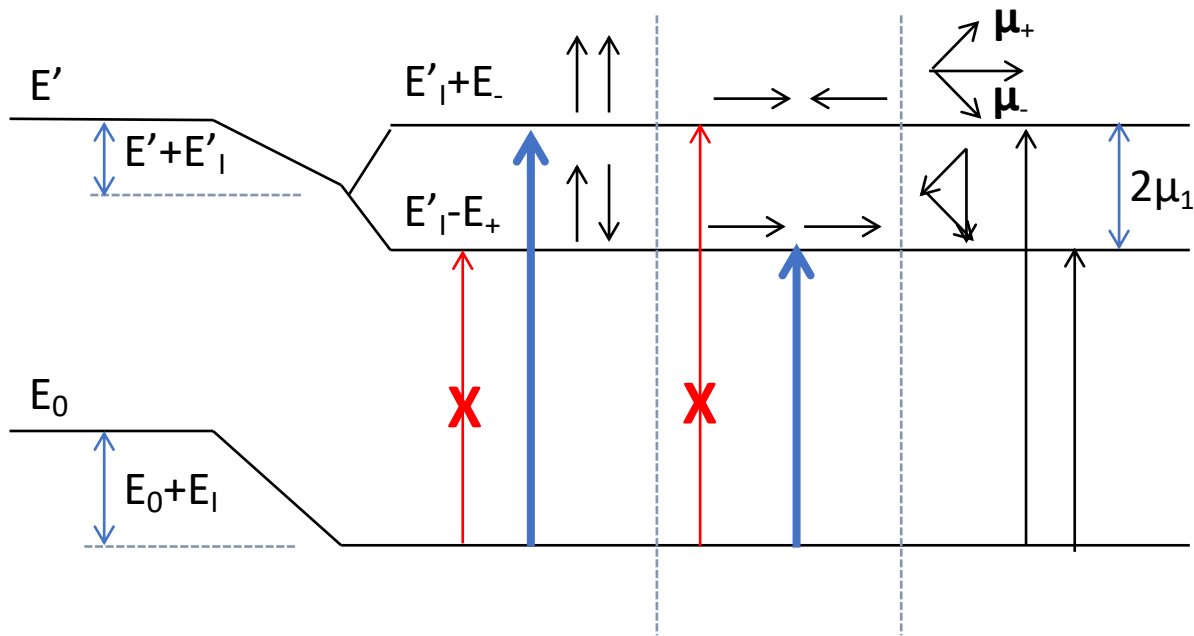
$$E'_I = \langle \psi'_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) | H_{\text{int}} | \psi'_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) \rangle \quad : \text{Coulomb energy}$$

$$E_{\pm} = \pm \langle \psi'_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) | H_{\text{int}} | \psi_1(\mathbf{r}_1)\psi'_2(\mathbf{r}_2) \rangle \quad : \text{Resonance energy}$$

Giving a total dimer energy of:  $E'_T = E_0 + E' + E'_I + E_{\pm}$

=Ground state + excited state of one molecule + energies of the pair

# The Dimer Spectrum



Olsen & Cox Photosynth. Res. 30, 35 (1991).

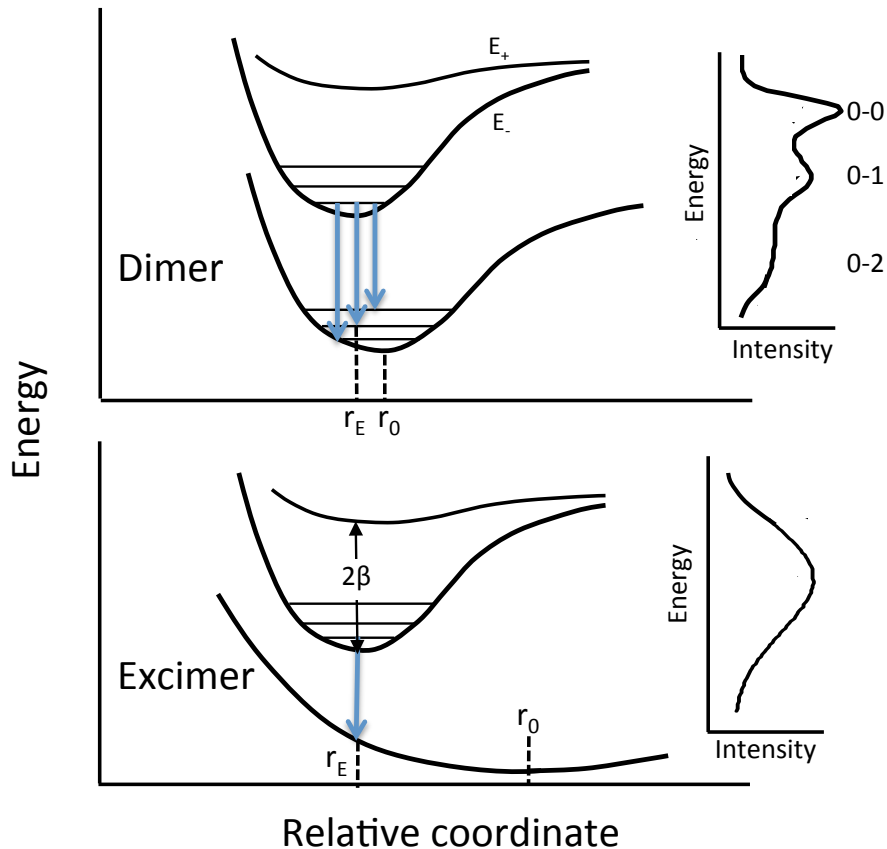
Symmetry prevents some transitions from occurring

Transition moment: 
$$\mu_{\pm} = -\frac{q}{\sqrt{2}} \langle \psi'_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) \pm \psi_1(\mathbf{r}_1)\psi'_2(\mathbf{r}_2) | \mathbf{r} | \psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) \rangle = \frac{1}{\sqrt{2}} (\mu_1 \pm \mu_2)$$



# Excimers and Exciplexes

- A dimer with no ground state is an **excimer**.
- A molecular couple comprised of two different molecular species is an **exciplex**.

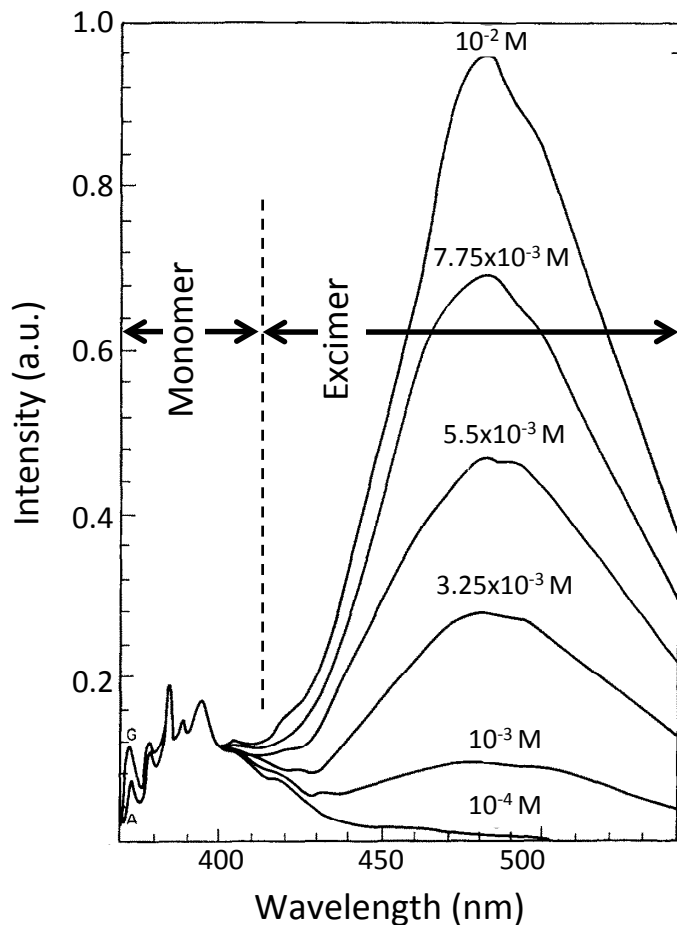


Getting to the excimer can be a multi-step process

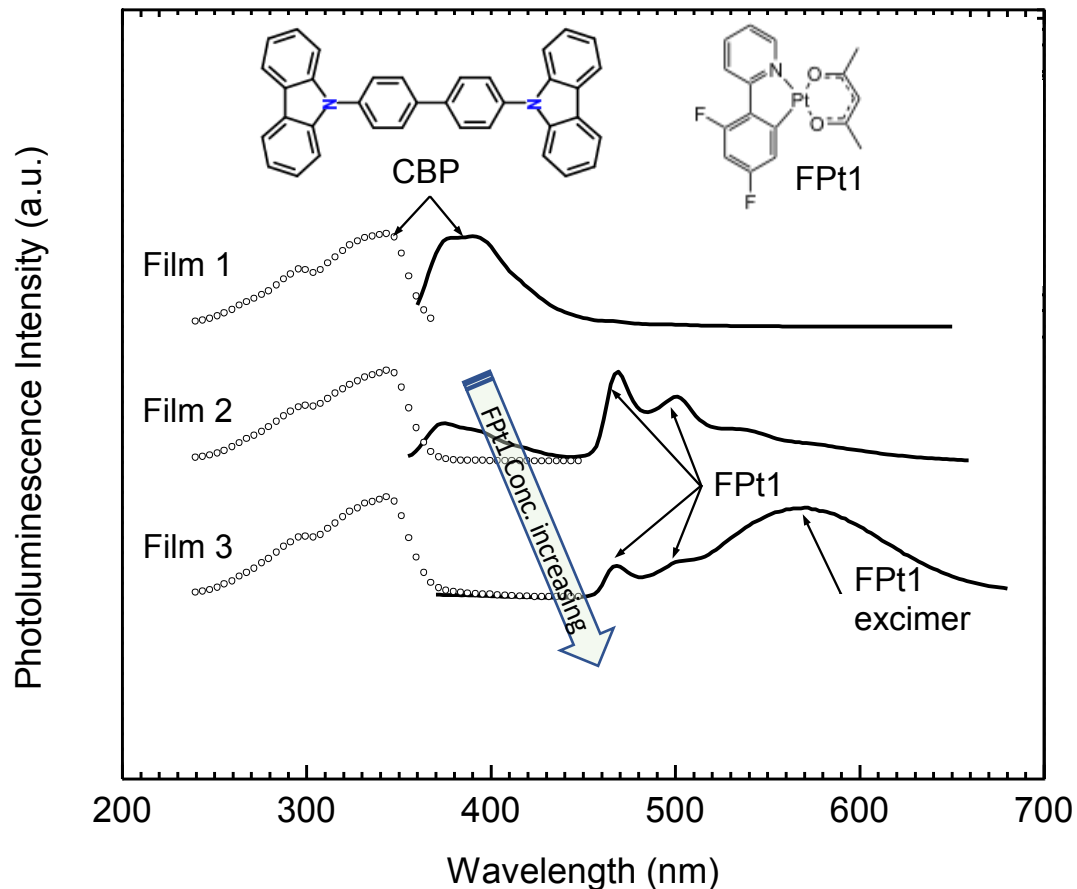


# Examples of Excimer Emission in Fluorophors and Phosphors

Excimer Fluorescence: Pyrene in solution  
Higher concentration=more excimer pairs



