

Week 4

Optical Properties 2

Building to Solids

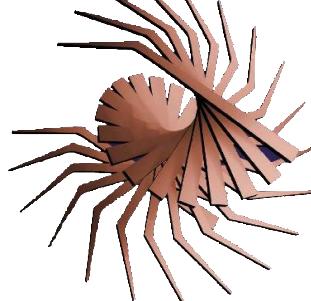
Excitons

Spin

Energy Transfer

Chapter 3.7-3.12

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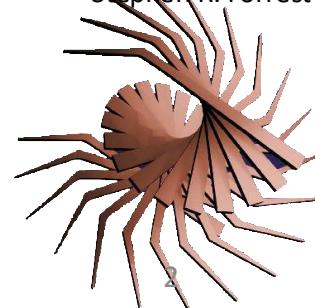
Building to solids

- Interaction of an isolated pair of molecules: Dimers
- 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_2 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): $H_{\text{int}} = -\frac{A_{12}}{r_{12}^6}$

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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:

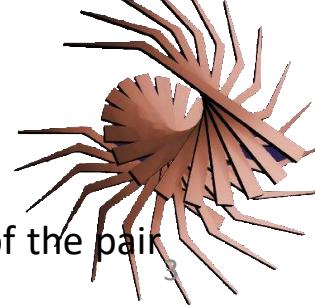
$$E'_I = \langle \psi'_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) | H_{\text{int}} | \psi'_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) \rangle : \text{Coulomb energy}$$

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

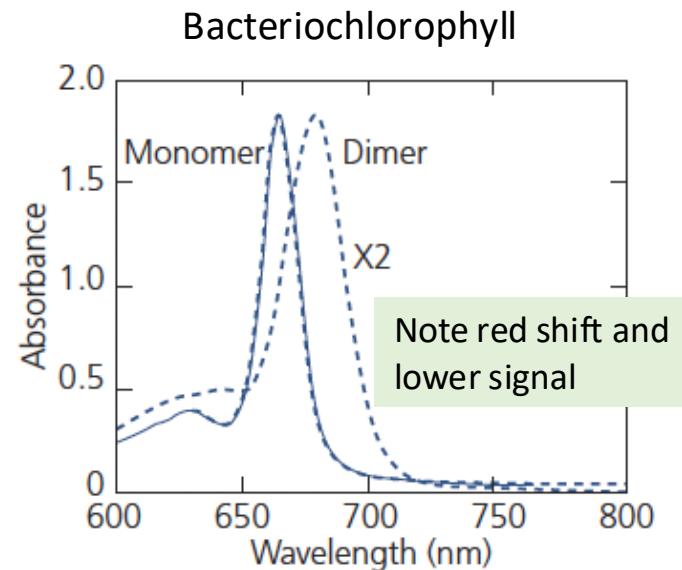
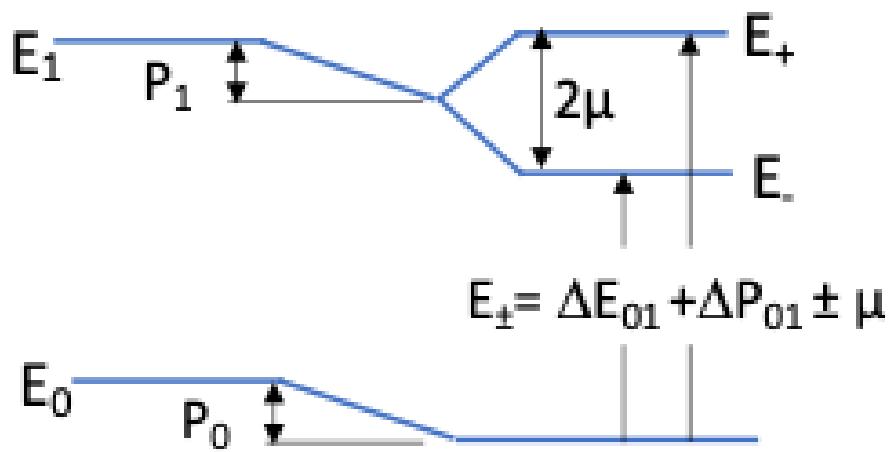
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Giving a total dimer energy of: $E'_T = E_0 + E' + E'_I + E_{\pm}$

