

# Week 4

Optical Properties 2

Excitons

Spin

Energy Transfer

Chapter 3.6, 3.7.1, 3.7.4, 3.8

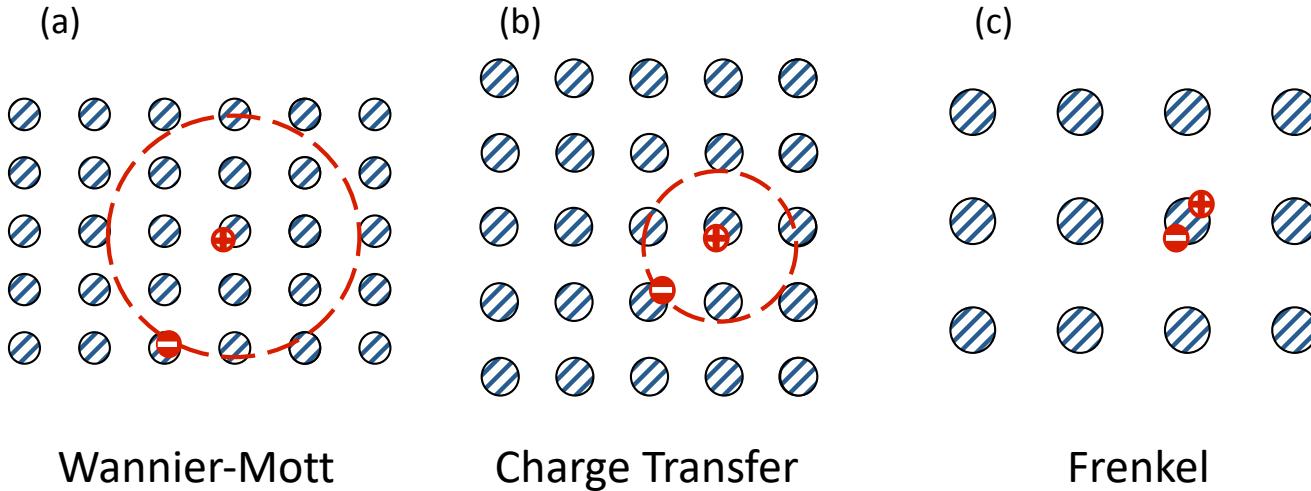
Organic Electronics  
Stephen R. Forrest



# 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



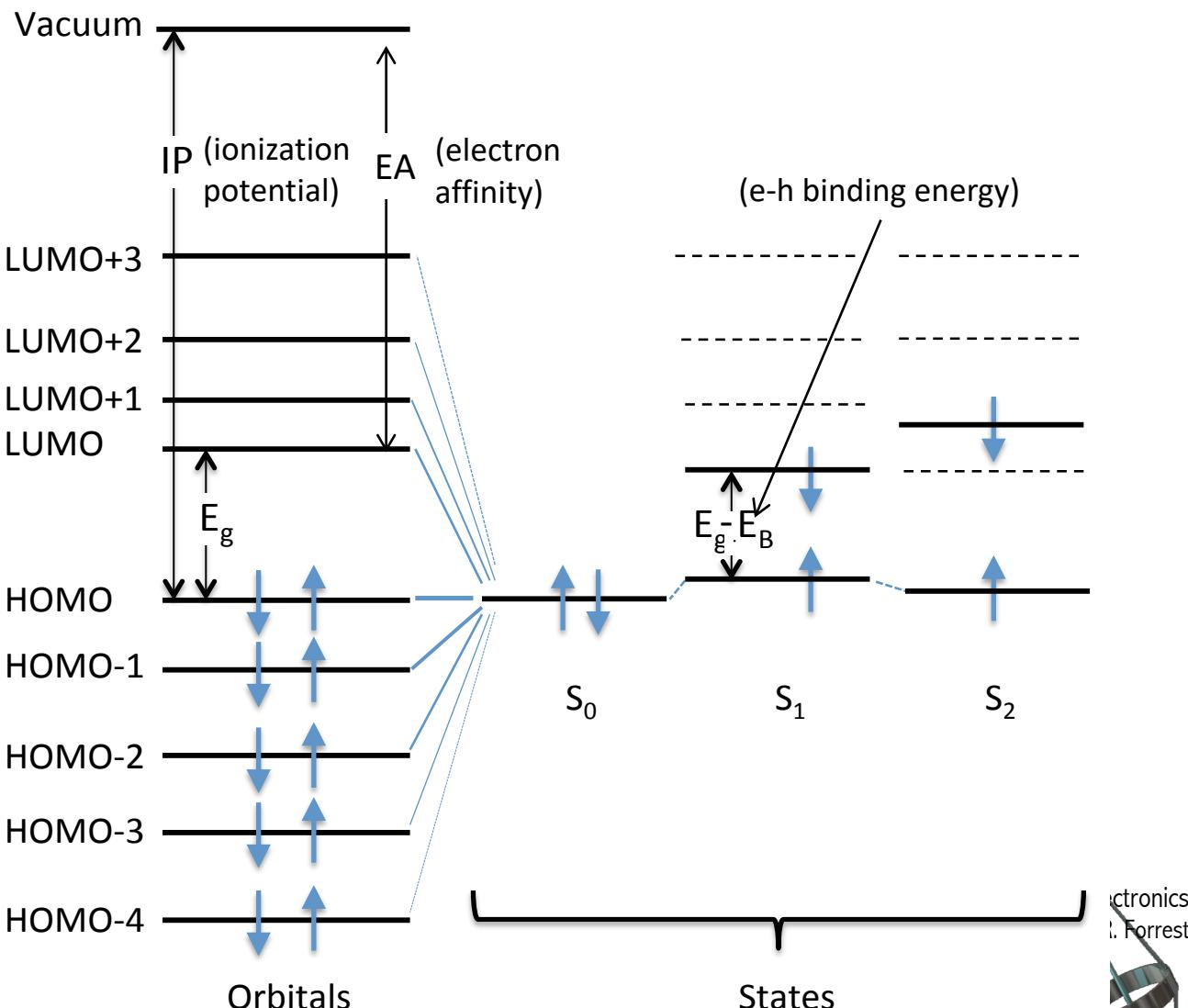
Bohr Model:

$$E_B = -\frac{q^2}{8\pi a_0 (\epsilon_r \epsilon_0)} \frac{1}{n^2} \quad a_0 = \frac{4\pi(\epsilon_0 \epsilon_r) \hbar^2}{m_r^* q^2}$$

| Medium                    | $\epsilon_r$ | $m_r^* / m_e$ | $a_0$<br>(Å) | $E_B$<br>(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         |

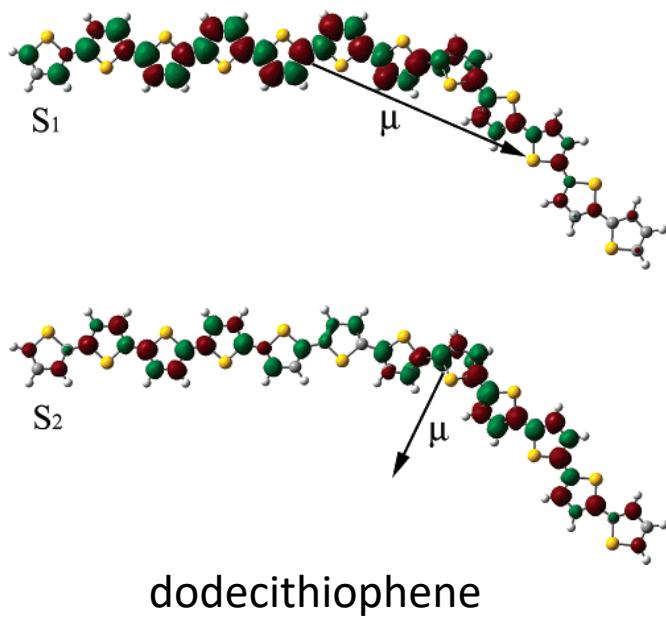
# Important distinctions between electronic *orbitals* and electronic *states*