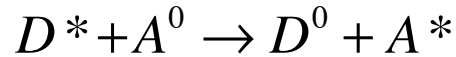
Excimer Phosphorescence  
Coexistence of monomer and excimer emission = white light



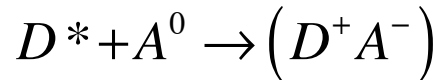
# Exciplexes

- Concept of **donor** and **acceptor** molecules:

- An excitation moves from an excited donor ( $D^*$ ) to a ground state acceptor ( $A^0$ )



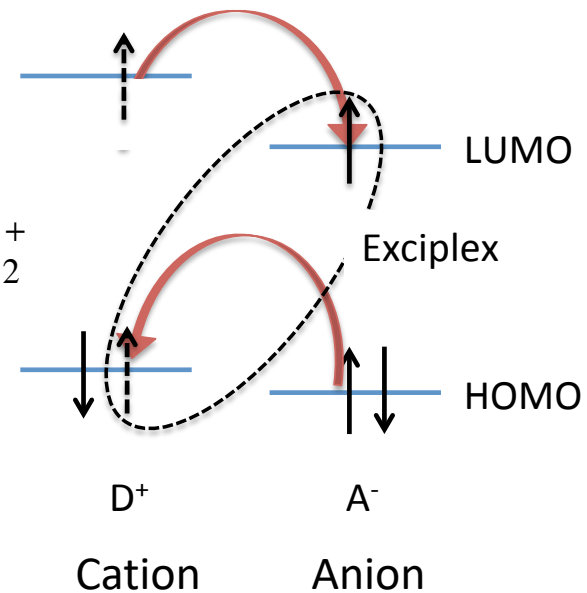
- Since there is an energy difference between D and A, an exciplex results in charge transfer (shared charge) between molecules:



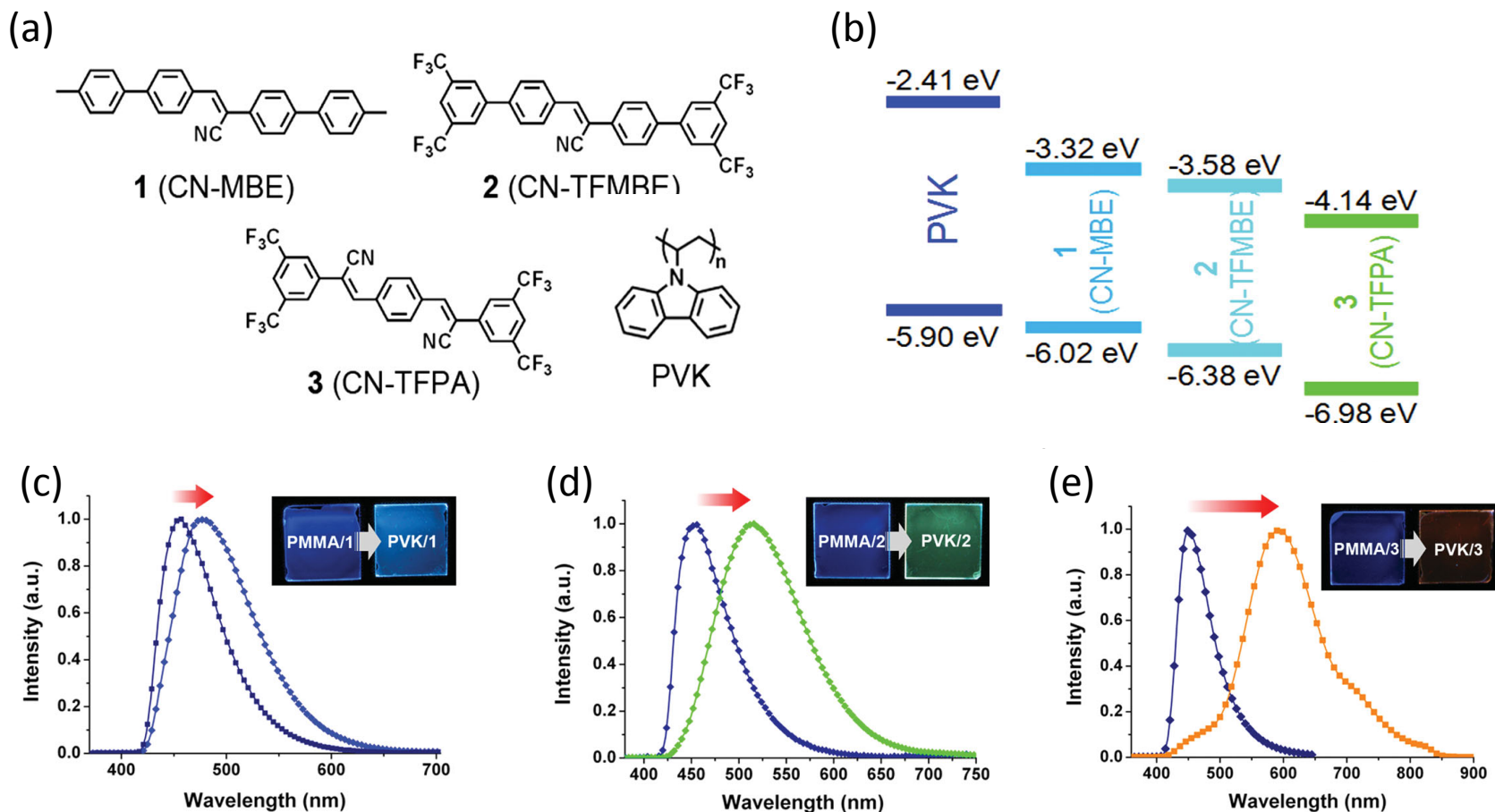
- Excitation shared by two different molecules forming a complex: the amount of charge transfer depends on energy asymmetry

$$\psi_T^0 = \alpha^0 \psi_1 \psi_2 + \gamma^0 \psi_1^+ \psi_2^- + \delta^0 \psi_1^- \psi_2^+$$

$$\psi_T' = \alpha \psi_1' \psi_2 + \beta \psi_1 \psi_2' + \gamma \psi_1^+ \psi_2^- + \delta \psi_1^- \psi_2^+$$



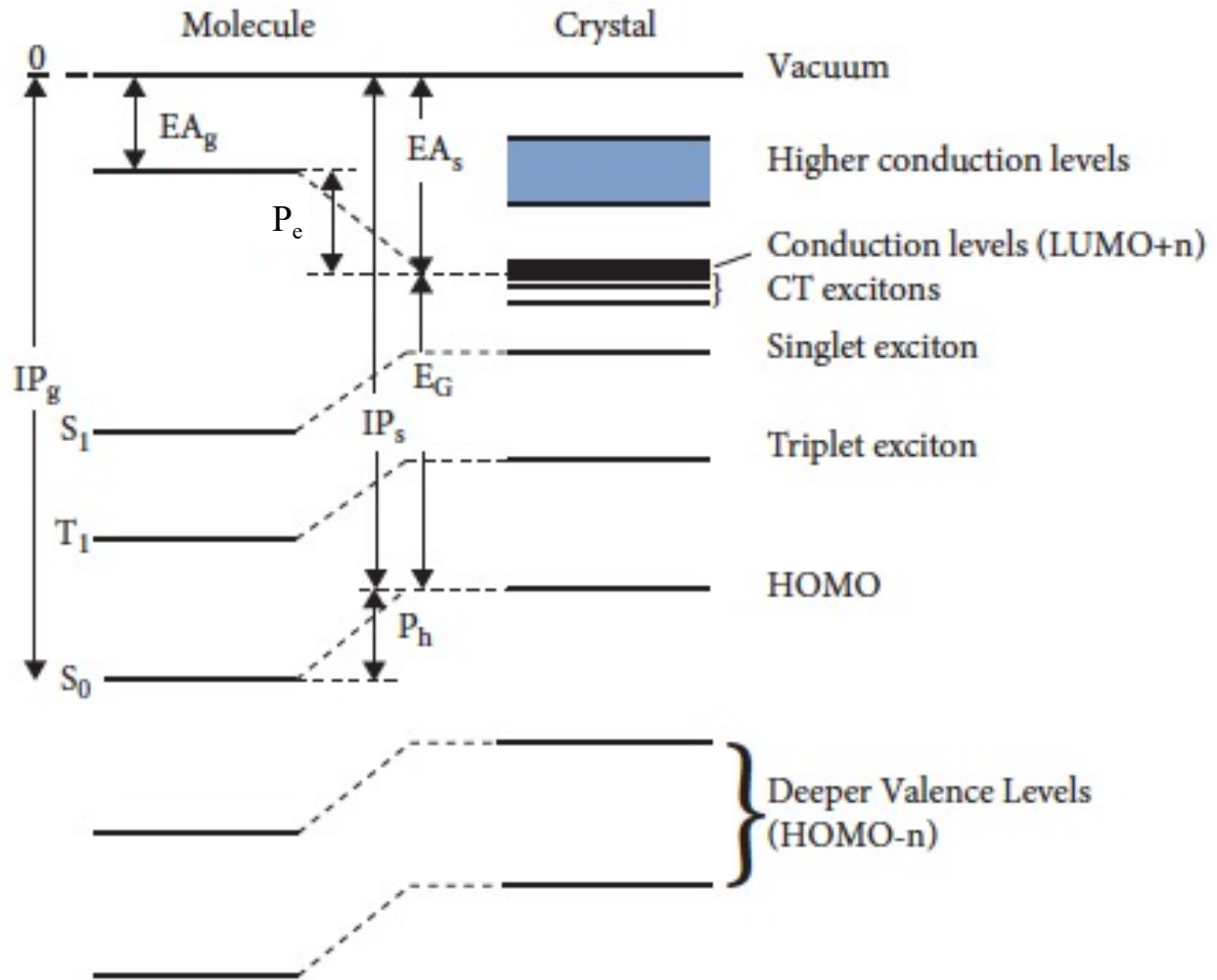
# Example of an Exciplex



Kim, J.-H., et al. 2014. Adv. Functional Mater., 24, 2746.

# The correspondence between a molecule and a solid

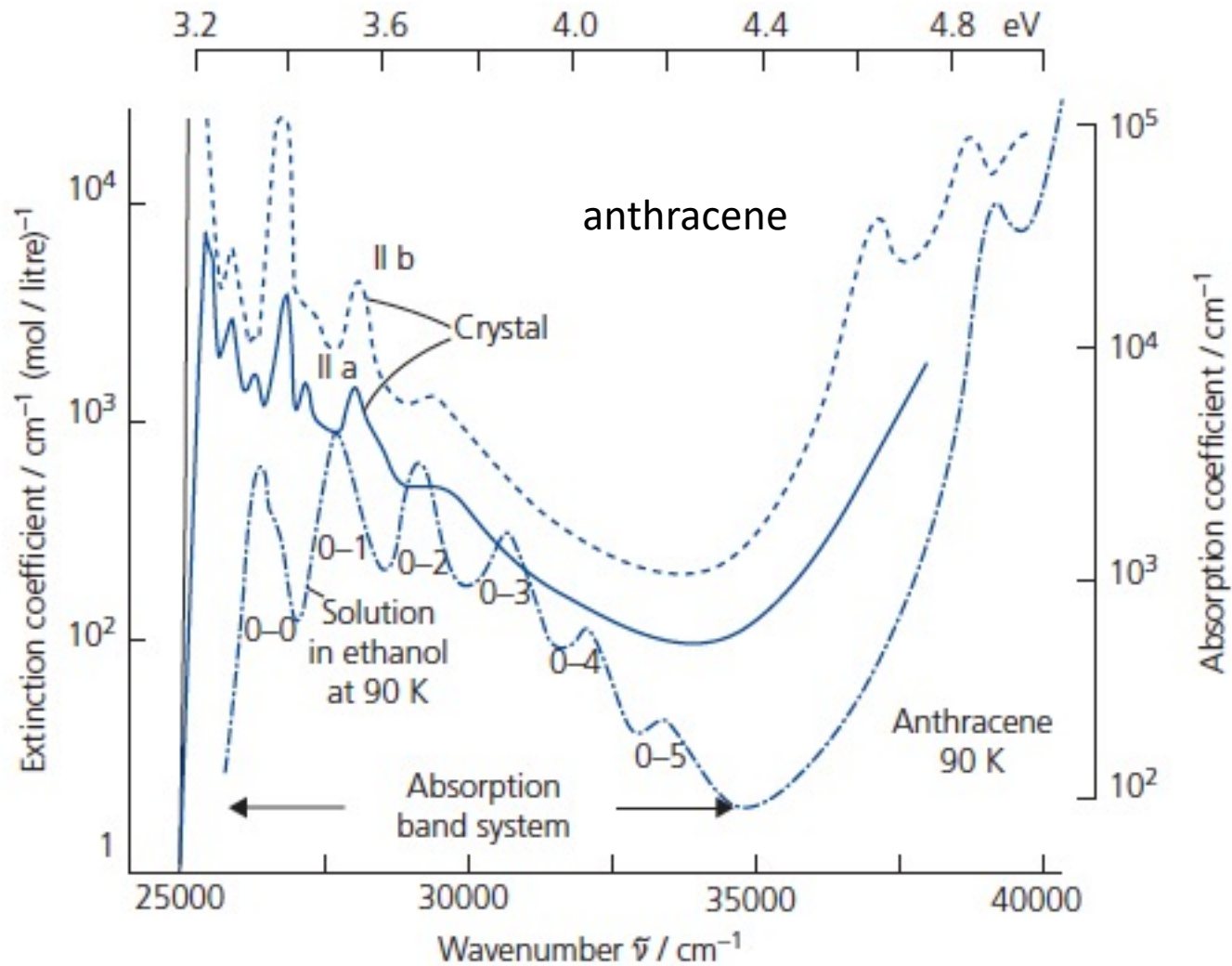
- IP=ionization poten
- EA=electron affinity
- P=Polarization ener
- g,s=gas, solid



Lyons Model



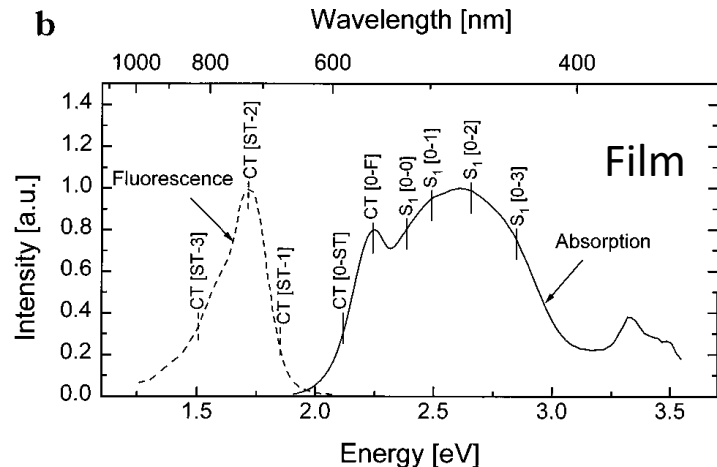
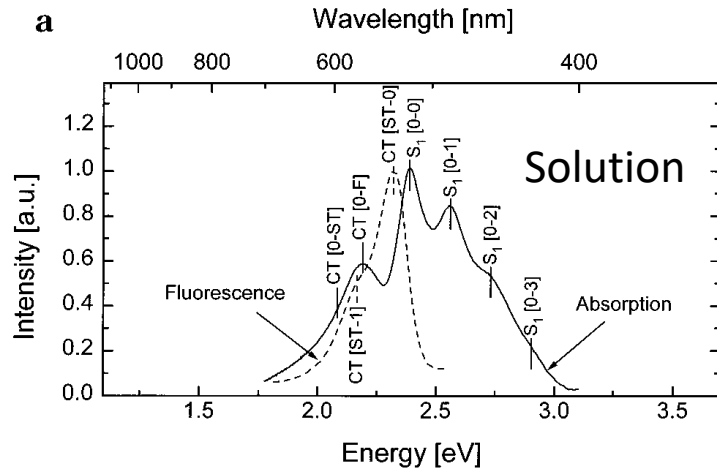
# Going from molecules to solids



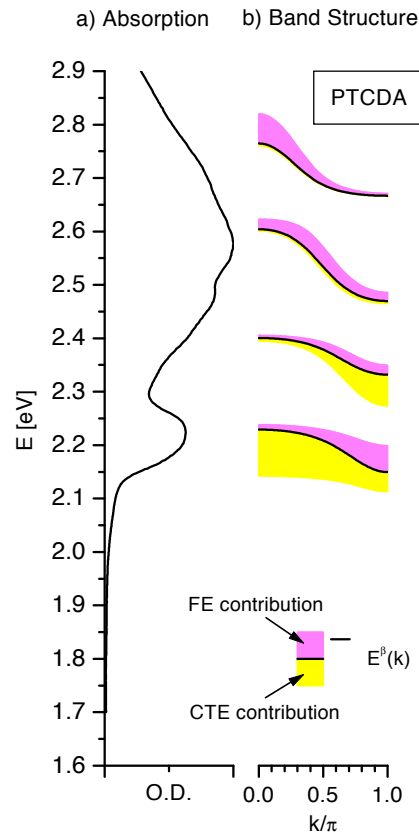
Vibronic progression loses definition in the solid: why?

# Charge Transfer States: Intermediates between molecule and solid

Tight packing in PTCDA leads to strong CT oscillator strength

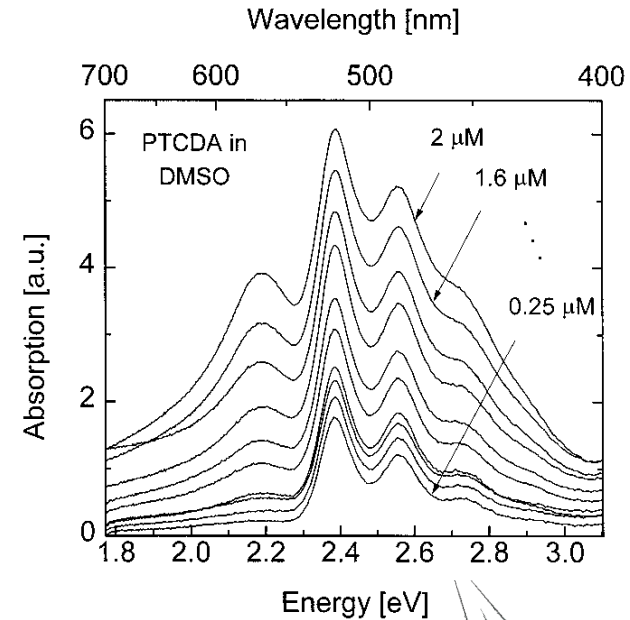


Bulovic, V., et al. 1996. *Chem. Phys.*, 210, 1.



Hoffmann, M., et al. 2000. *Chem. Phys.*, 258, 73.

How can we be sure it's a  
CT state?

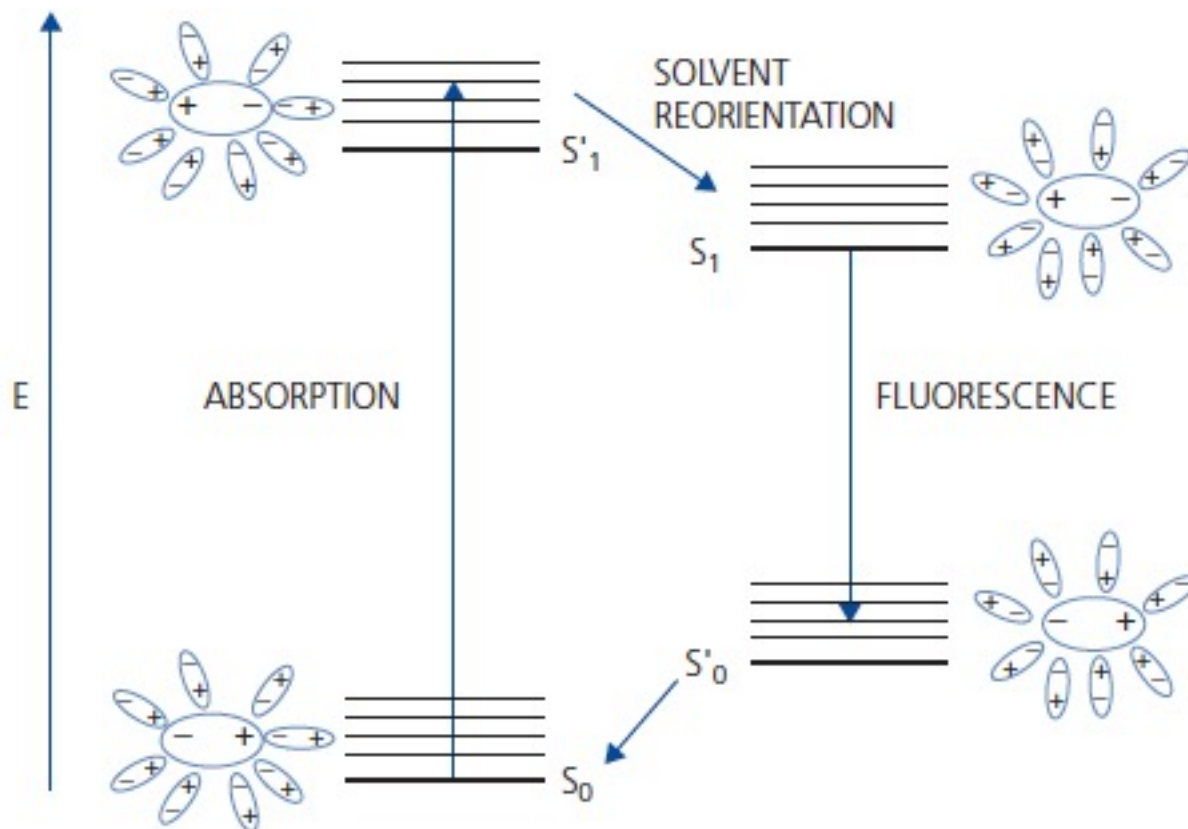


Bulovic, V., et al. 1996. *Chem. Phys.*, 210, 1.