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

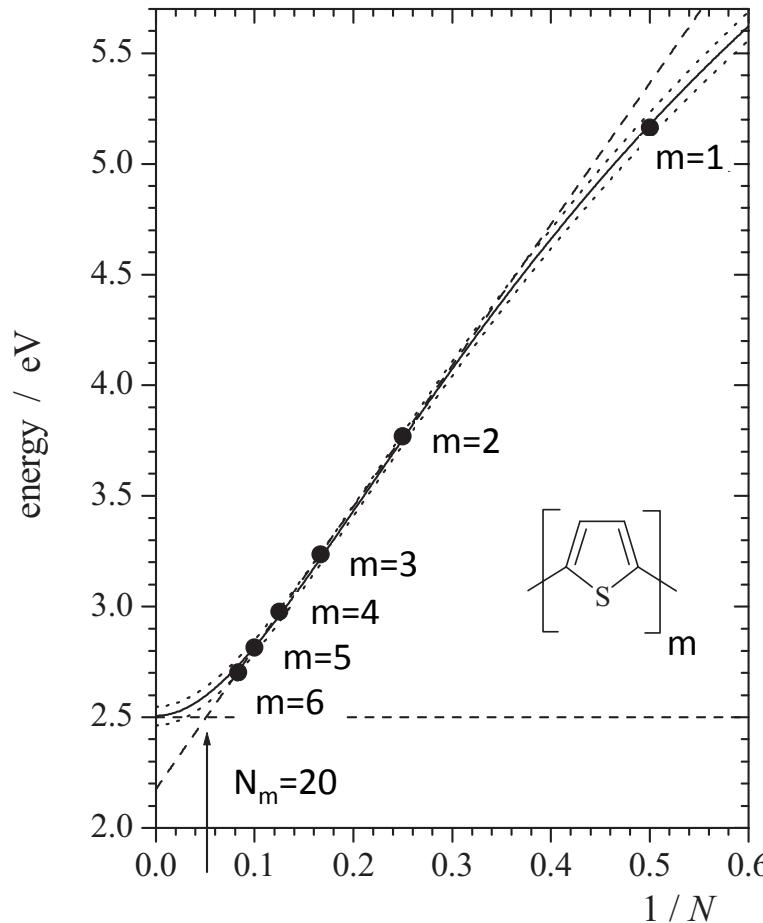


# How big is the excited state?

- 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

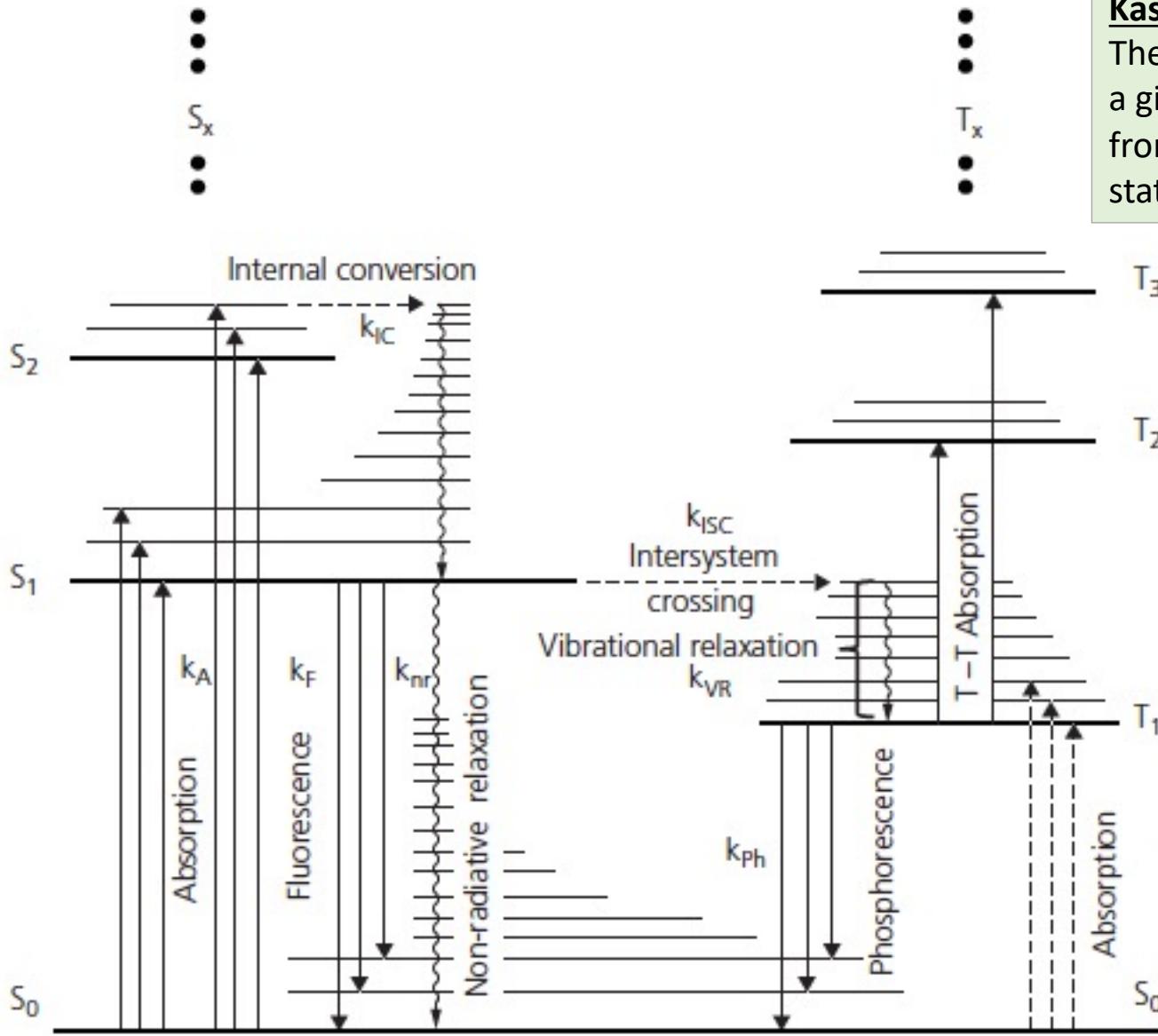


## Low energy absorption cutoff of thiophene oligomers vs. no. of monomer segments, $m$ .



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

# 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  $|\mu_{if,e}|^2 FC_{if}$

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

Ave. emission freq.

Einstein spontan. abs.

Normalized lineshape

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

This leads to more practical expressions for the oscillator strength:

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

Decadic molar absorption  
Coefficient [ $\text{l}\cdot\text{cm}^{-1}\cdot\text{M}^{-1}$ ]

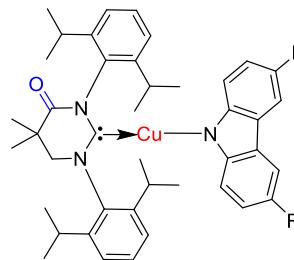
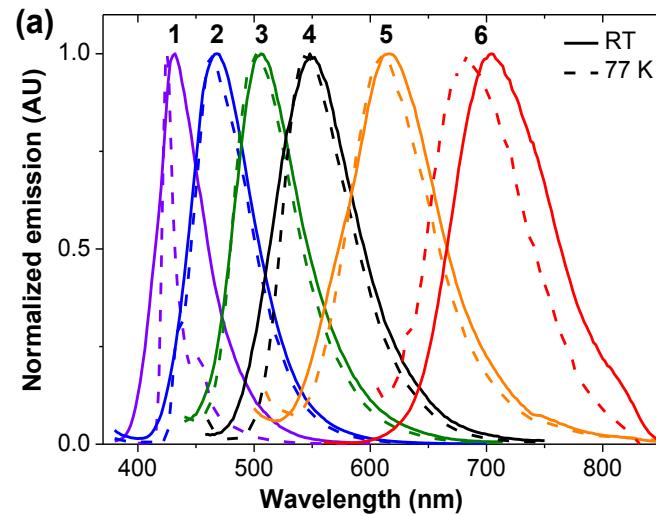
wavenumber= $v/c$

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

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.

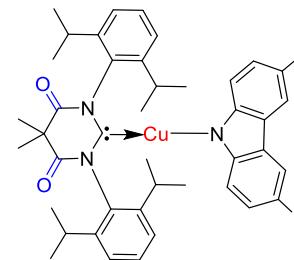


Carbene = MAC\*

R, R' = CN (1)

R = CN, R' = H (2)

R, R' = H (3)

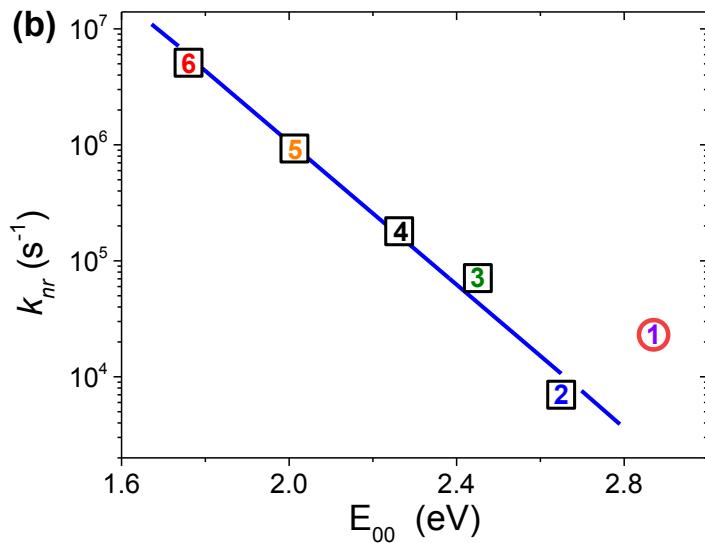


Carbene = DAC\*

R, R' = CN (4)

R = CN, R' = H (5)

R, R' = H (6)



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

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

$\Omega$  = number of modes contributing to the maximum phonon energy,  
 $= \frac{1}{2}$  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  $\text{H}_2$  molecule.
  - Ground state:  $\psi_G(\mathbf{r}_1, \mathbf{r}_2) = \psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2)$ :  $\psi(\mathbf{r}_{1,2})$  = 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:

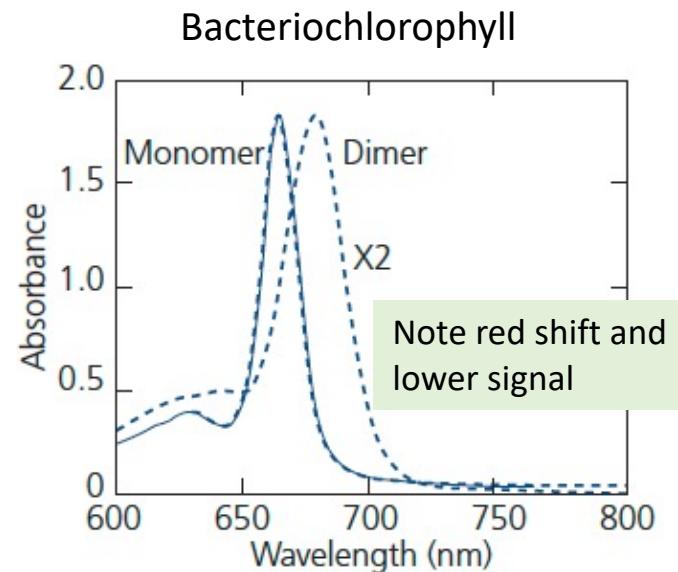
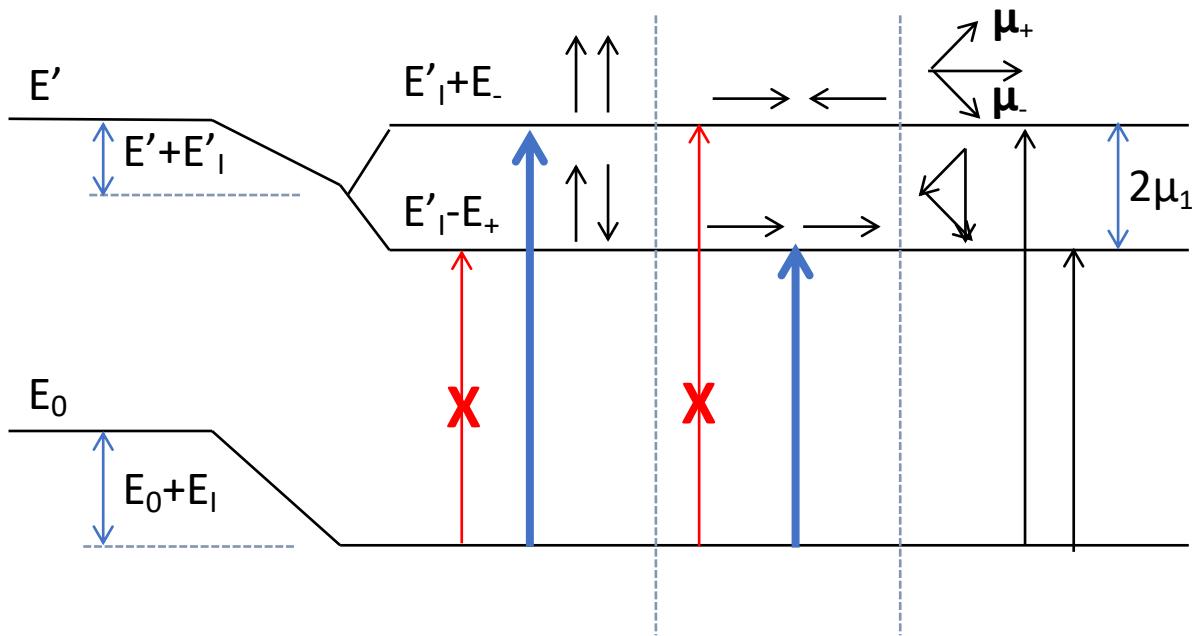
$$E'_I = \langle \psi'_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) | H_{\text{int}} | \psi'_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) \rangle : \text{Coulomb energy}$$

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

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

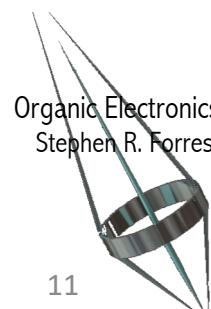
# The Dimer Spectrum



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

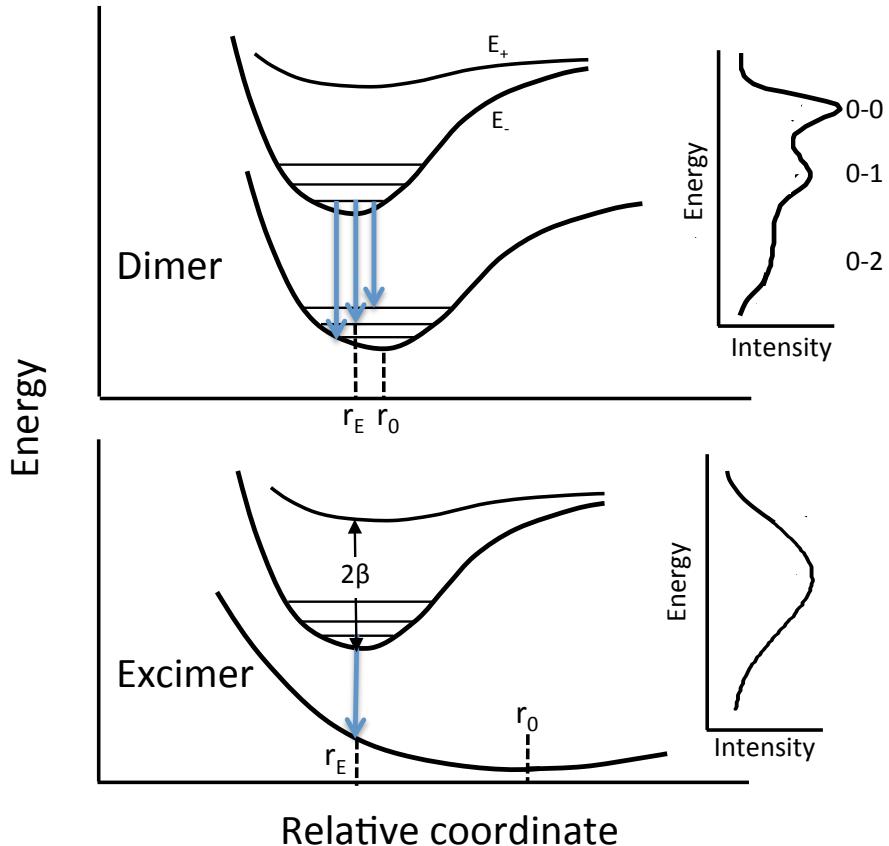
Symmetry prevents some transitions from occurring