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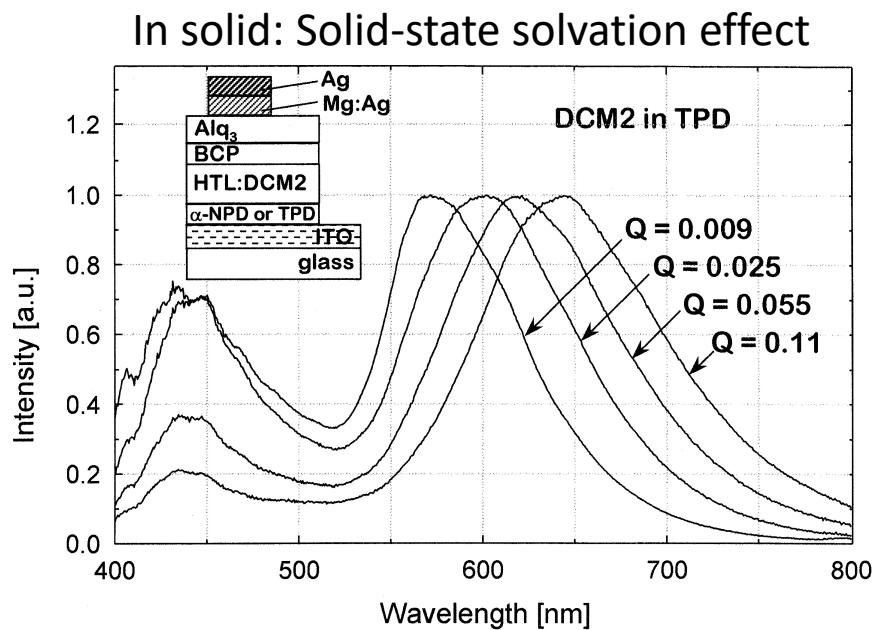
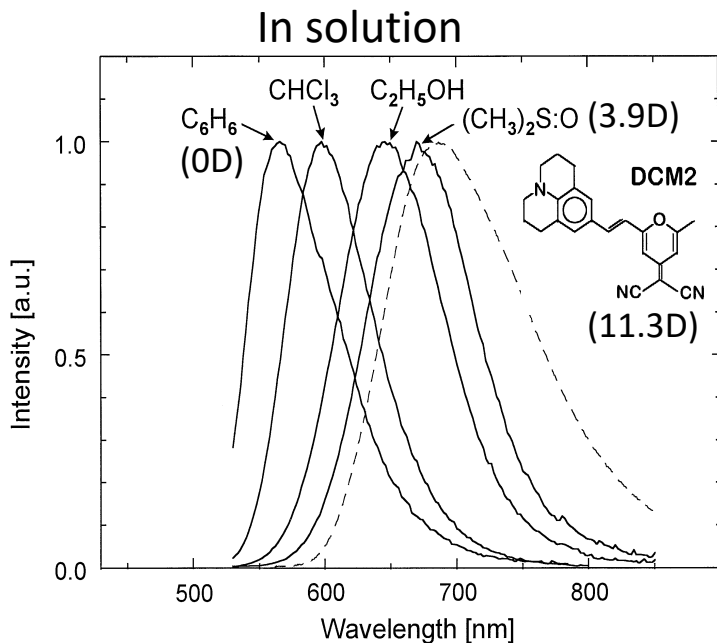


# Solvatochromism and Polarization



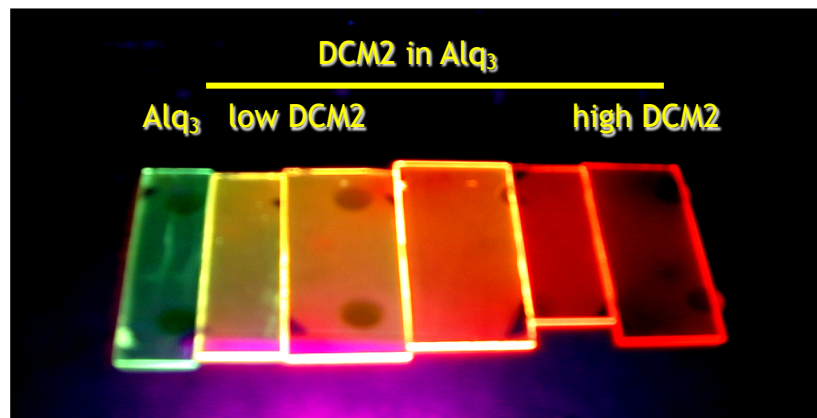
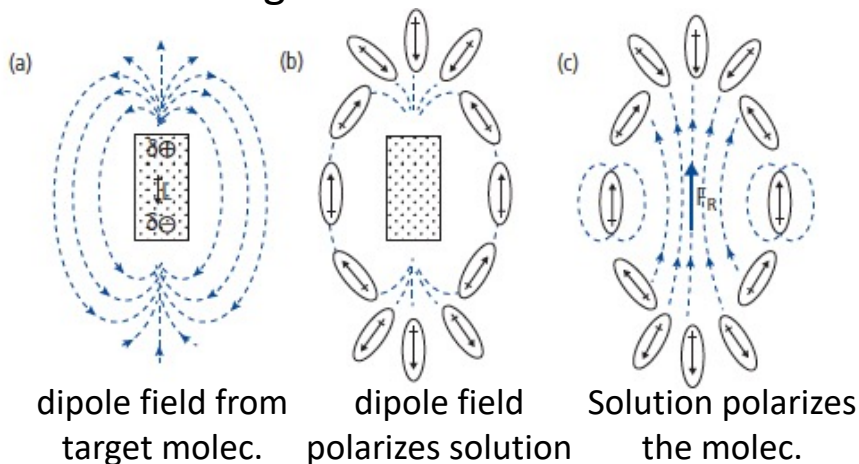
- The environment responds to changes in the dipole of the central molecule.
- The energy difference due to this response is the polarization energy
- *Positive solvatochromism* = red spectral shift = *bathochromic shift*.
- *Negative solvatochromism* = blue spectral shift = *hypsochromic shift*.

# Place a dipolar (fluorescent) molecule in increasingly polar solvents

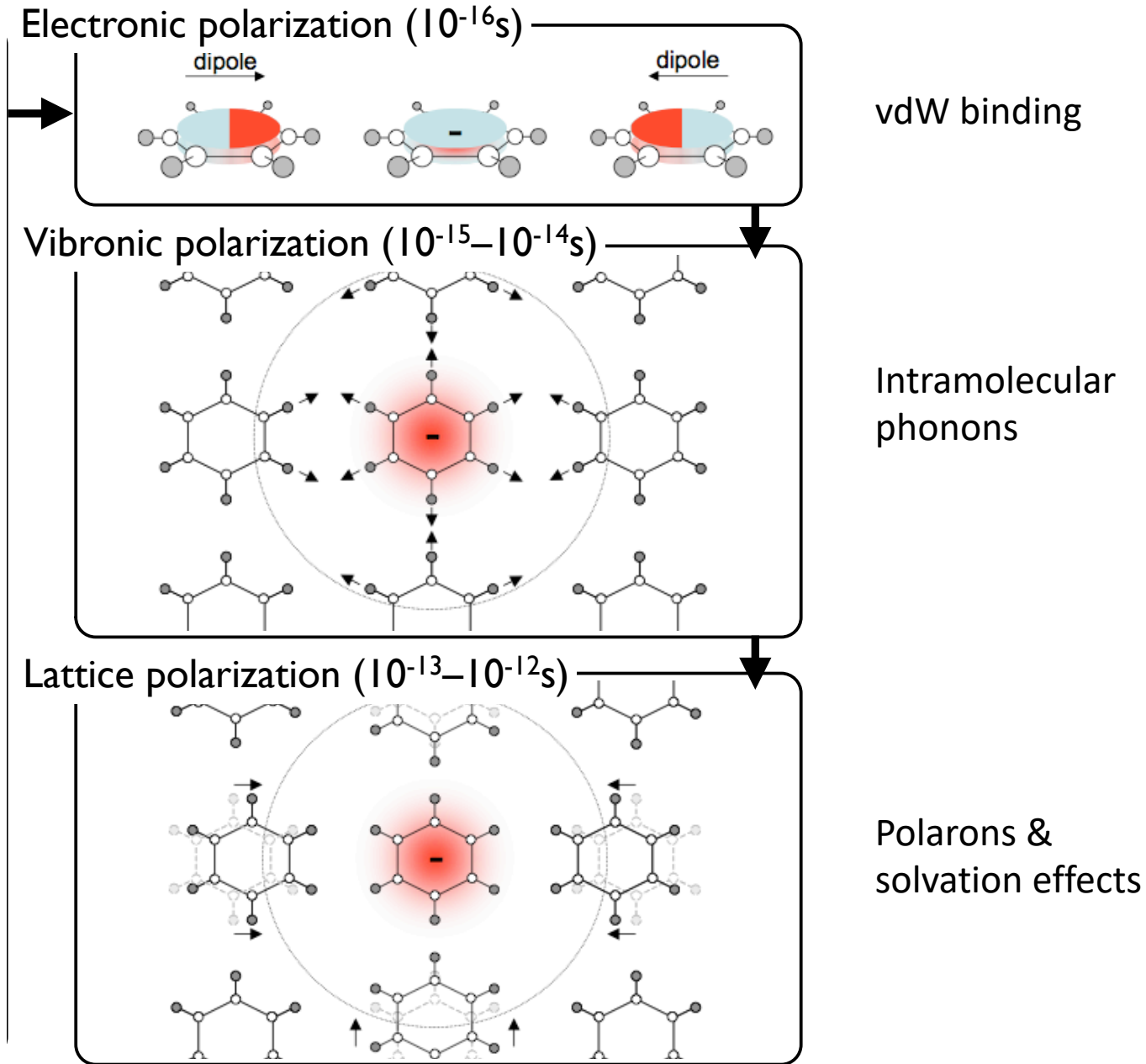


Bulovic, V., et al.. *Chem. Phys. Lett.*, 287, 455.

## The origin of solvatochromism



# Putting polarization in context



# Exciton Spin

- Organic solids are not strongly coupled
  - Individual molecular properties retained in the solid
  - Lack of degeneracy in the bands

⇒ Spin of individual molecules largely preserved in the solid

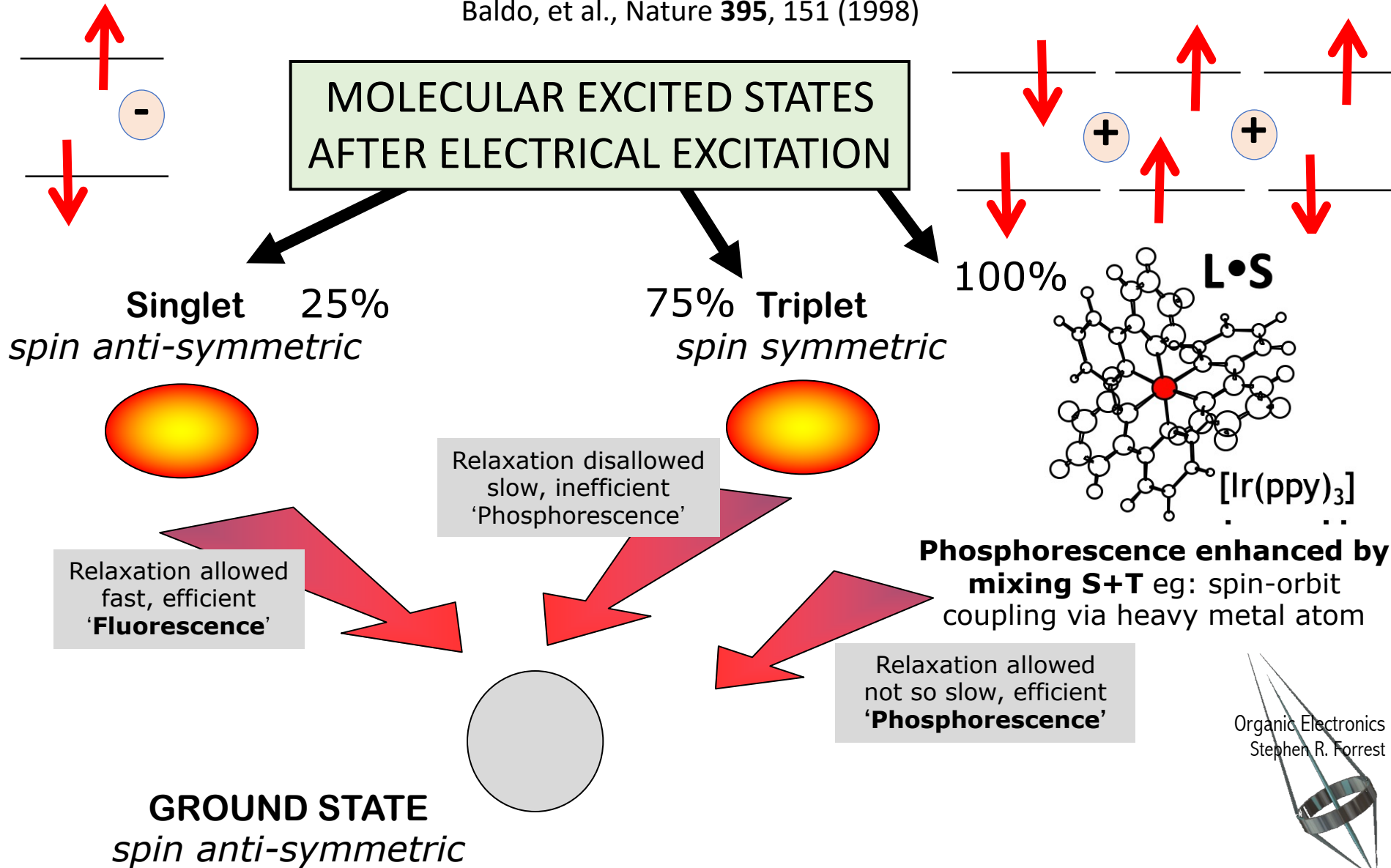
This situation is substantially different than for strongly correlated inorganic semiconductors and metals.

- Spin multiplicity (and its violation) determines optical properties
  - $S=0$ , singlets;  $S=1$ , triplets

# 100% Internal Efficiency via Spin-Orbit Coupling

Heavy metal induced electrophosphorescence  $\sim 100\%$  QE

Baldo, et al., Nature **395**, 151 (1998)



# Spin-Orbit Coupling

- Primary mechanism that results in violation of spin conservation
- Results in phosphorescence
- A result of quantum mechanical interactions of electron spin and relativistic orbital angular momentum

Magnetic field due to a charge of velocity  $\mathbf{v}$  in field  $\mathbf{F}$ :  $\mathbf{B} = -\frac{\mathbf{v} \times \mathbf{F}}{c^2}$

$$\text{and } \mathbf{F}(\mathbf{r}) = -\hat{\mathbf{r}} \frac{dV}{dr} \quad \mathbf{B} = \frac{\mathbf{v} \times \hat{\mathbf{r}}}{c^2} \frac{dV}{dr}$$

Orbital angular momentum is given by:  $\mathbf{l} = \mathbf{r} \times m_e \mathbf{v}$

Giving: 
$$\mathbf{B} = -\frac{1}{m_e r c^2} \frac{dV}{dr} \mathbf{l}$$

As in the case for an electric dipole, the energy due to a magnetic dipole moment,  $\mathbf{m}$  is

$$E_{\text{int}} = -\mathbf{m} \cdot \mathbf{B}$$





# Spin-Orbit Coupling, cont'd

The magnetic moment due to electron spin is:  $\mathbf{m}_s = -g_s \mu_B \frac{\mathbf{s}}{\hbar} = -g_s \frac{q}{2m_e} \mathbf{s}$

This gives spin-orbit coupling *in the electron reference frame* of

$$H_{so} = -g_s \frac{q}{2m_e^2 c^2} \frac{1}{r} \frac{dV}{dr} \mathbf{l} \cdot \mathbf{s}$$

Relativistic effects: precession of the spin in its orbit in the laboratory frame gives:

$$\mathbf{B} \rightarrow -\frac{\mathbf{v} \times \mathbf{F}}{2c^2}$$

From which we finally arrive at:

$$H_{so} = -\frac{q}{2m_e^2 c^2} \frac{1}{r} \frac{dV}{dr} \mathbf{l} \cdot \mathbf{s} = \xi(r) \mathbf{l} \cdot \mathbf{s}$$

Now, for a hydrogenic atom:  $V(r) = -Zq / 4\pi\epsilon_0 r$  such that:  $\xi(r) = -\frac{Zq^2}{8\pi\epsilon_0 m_e^2 c^2} \frac{1}{r^3}$

$$(R_{nl} \sim (Z/a_0)^{3/2})$$

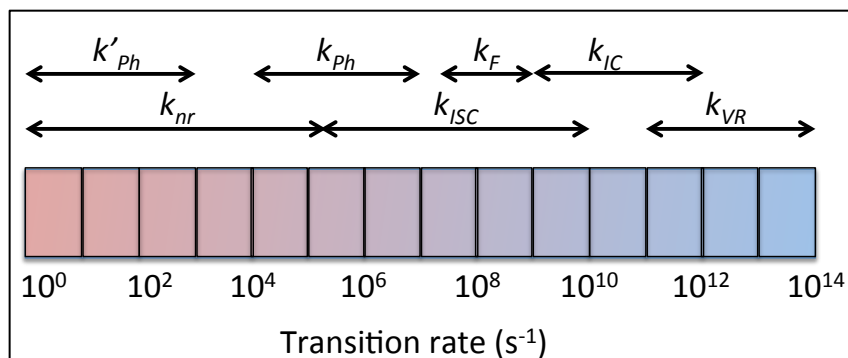
Using the hydrogenic wavefunctions  $|nlm_l\rangle = R_{nl}(r)Y_{lm_l}(\theta, \phi)$

$$E_{so} = \frac{2\pi\alpha^2 R_{nl} Z^4 c}{n^3 l(l+\frac{1}{2})(l+1)\hbar} \langle \mathbf{l} \cdot \mathbf{s} \rangle$$

Fine structure

Rydberg

# Characteristic Transition Rates



$k_{ph}'$  = phosphorescent transition rate in the absence of S-O coupling  
 $k_{ph}$  = phosphorescent transition rate in the presence of S-O coupling

Quantum yields: (Ratio of photons emitted to photons absorbed into  $4\pi$  solid angle)

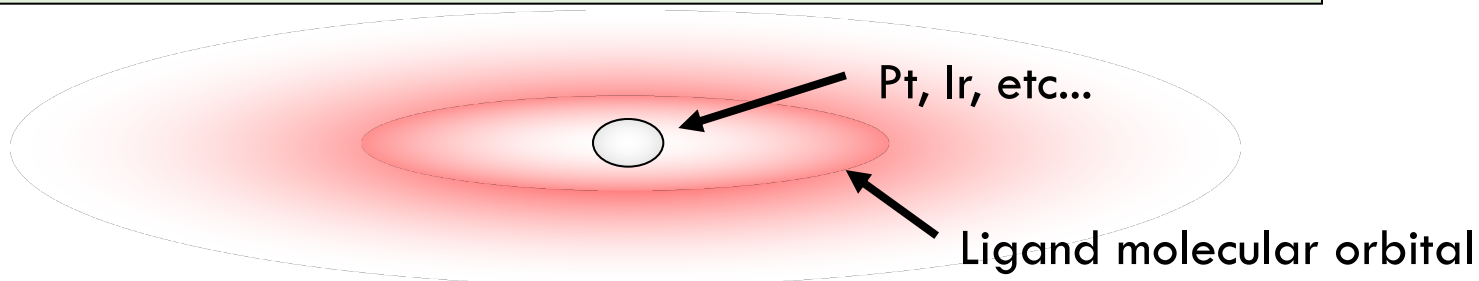
Fluorescence: 
$$\Phi_F = \frac{k_F}{k_F + k_{nrS} + k_{ISC}}$$

Phosphorescence: 
$$\Phi_P = \frac{\Phi_{ISC} k_{Ph}}{k_{Ph} + k_{nrT}} \quad ; \quad \Phi_{ISC} = \frac{k_{ISC}}{k_{ISC} + k_F + k_{nrS}}$$

# Electrophosphorescence: 100% IQE Achieved

- Need to mix singlet and triplet states:  
- make both singlet and triplet decay allowed.