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



# Excimers and Exciplexes

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

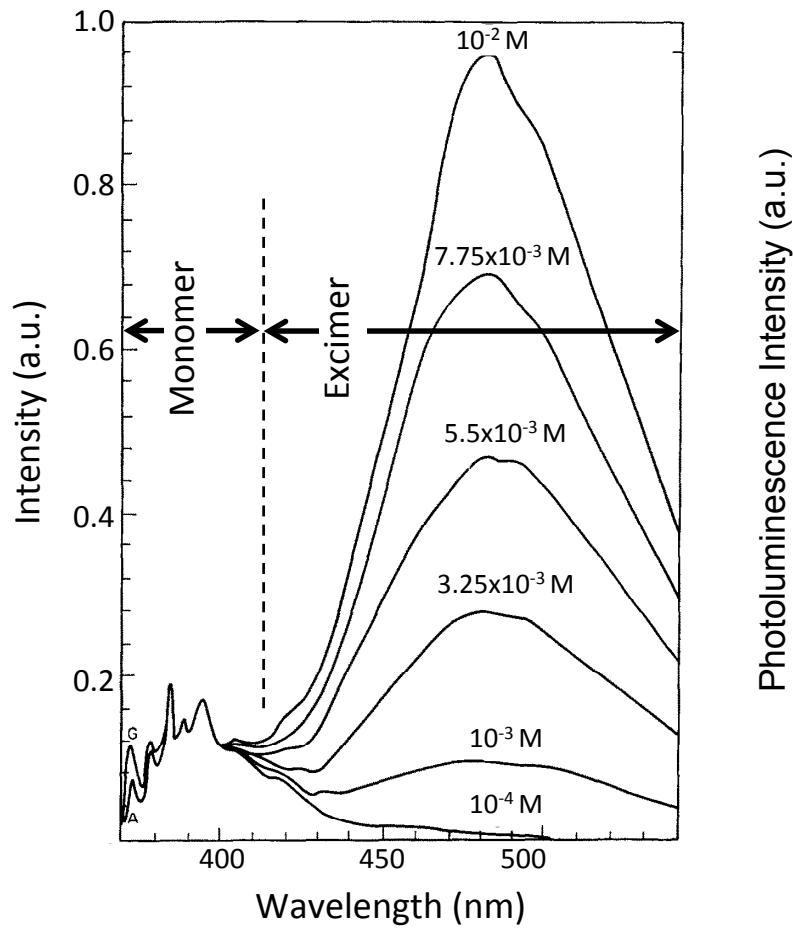


Getting to the excimer can  
be a multi-step process

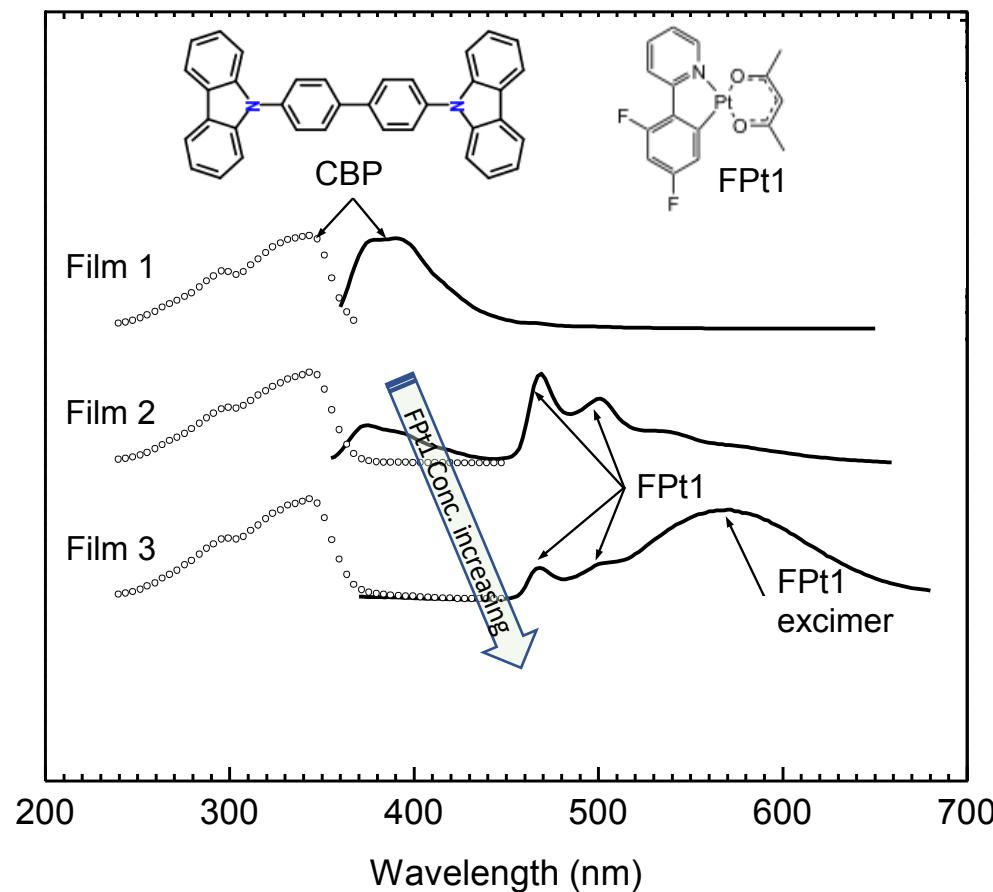


# Examples of Excimer Emission in Fluorophors and Phosphors

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



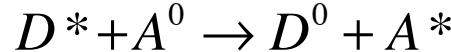
Excimer Phosphorescence  
Coexistence of monomer and excimer emission = white light



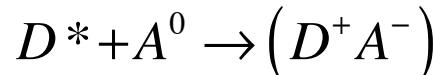
# Exciplexes

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

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



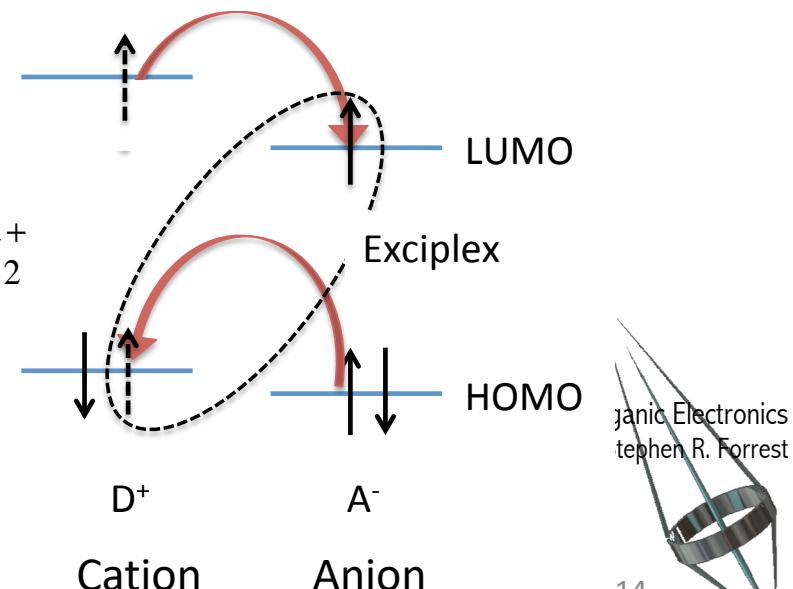
- Since there is an energy difference between D and A, an exciplex results in charge transfer (shared charge) between molecules:



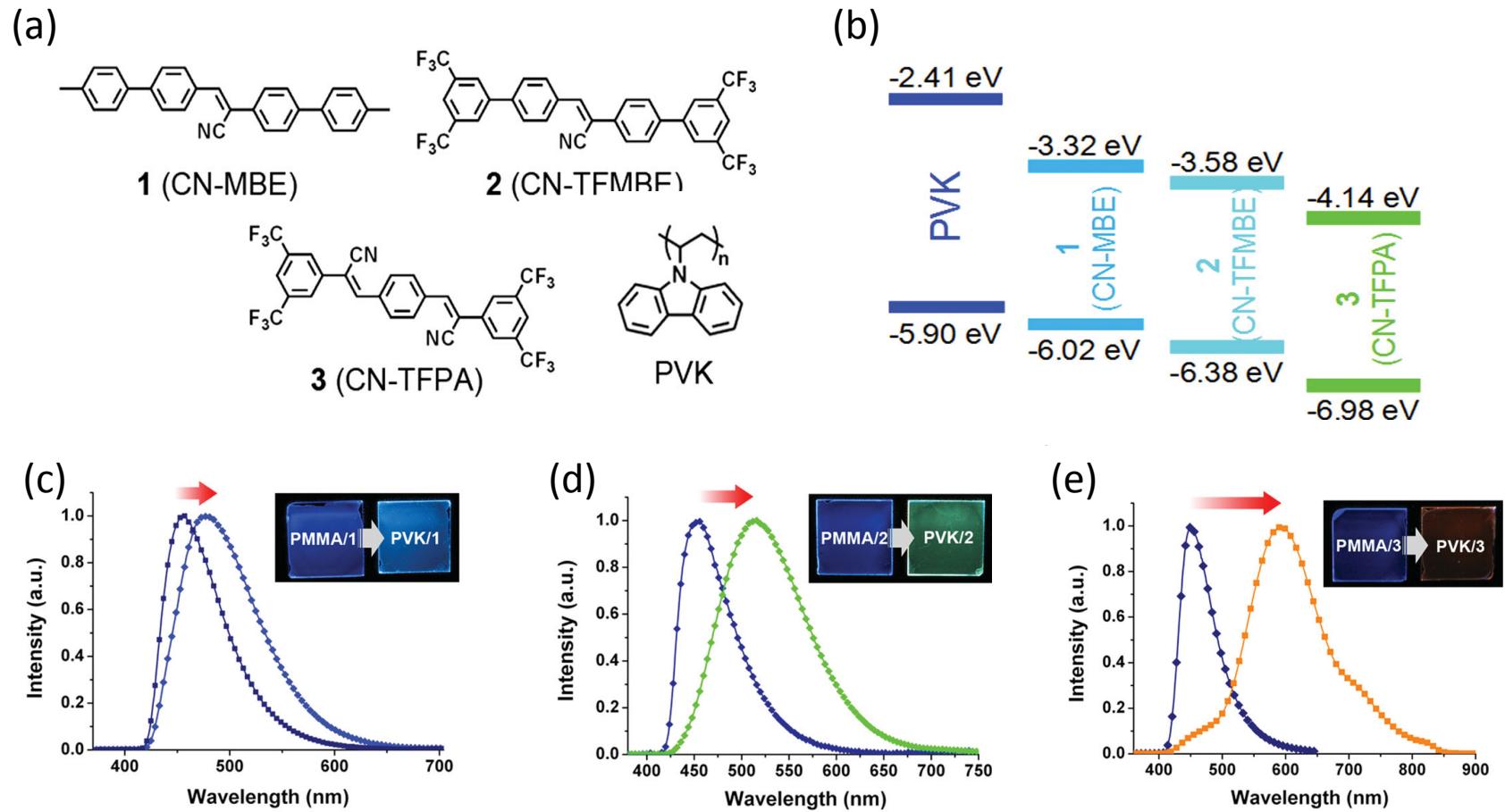
- Excitation shared by two different molecules forming a complex: the amount of charge transfer depends on energy asymmetry

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

$$\psi'_T = \alpha \psi'_1 \psi_2 + \beta \psi_1 \psi'_2 + \gamma \psi_1^+ \psi_2^- + \delta \psi_1^- \psi_2^+$$



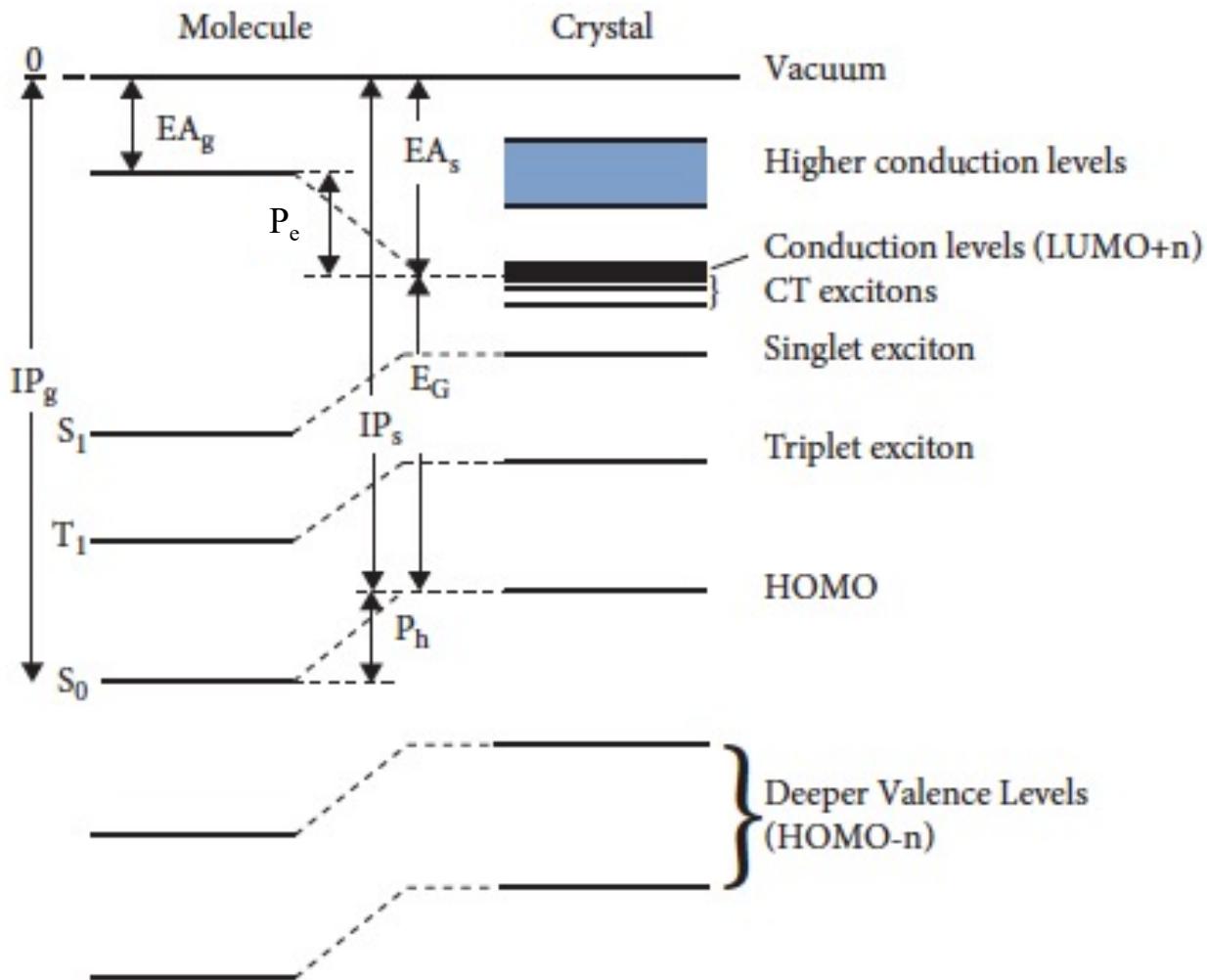
# Example of an Exciplex



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

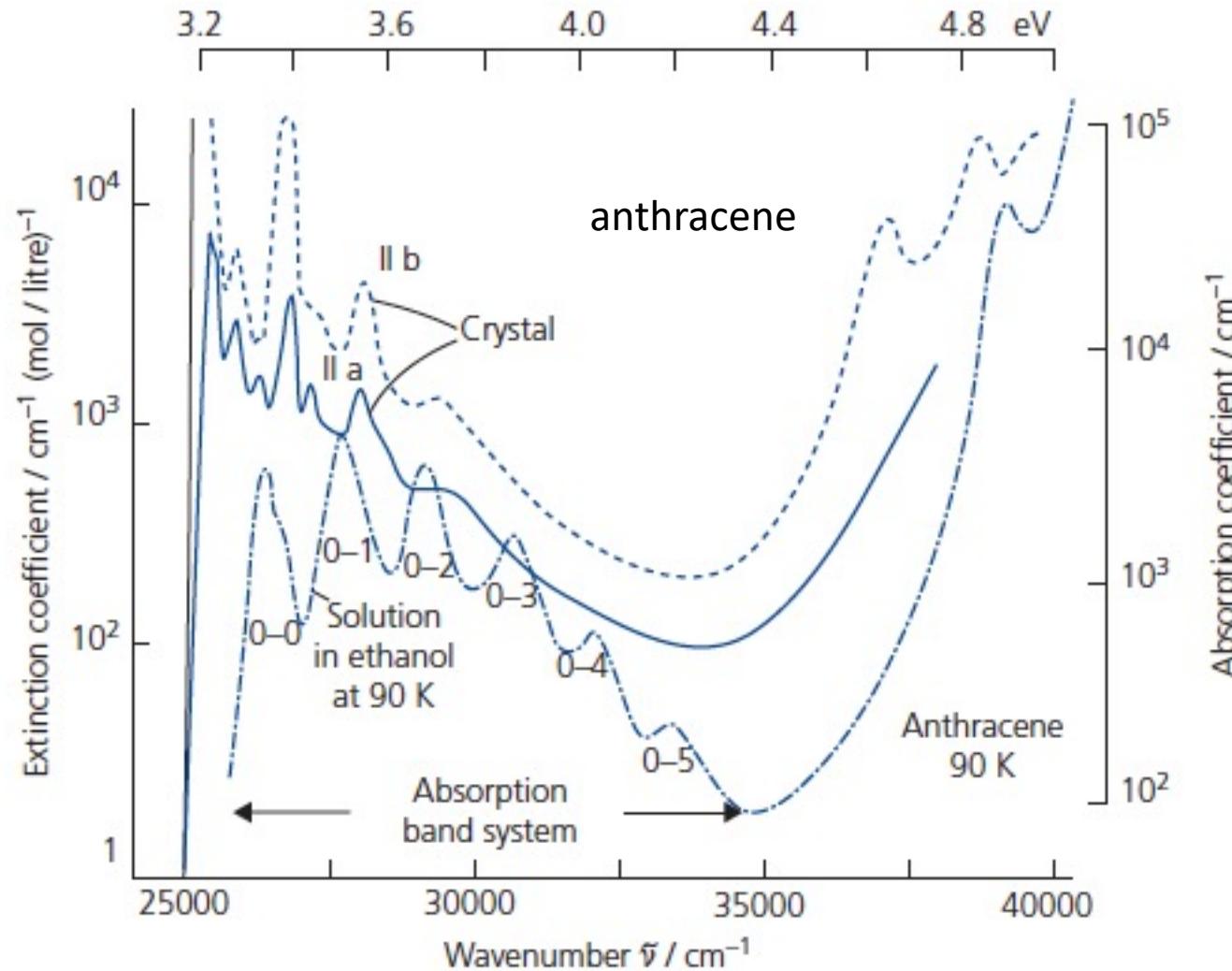
# The correspondence between a molecule and a solid

- IP=ionization potential
- EA=electron affinity
- P=Polarization energy
- g,s=gas, solid



Lyons Model

# Going from molecules to solids

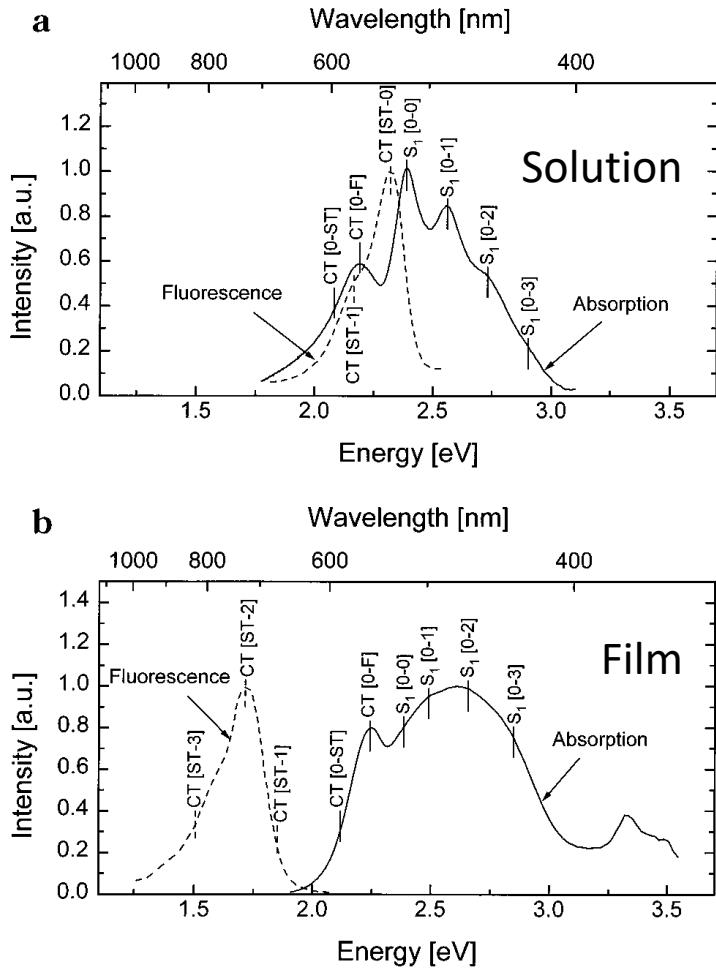


Vibronic progression loses definition in the solid: why?