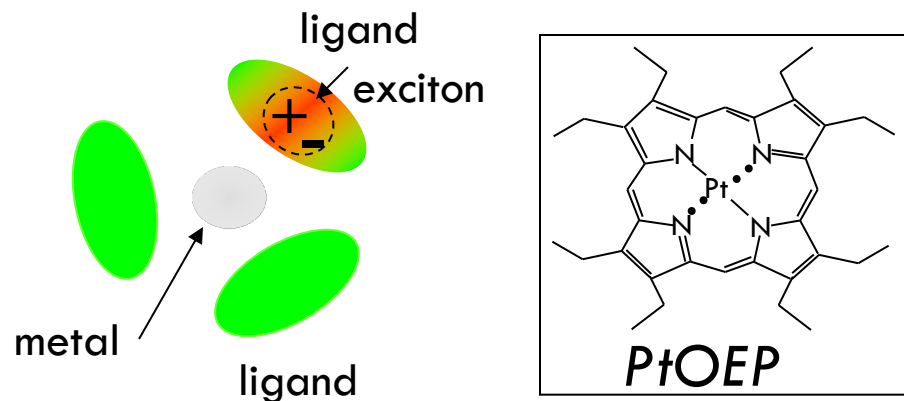
Use metal-organic complexes with heavy transition metals



**Spin orbit coupling mixes states: proportional to atomic number:  $Z^4$**

## Type I phosphor

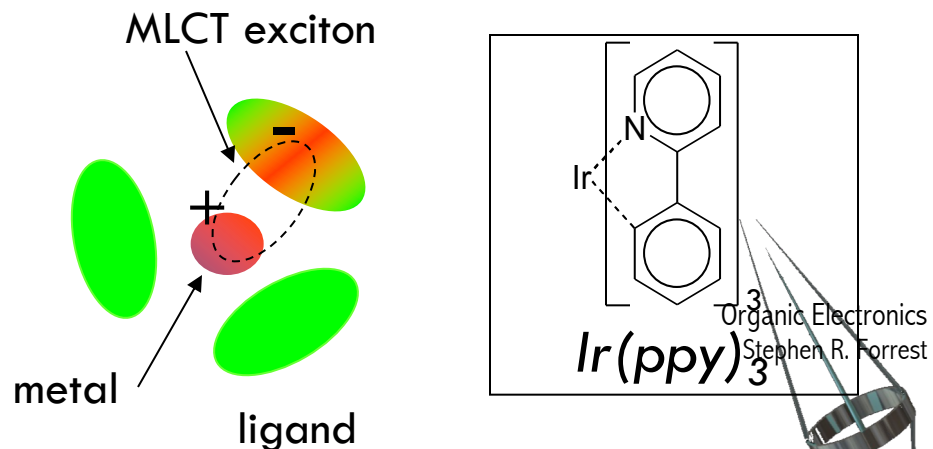
Exciton localized on organic



less mixing  $\sim 100 \mu\text{s}$  triplet lifetime

## Type II phosphor

Metal-ligand charge transfer exciton



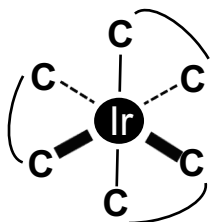
most mixing  $\sim 1 \mu\text{s}$  triplet lifetime

# Differences between Type I and Type II Phosphors

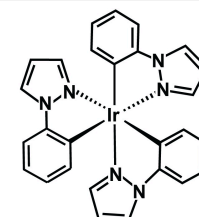
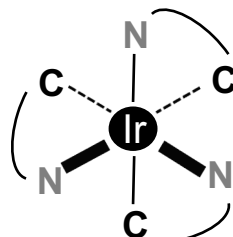
N-Heterocyclic carbene (NHC) ligand for blue

NHC Ir (III) complex =  $\text{Ir}(\text{C}^{\wedge}\text{C}:)_3$

Conventional design =  $\text{Ir}(\text{C}^{\wedge}\text{N})_3$

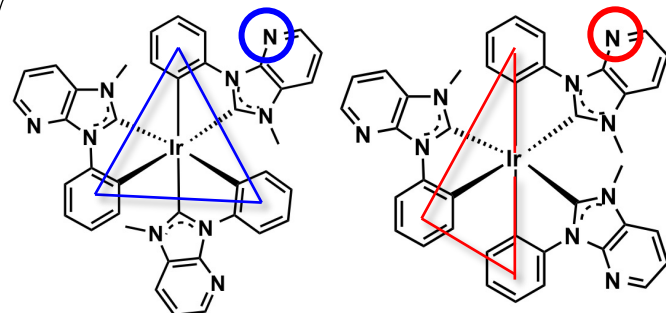


vs.



*fac*-Ir(ppz)<sub>3</sub>

PL (a.u.)



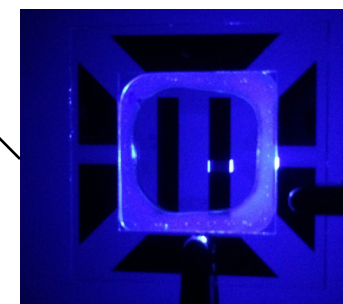
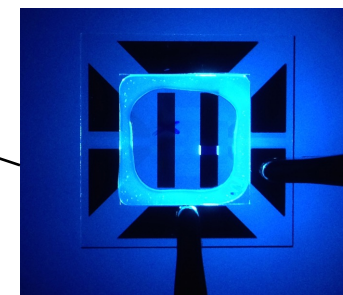
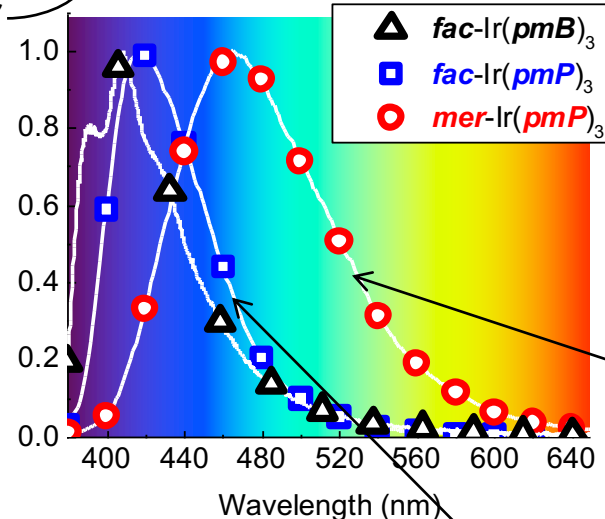
*fac*-Ir(pmP)<sub>3</sub>

Type I

*mer*-Ir(pmP)<sub>3</sub>

Type II

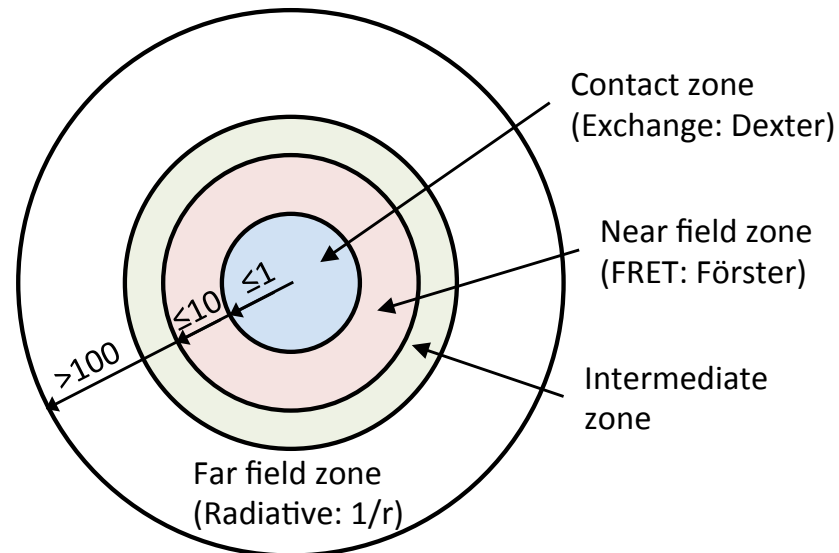
J. Lee, et al. Nat. Mater., 14, 92 (2016)



Property	<i>fac</i> -Ir(pmP) <sub>3</sub>	<i>mer</i> -Ir(pmP) <sub>3</sub>
Emission energy	3.0 eV	2.7 eV
Solvatochromism (in DCM)	-0.19 eV	-0.33 eV
Rigidochromic shift (300 → 77K)	+0.19 eV	+0.34 eV
FWHM change (300 → 77K)	58 → 30 nm	93 → 55 nm
Excited state dipole	Small (localized)	Large (extended)

# Energy Transfer

- If excitons are mobile in the solid, they must move from molecule to molecule
  - ✧ The microscopic “hopping” between neighboring molecules = energy transfer

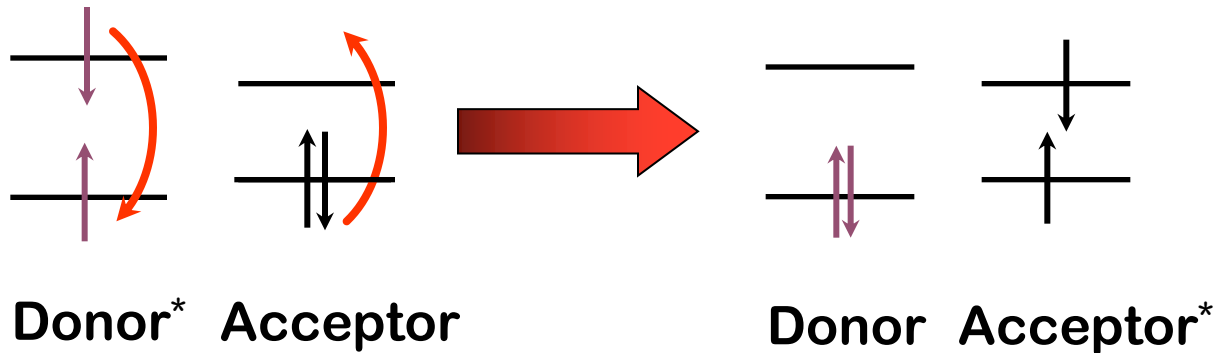
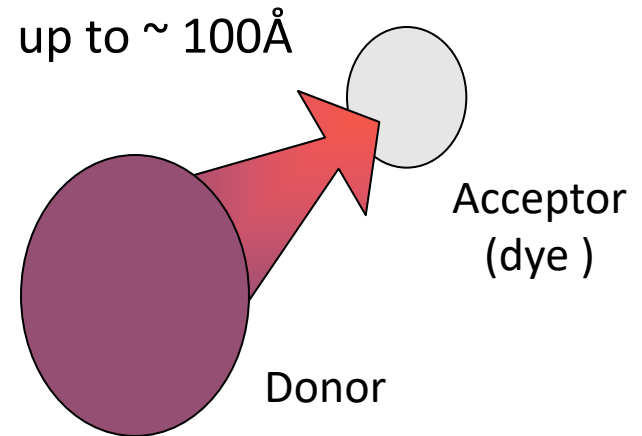


Different transfer ranges accessed by different processes

# Förster Resonant Energy Transfer (FRET)

- Förster, T. 1948. Zwischenmolekulare Energiewanderung Und Fluoreszenz. *Ann. Physik*, 55, 2.
- Förster, T. 1959. 10th Spiers Memorial Lecture: Transfer Mechanisms of Electronic Excitations. *Disc. Faraday Soc.*, 27, 7.