# Charge Transfer States: Intermediates between molecule and solid

Tight packing in PTCDA leads to strong CT oscillator strength

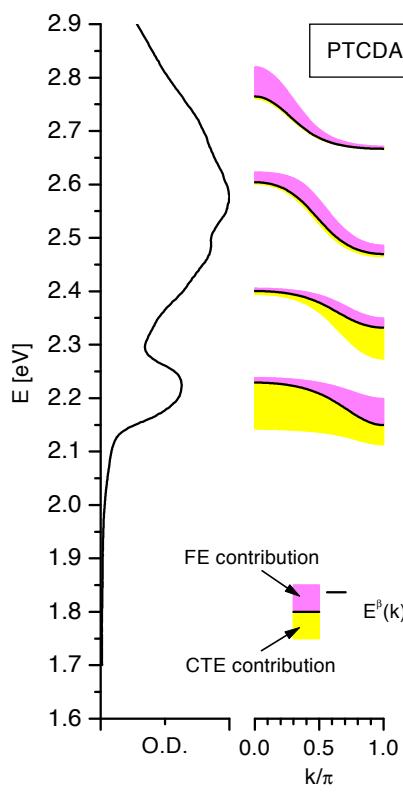
a



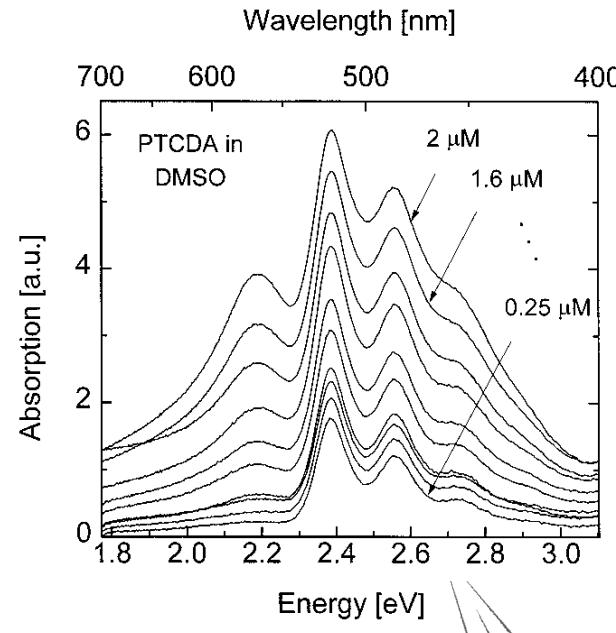
Bulovic, V., et al. 1996. *Chem. Phys.*, 210, 1.

a) Absorption

b) Band Structure



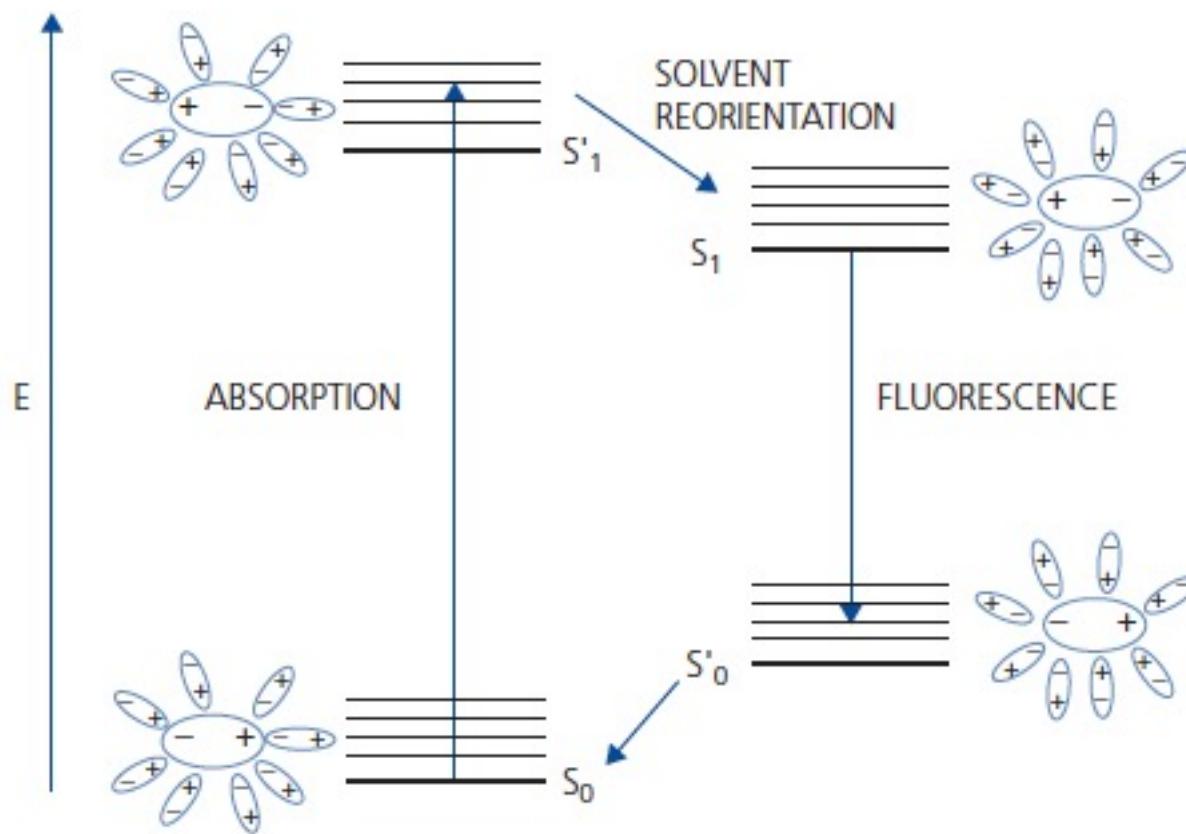
How can we be sure it's a  
CT state?



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

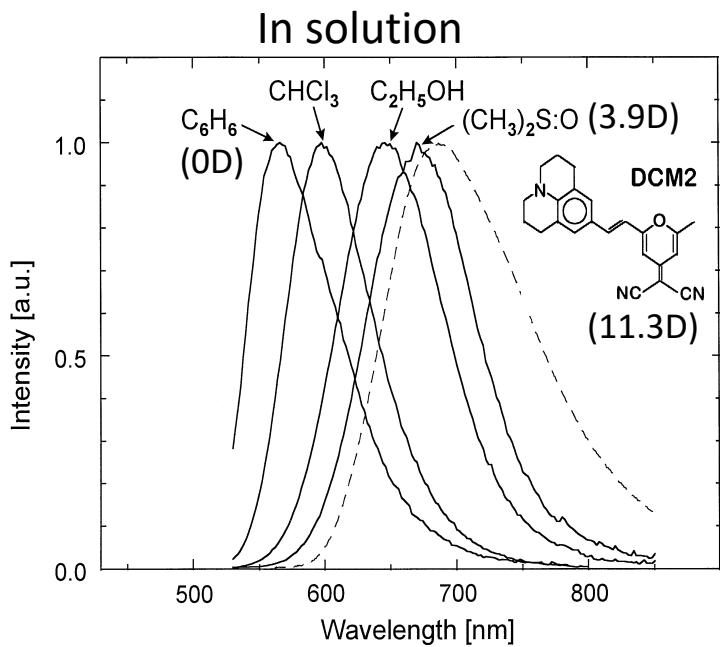
Hoffmann, M., et al. 2000. *Chem. Phys.*, 258, 73.

# Solvatochromism and Polarization

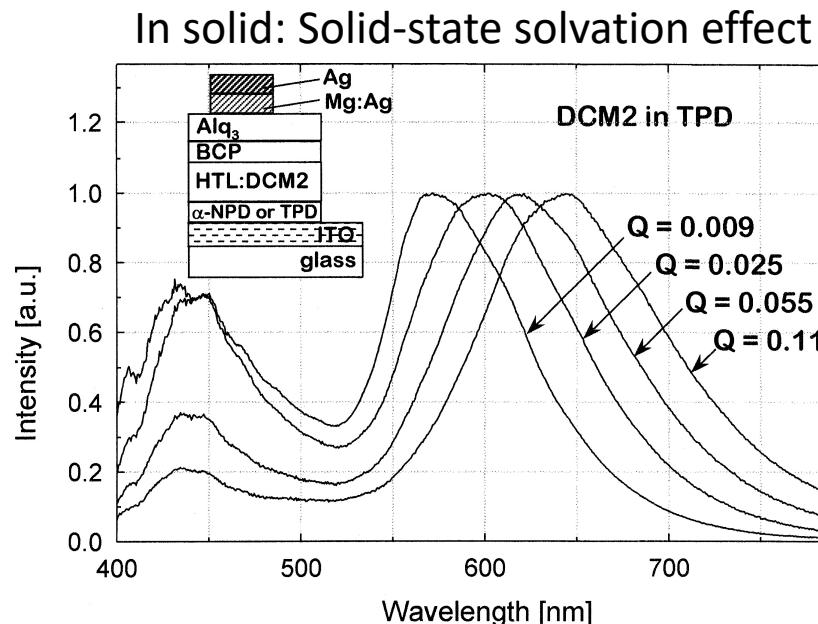
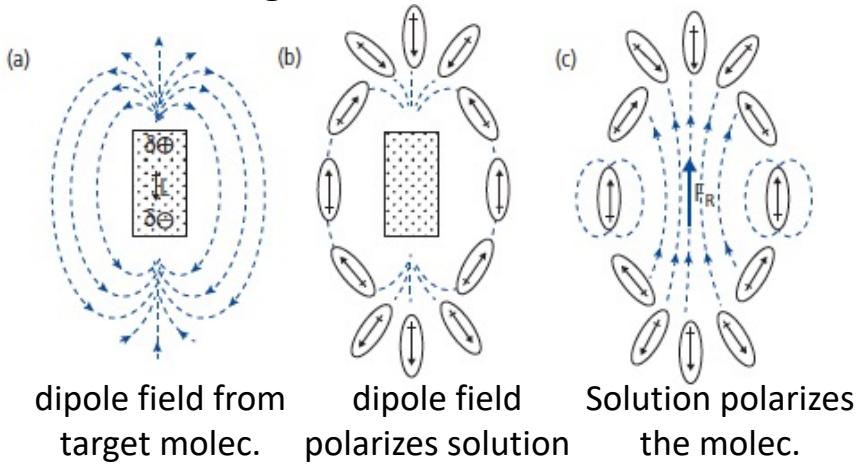


- The environment responds to changes in the dipole of the central molecule.
- The energy difference due to this response is the polarization energy
- *Positive solvatochromism* = red spectral shift = *bathochromic shift*.
- *Negative solvatochromism* = blue spectral shift = *hypsochromic shift*.

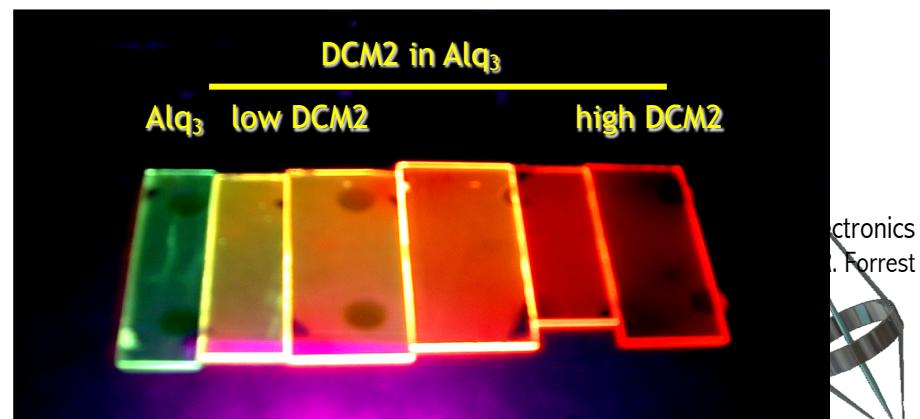
# Place a dipolar (fluorescent) molecule in increasingly polar solvents



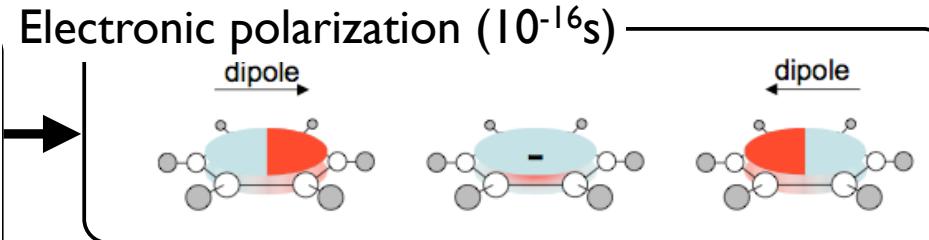
## The origin of solvatochromism



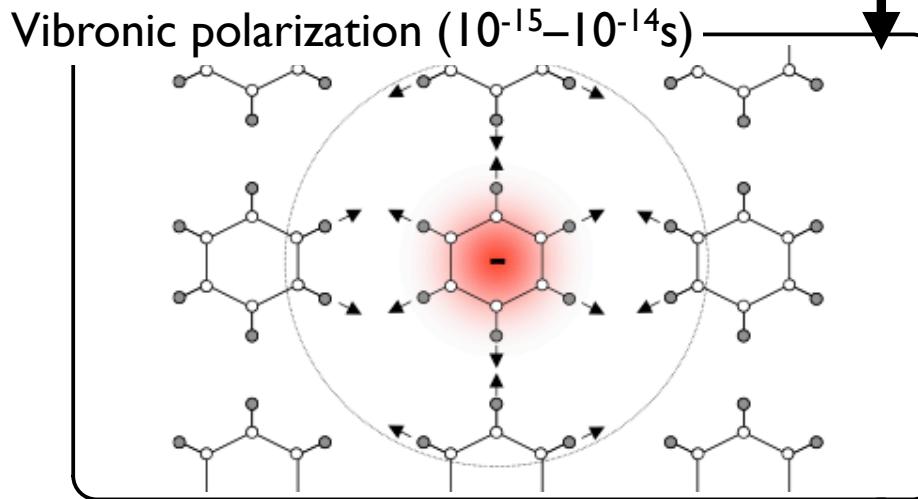
Bulovic, V., et al.. *Chem. Phys. Lett.*, 287, 455.



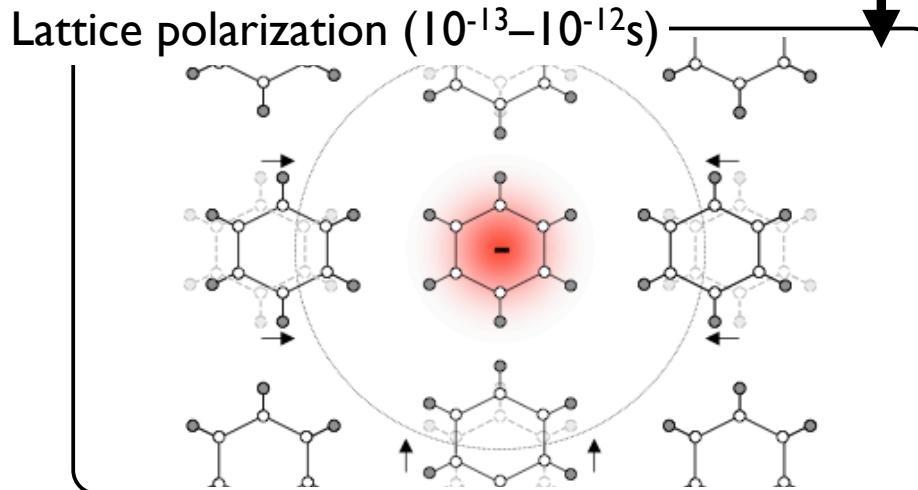
# Putting polarization in context



vdW binding



Intramolecular phonons



Polarons & solvation effects

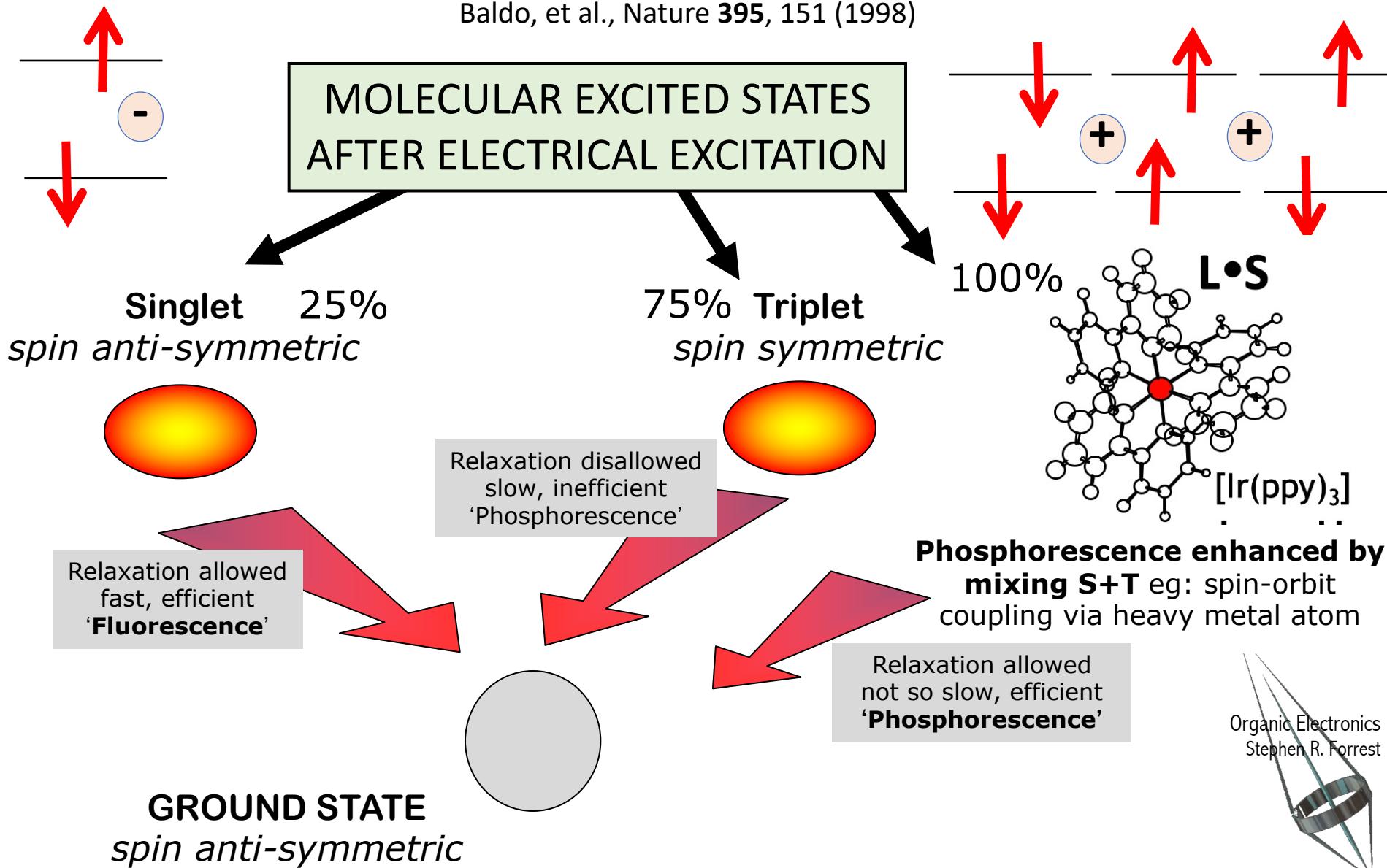
# Exciton Spin

- 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 ~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  $\mathbf{F}$ :  $\mathbf{B} = -\frac{\mathbf{v} \times \mathbf{F}}{c^2}$

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

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:  $\mathbf{m}_s = -g_s \mu_B \frac{\mathbf{s}}{\hbar} = -g_s \frac{q}{2m_e} \mathbf{s}$

↑      ↑  
g-factor   Bohr magneton  
≈ 2

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

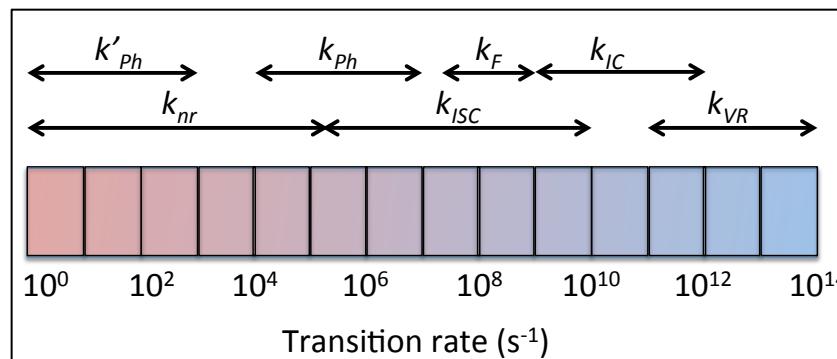
$$E_{so} = \frac{2\pi\alpha^2 R_\infty Z^4 c}{n^3 l(l+\frac{1}{2})(l+1)\hbar} \langle \mathbf{l} \cdot \mathbf{s} \rangle$$

Fine structure

Rydberg

Organic Electronics  
Stephen D. Forrest

# 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)

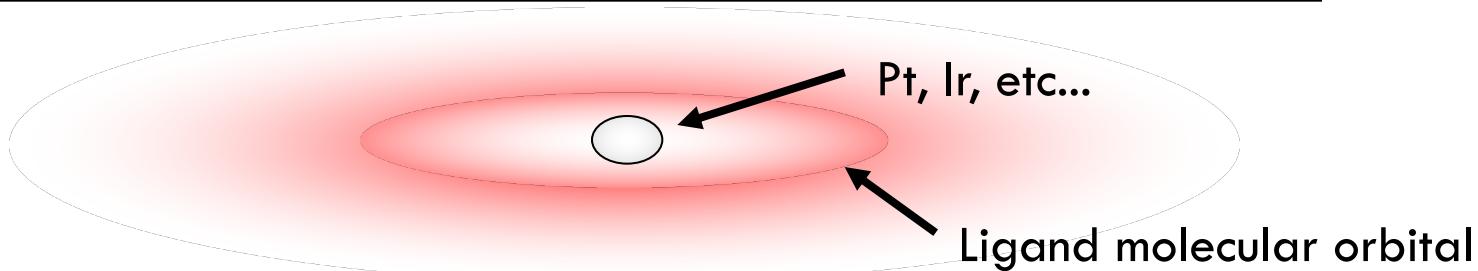
$$\text{Fluorescence: } \Phi_F = \frac{k_F}{k_F + k_{nrS} + k_{ISC}}$$

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

# Electrophosphorescence: 100% IQE Achieved

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

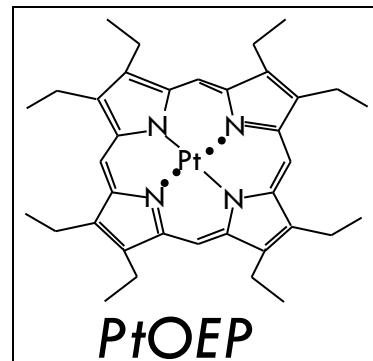
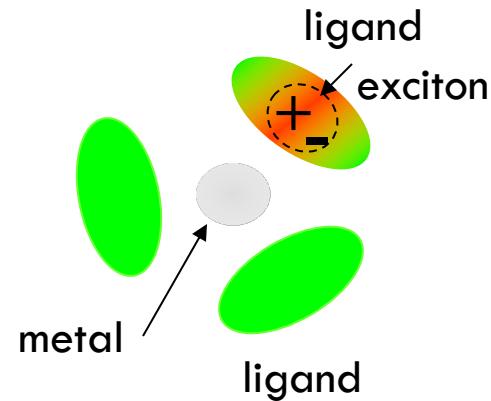
Use metal-organic complexes with heavy transition metals



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

## Type I phosphor

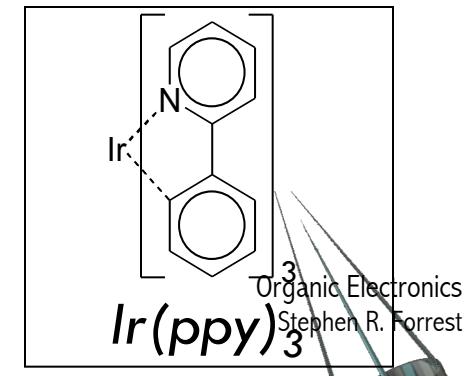
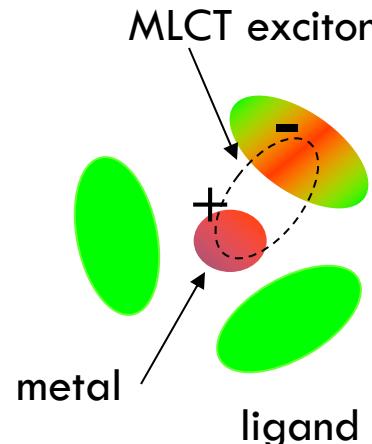
Exciton localized on organic