- resonant dipole-dipole coupling
- donor and acceptor transitions must be allowed



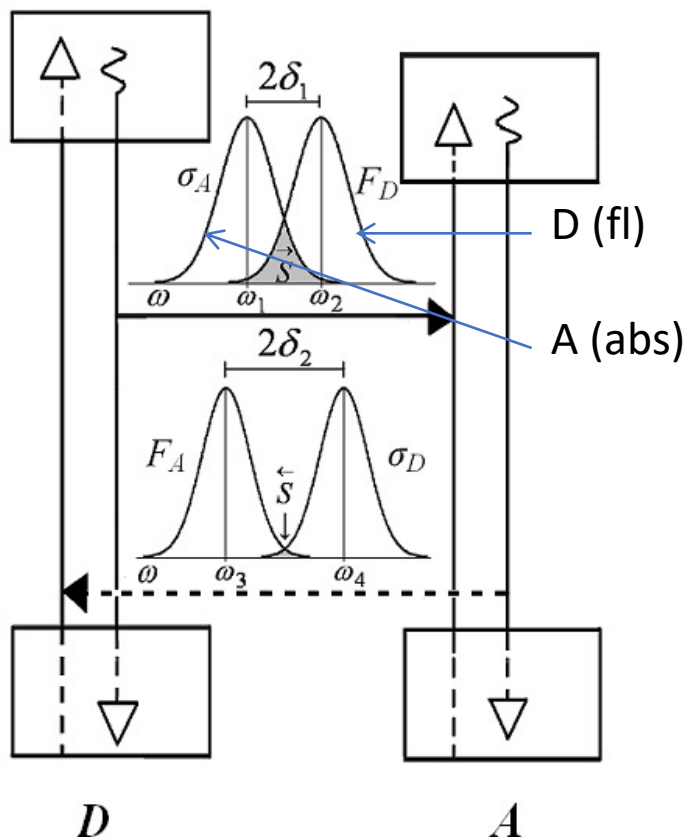
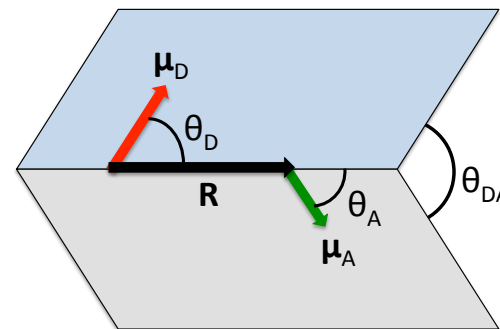
Efficient method for singlet transfer to fluorescent dye  
Triplet-singlet transfer possible if donor is strongly phosphorescent



# Transfer occurs via electric dipole interactions

$$H_{\text{int}} = \frac{q^2}{4\pi\epsilon_0\epsilon_r R^3} \left\{ \mathbf{r}_D \cdot \mathbf{r}_A - \frac{3(\mathbf{r}_D \cdot \mathbf{R})(\mathbf{r}_A \cdot \mathbf{R})}{R^2} \right\} + O\left(\frac{1}{R^4}\right) + \dots$$

Relative orientation of *excited state* donor and *ground state* acceptor dipoles determines coupling strength (i.e. its efficiency):



Calculating the transfer rate: FGR to the rescue!

$$k_{ET}(E) = \frac{2\pi}{\hbar} \left| \langle \Phi_f | H_{\text{int}} | \Phi_i \rangle \right|^2 \rho(E) = \frac{2\pi}{\hbar} |M_{fi}|^2 \rho(E)$$

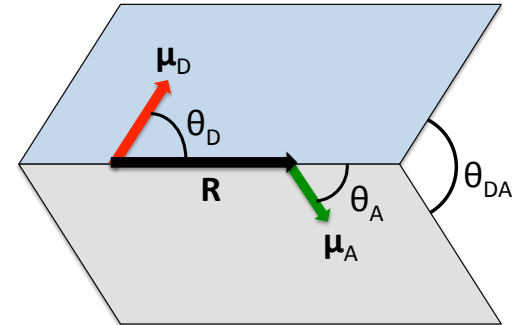
Overlap of the initial and final state energies simply equals the overlap of the donor fluorescence and acceptor absorption spectra!

# Calculating FRET

$$q^2 \left\{ \mathbf{r}_D \cdot \mathbf{r}_A - \frac{3(\mathbf{r}_D \cdot \mathbf{R})(\mathbf{r}_A \cdot \mathbf{R})}{R^2} \right\} = q^2 r_D r_A \{ \cos \theta_{DA} - 3 \cos \theta_D \cos \theta_A \} = \kappa_F \mu_D \mu_A$$

This gives us the **orientation factor**:

$$\kappa_F^2 = (\cos \theta_{DA} - 3 \cos \theta_D \cos \theta_A)^2$$



That is, FRET can only occur if the initial and final dipoles are non-orthogonal

and

$$|M_{fi}|^2 = \frac{\kappa_F^2 \mu_D^2 \mu_A^2}{(4\pi\epsilon_0)^2 n_r^4 R_{DA}^6} FC(E_{D^*}; E_{D^*} - \hbar\omega) \times FC(E_{A^0}; E_{A^0} + \hbar\omega)$$

Distance between dipoles  $\sim$  vdW energy!

$$k_{ET} = \frac{9c^4}{128\pi^5} \frac{\Phi_D}{N_A n_r^4 \tau_D} \frac{\kappa^2}{R_{DA}^6} \frac{M_{wA}}{\rho_{MA}} \int \frac{f_D(\nu) \alpha_A(\nu)}{\nu^4} d\nu$$

Absorption coeff't of acceptor

Fluorescence quantum yield of donor

Donor natural lifetime

Normalized fluorescence spectrum of donor

Molar mass/mass density of acceptor



# What FRET Implies

Simply put:

$$k_{ET} = \frac{1}{\tau_D} \left( \frac{R_0}{R_{DA}} \right)^6$$

Where

$$R_0^6 = \frac{9c^4}{128\pi^5} \frac{\kappa^2 \Phi_D}{N_A n_r^4} \frac{M_{wA}}{\rho_{MA}} \int \frac{f_D(\nu) \alpha_A(\nu)}{\nu^4} d\nu = KJ_\nu$$

$R_0$  is the **Förster radius**, or transfer distance.

That is, when  $R_0 = R_{DA}$ , then  $k_{ET} = 1/\tau_D$ , the natural radiative lifetime. Thus, the transfer efficiency is:

$$\eta_{ET} = \frac{\tau_D + \tau_{NR}}{\tau_{ET} + \tau_D + \tau_{NR}} \rightarrow \frac{1}{2}$$

(i.e. half of the energy is lost to transfer)

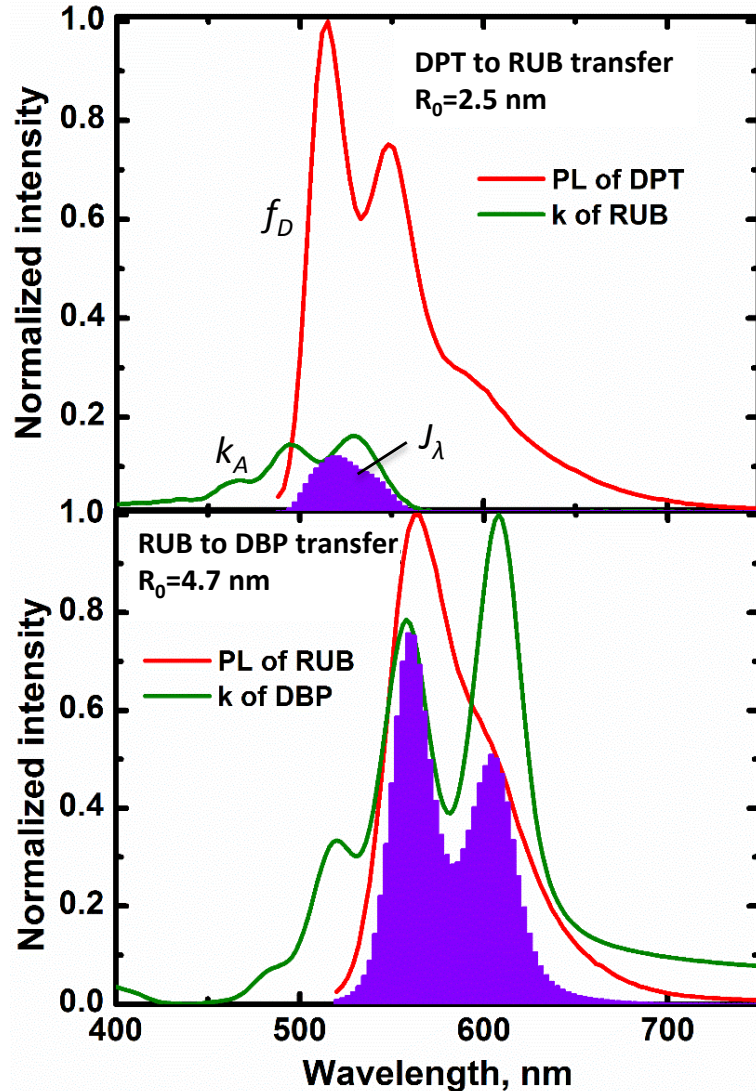
- Keep in mind that **FRET is orientation dependent** : this makes it a probe of molecular orientation by using polarized input light, and determining the polarization of the light emitted from the acceptors
- **FRET transfer time ~ radiative emission time:**  $k_{ET} \sim 1-10$  ns.
- Primary route to diffusion



# Two examples

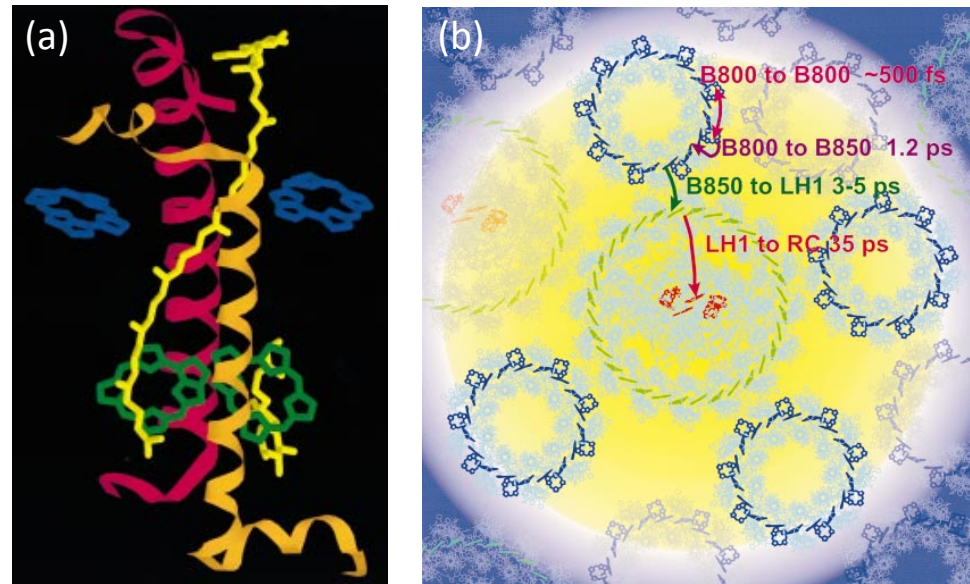
FRET is important in OLEDs, OPVs, biology,....