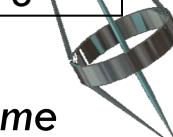
less mixing  $\sim 100 \mu\text{s}$  triplet lifetime

## Type II phosphor

Metal-ligand charge transfer exciton



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

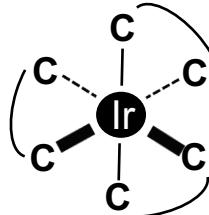


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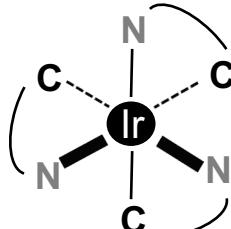
# Differences between Type I and Type II Phosphors

N-Heterocyclic carbene (NHC) ligand for blue

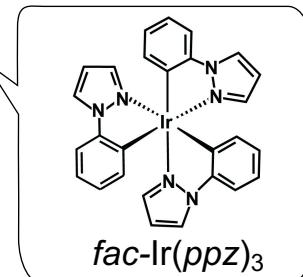
**NHC Ir (III) complex =  $\text{Ir}(\text{C}^{\wedge}\text{C}:)_3$**



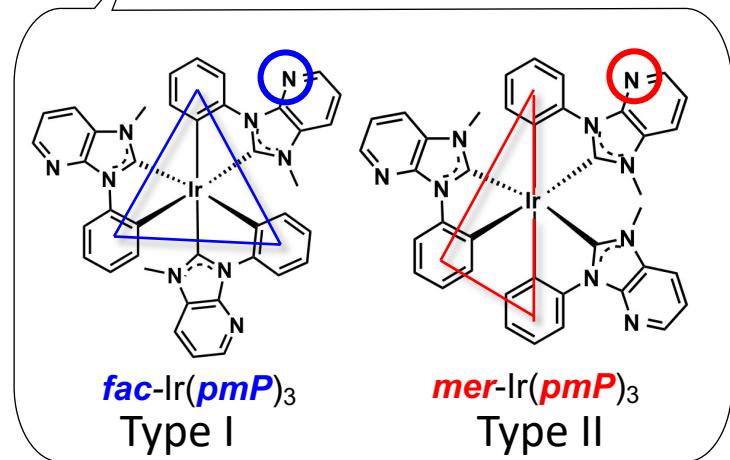
**Conventional design =  $\text{Ir}(\text{C}^{\wedge}\text{N})_3$**



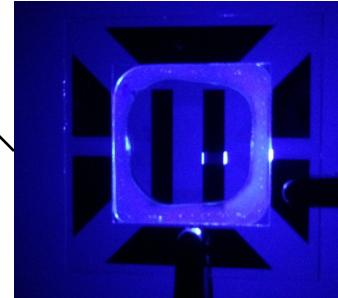
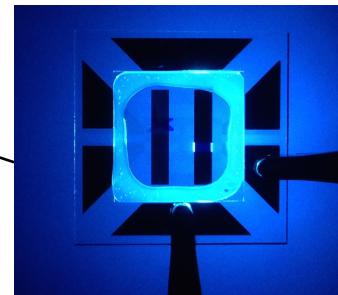
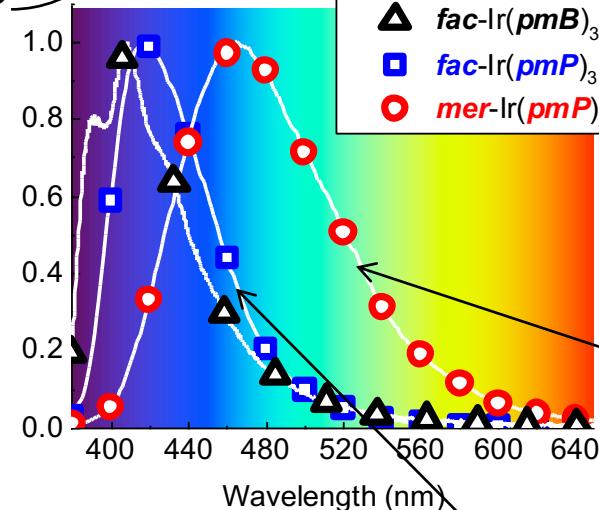
vs.



PL (a.u.)



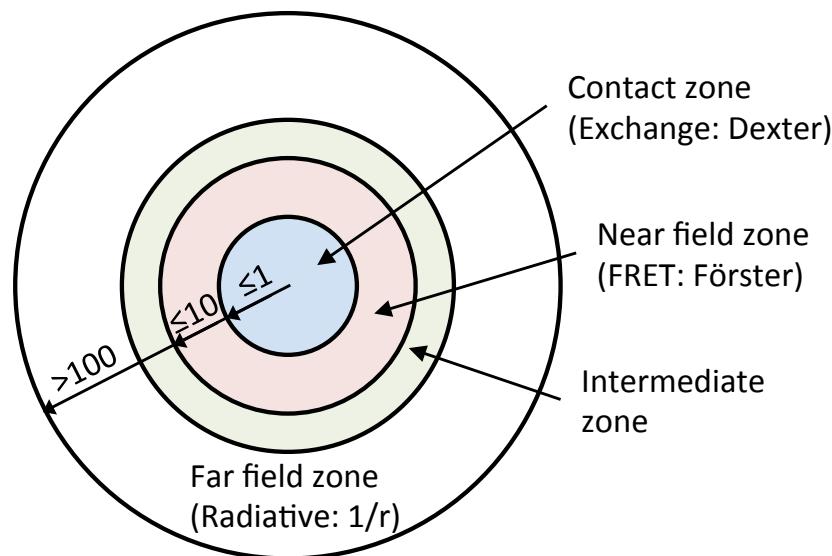
J. Lee, et al. Nat. Mater., 14, 92 (2016)



| Property                        | <i>fac</i> - $\text{Ir}(pmP)_3$ | <i>mer</i> - $\text{Ir}(pmP)_3$ |
|---------------------------------|---------------------------------|---------------------------------|
| 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

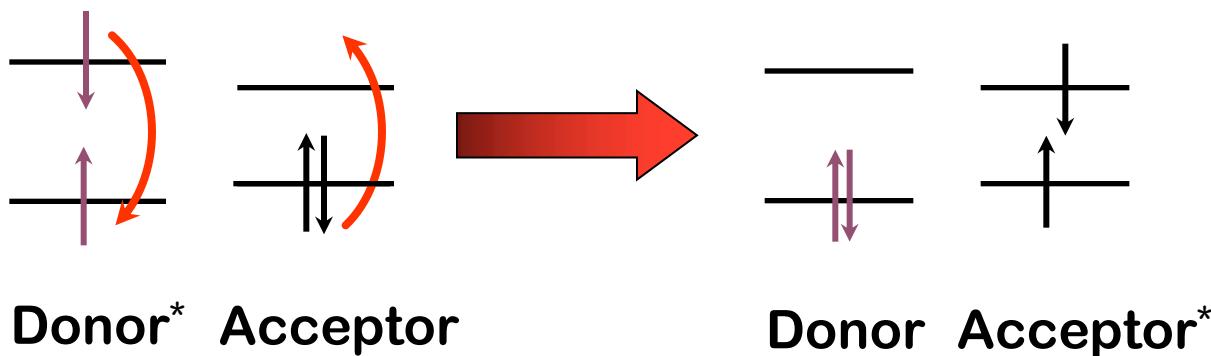
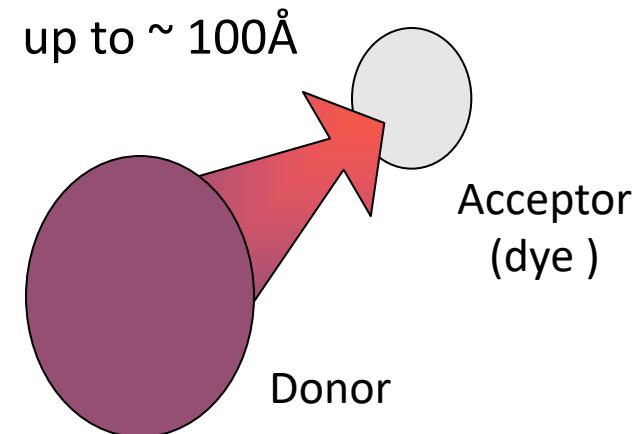
- If excitons are mobile in the solid, they must move from molecule to molecule
  - ✧ The microscopic “hopping” between neighboring molecules = energy transfer



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



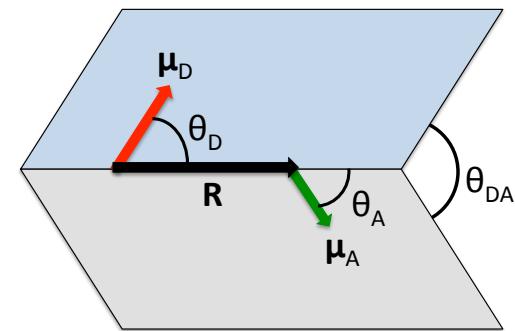
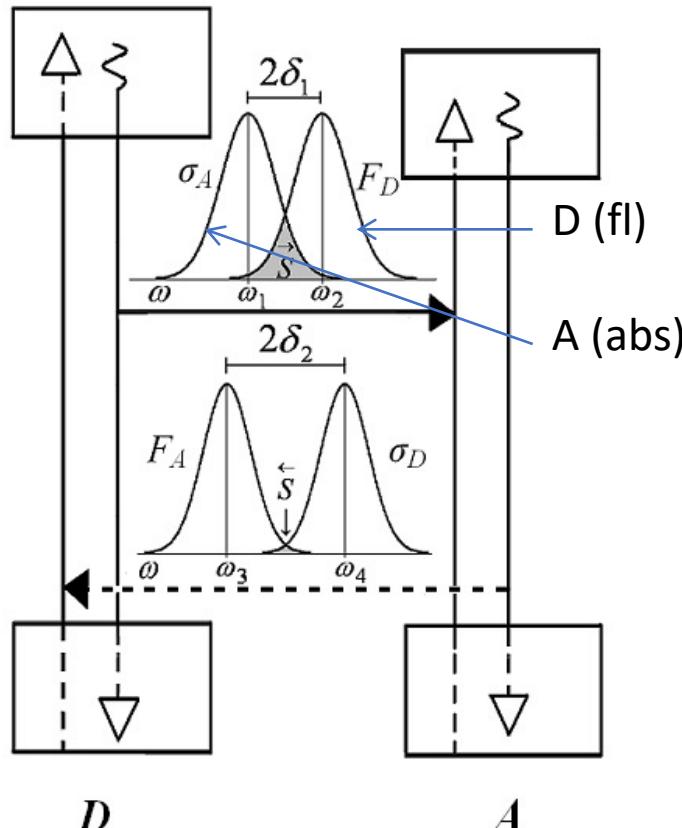
Efficient method for singlet transfer to fluorescent dye  
Triplet-singlet transfer possible if donor is strongly phosphorescent



# 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!

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

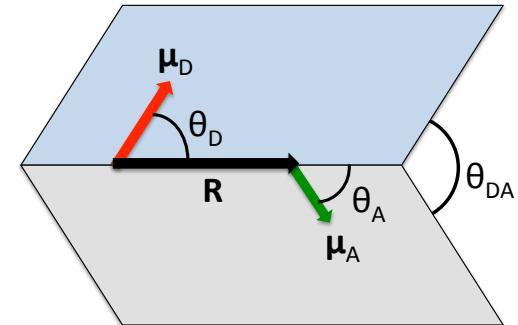
Overlap of the initial and final state energies simply equals the overlap of the donor fluorescence and acceptor absorption spectra!

# 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!

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

Fluorescence quantum yield of donor

Donor natural lifetime

Normalized fluorescence spectrum of donor

Absorption coeff't of acceptor

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# What FRET Implies

Simply put:

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

Where

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

$R_0$  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)

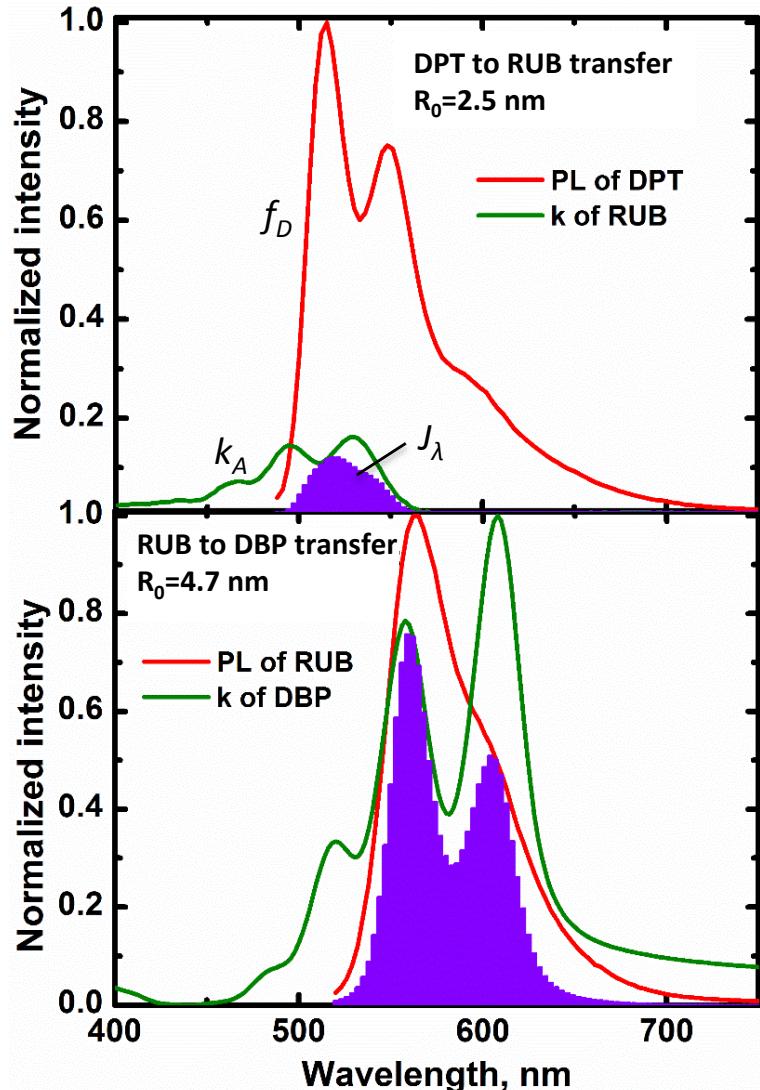
- Keep in mind that **FRET is orientation dependent** : this makes it a probe of molecular orientation by using polarized input light, and determining the polarization of the light emitted from the acceptors
- **FRET transfer time ~ radiative emission time**:  $k_{ET} \sim 1-10$  ns.
- Primary route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



# Two examples

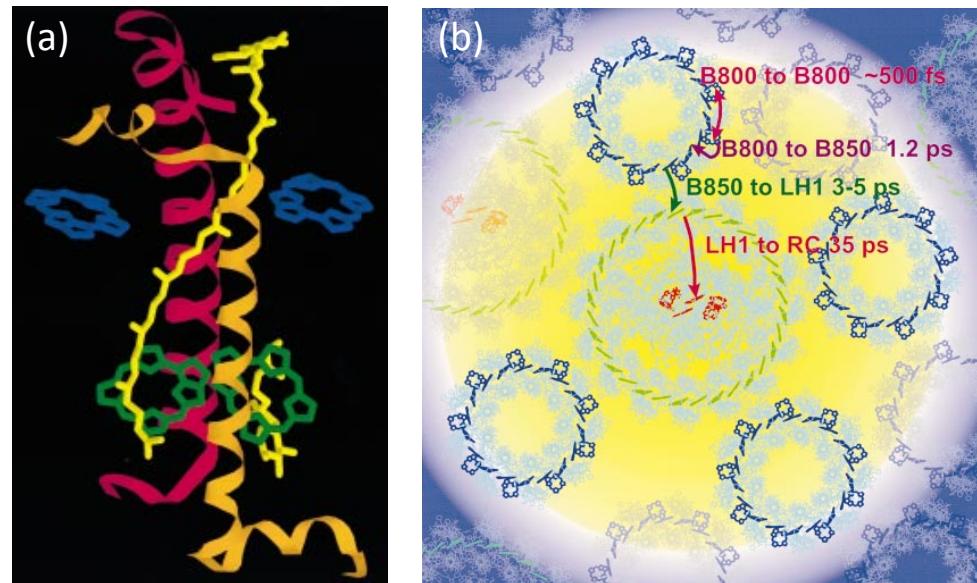
FRET is important in OPVs, OLEDs, biology,....

Typical molecules used in OPVs and OLEDs



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

Photosynthetic light harvesting complex LH2



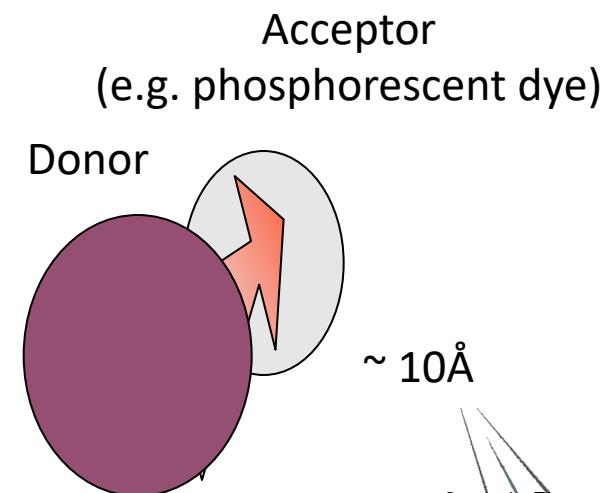
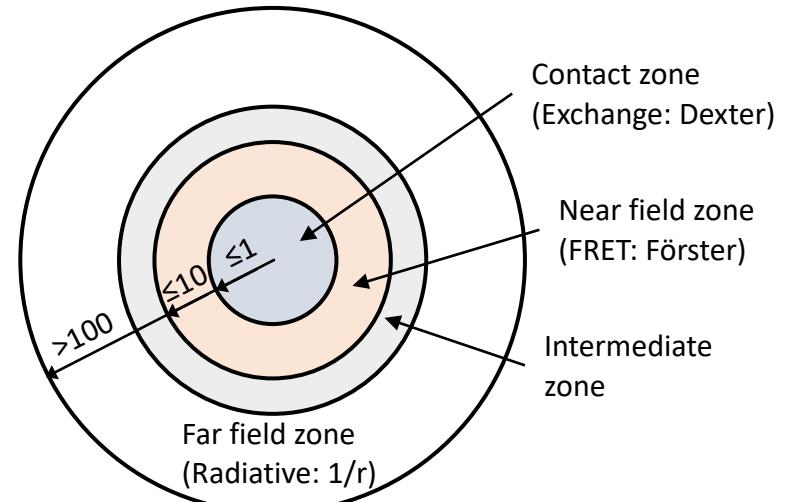
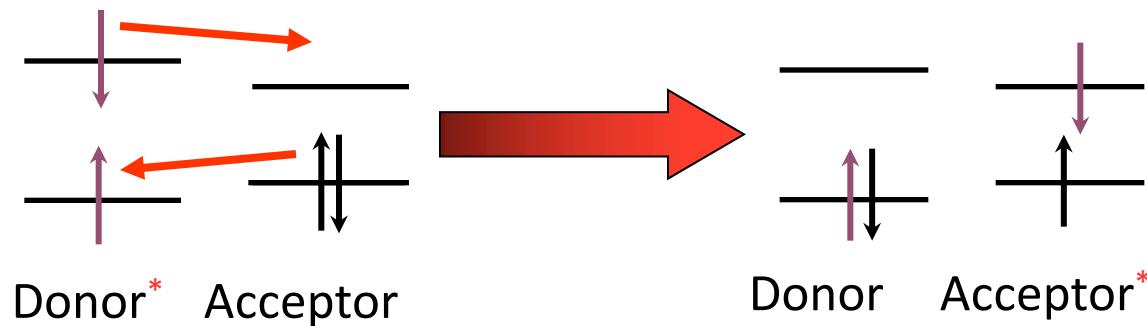
Sundström et al., J. Phys. Chem. B, 103, 2327 (1999).

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# Exchange Energy Transfer

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

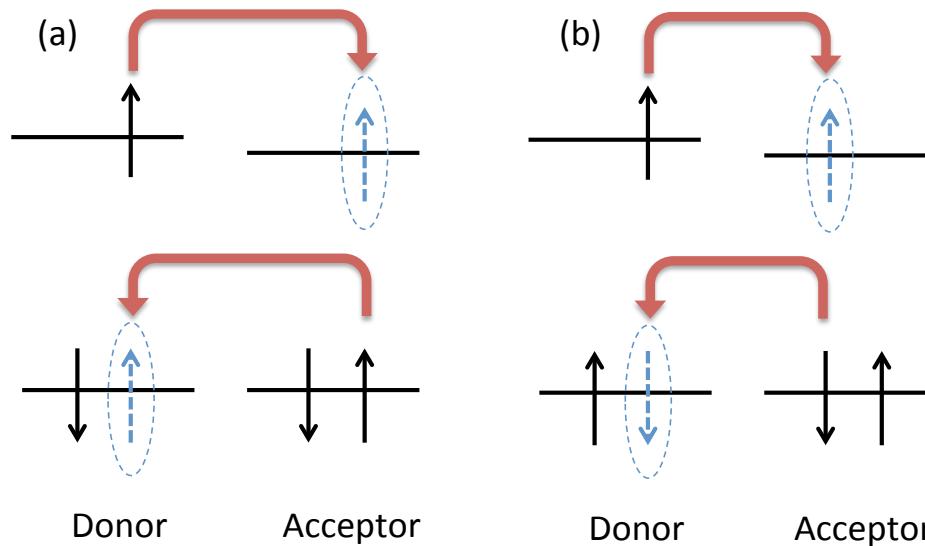
*spin is conserved: e.g. singlet-singlet or triplet-triplet*



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

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# Spin conserving exchange interactions



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

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 hyrdogenic 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:

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

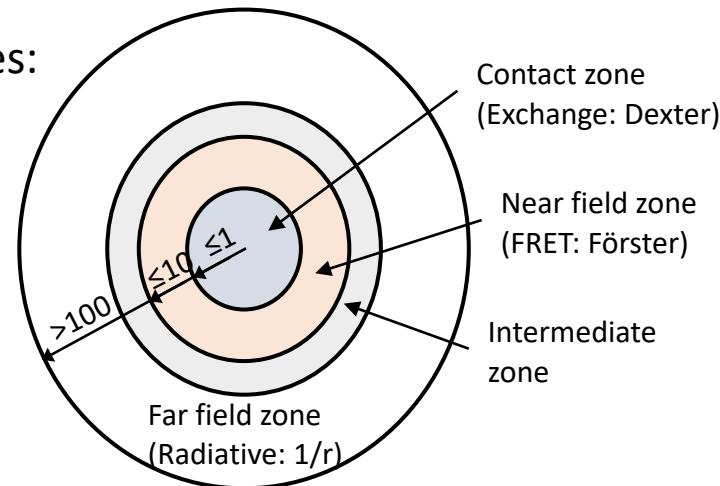
# Important facts about Dexter exchange

- **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**
  - $k_{ET} \sim 10^{10} - 10^{11} s^{-1}$

# 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                          |