Typical molecules used in OPVs and OLEDs



Griffith & Forrest, Nano Lett., 14, 2353 (2014).

Photosynthetic light harvesting complex LH2

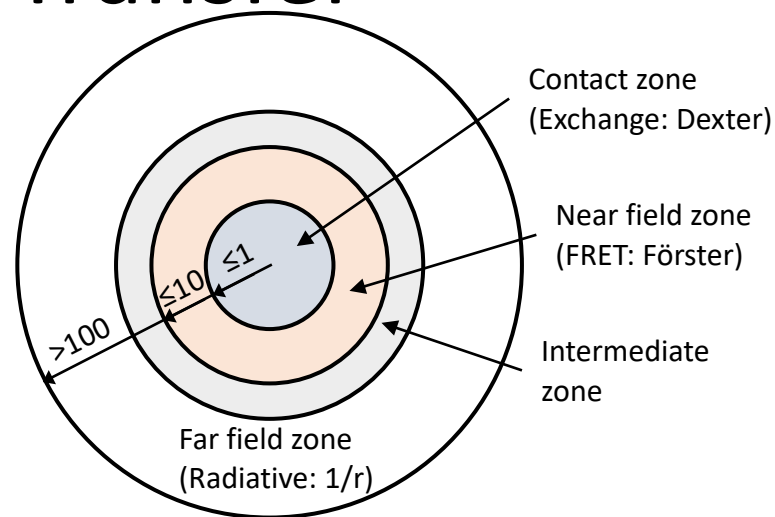


Sundström et al., J. Phys. Chem. B, 103, 2327 (1999).

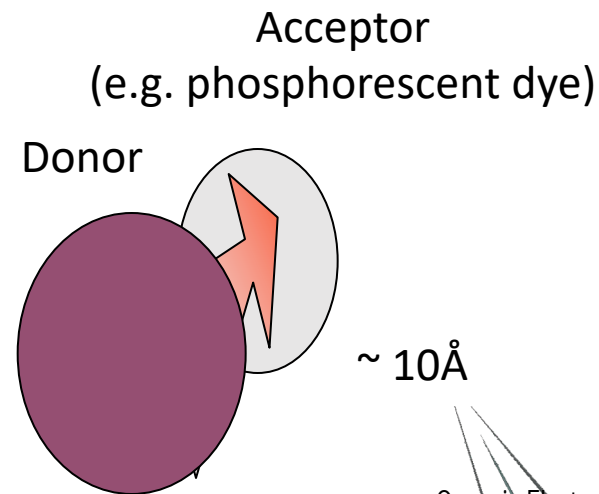
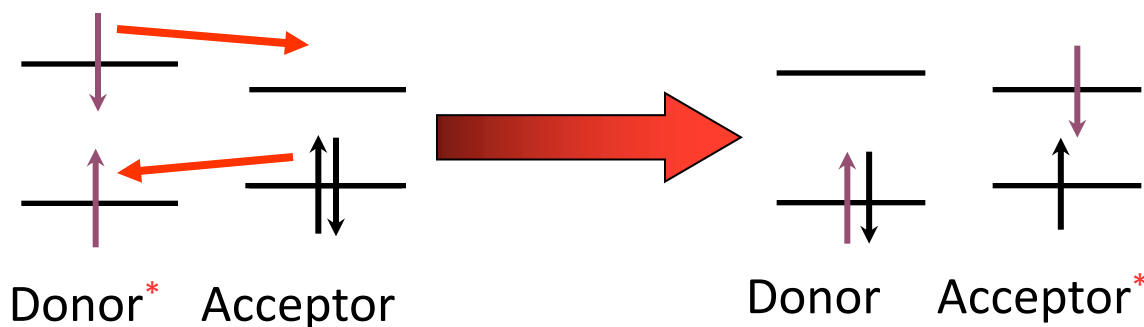
Organic Electronics  
 Stephen R. Forrest

# Exchange Energy Transfer

- Coherent transfer of excitons from donor to acceptor by simultaneous charge exchange in the contact zone
- Also known as **Dexter transfer**



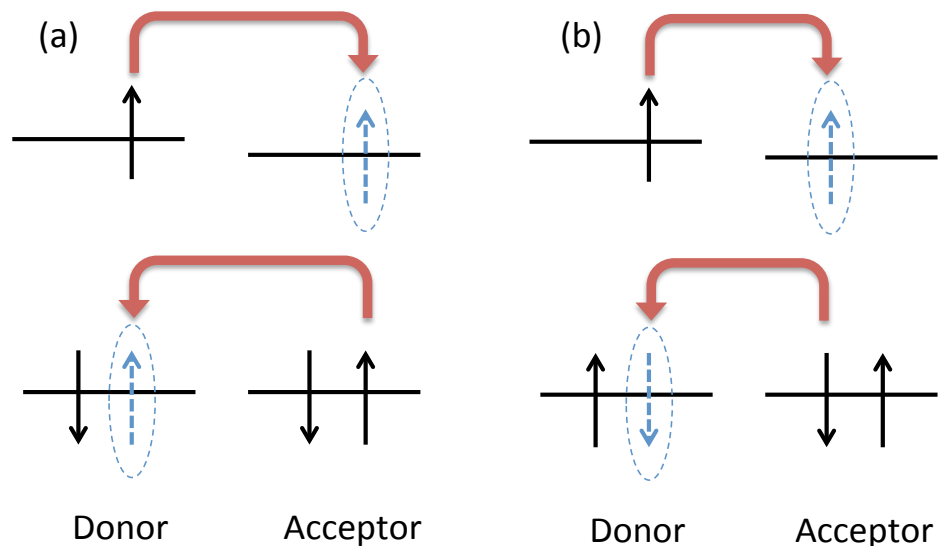
*spin is conserved: e.g. singlet-singlet or triplet-triplet*



Dexter, L. 1953. A Theory of Sensitized Luminescence in Solids. *J. Chem. Phys.* , 21, 836.



# Spin conserving exchange interactions



# Dexter Also Requires Resonance between D\* and A<sup>0</sup>


$$\text{FGR: } k_{ET} = \frac{2\pi}{\hbar} \Gamma^2 \int f_D(\omega) \sigma_A(\omega) d\omega$$

Overlap,  $\Gamma$ , is due to sum of the transition matrix elements over all initial and final states

$$\Gamma = \sum_{if} M_{fi} = \sum_{i,f} \langle \psi_f(\mathbf{r}_f, Q_f) | q^2 / 4\pi\epsilon_0 \epsilon_r R_{DA} | \psi_i(\mathbf{r}_i, Q_i) \rangle$$

For hydrogenic initial and final states, we get approximately

$$\Gamma^2 \propto \frac{q^2}{(4\pi\epsilon_0)^2 n_r R_{DA}^2} \exp(-2R_{DA} / L)$$

vdW radius 

Very rapidly decreasing  
“tunneling” between nearest  
neighbors

Finally resulting in the Dexter transfer equation:

$$k_{ET} \approx K \frac{q^2}{8\pi\epsilon_0^2 \hbar n_r R_{DA}^2} \left\{ \int f_D(\omega) \sigma_A(\omega) d\omega \right\} \exp(-2R_{DA} / L) = \frac{K' J_\omega}{R_{DA}^2} \exp(-2R_{DA} / L)$$

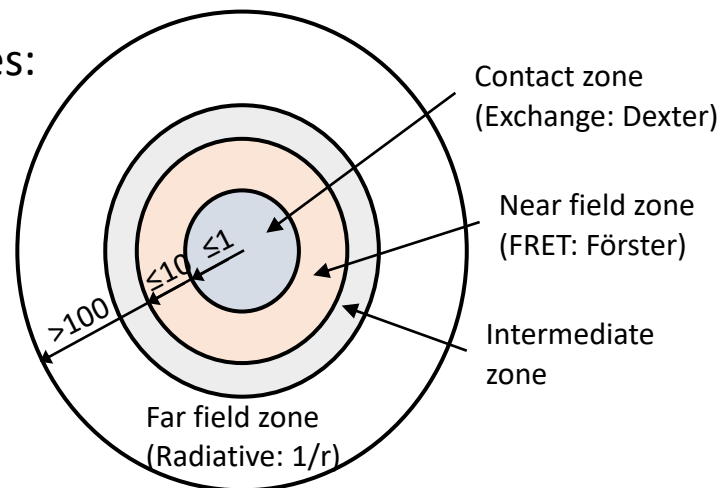
# Important facts about Dexter exchange

- **Spin of the donor and acceptor can change during exchange**
  - Spin of the excited and ground states cannot change
  - Effective in transfer of non-radiative triplet states (FRET is not since triplets are *generally* non-radiative)
- **Transfer is in the contact zone, only between nearest neighbors**
  - Range determined by vdW radius of the molecules
- **To first order (s-like states), there is no dependence on orientation**
  - $\kappa$  in FRET not found in exchange equation
  - Not due to dipole-dipole coupling; only Coulomb forces
- **Rate of exchange is on the order of a tunneling time**
  - $k_{ET} \sim 10^{10} - 10^{11} \text{s}^{-1}$

# Summarizing our discussion on energy transfer

The total rate is equal to the sum of the individual rates:

$$k_{ET,tot} = k_{ET,exch} + k_{ET,FRET} + k_{ET,rad}$$



Process	Transfer rate	Distance Dependence	Zone	Characteristic transfer distance
Exchange (Dexter)	$k_{ET,exch}$	$\frac{1}{R_{DA}^2} \exp(-2R_{DA} / L)$	Contact	$< 1$ nm
FRET	$k_{ET,FRET}$	$\frac{1}{R_{DA}^6}$	Near	$< 10$ nm
Radiative	$k_{ET,rad}$	$\frac{1}{R_{DA}^2} \exp(-\alpha_A R_{DA})$	Far	$> 100$ nm