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



The Dimer Spectrum

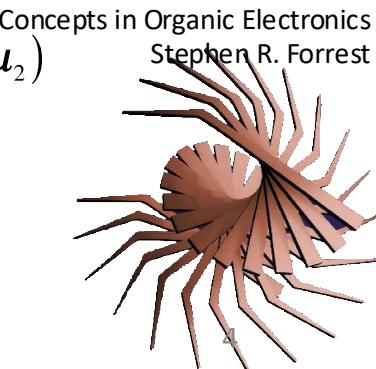


Olsen & Cox Photosynth. Res. **30**, 35 (1991).

Symmetry prevents some transitions from occurring

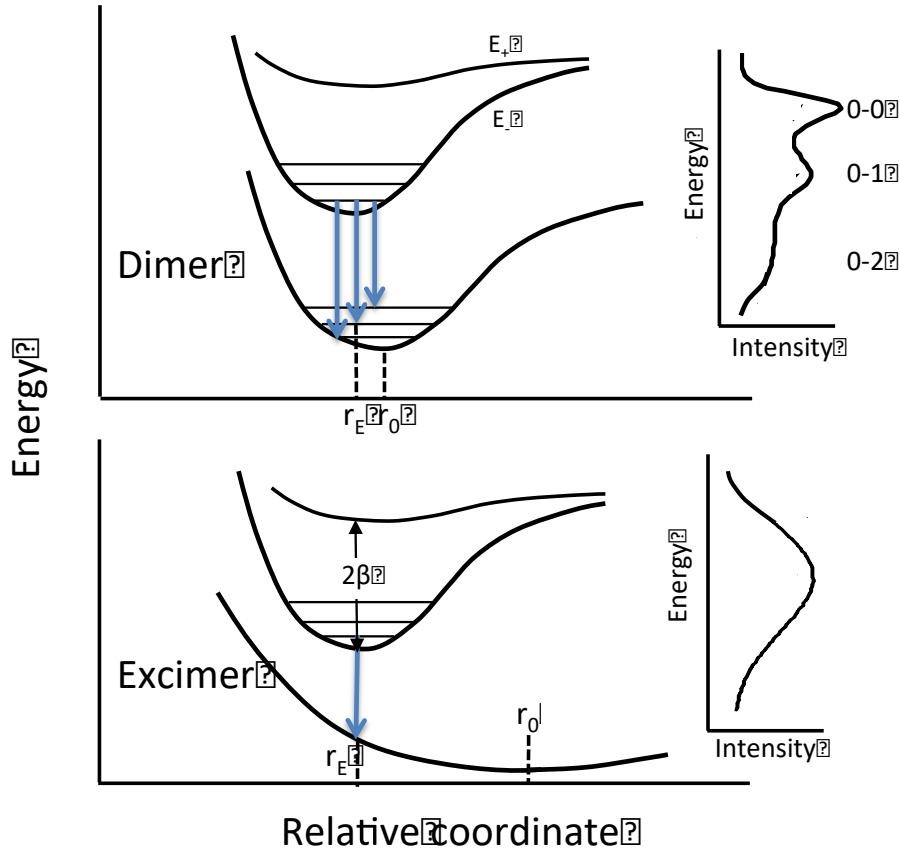
Transition dipole moment: $\mu_{\pm} = -\frac{q}{\sqrt{2}} \langle \psi'_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) \pm \psi_1(\mathbf{r}_1)\psi'_2(\mathbf{r}_2) | \mathbf{r} | \psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) \rangle = \frac{1}{\sqrt{2}} (\mu_1 \pm \mu_2)$

dipole operator

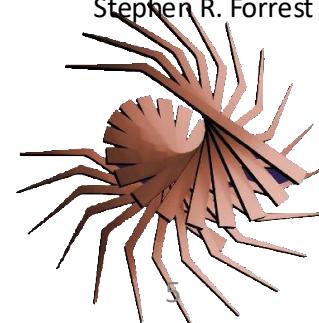


Excimers and Exciplexes

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



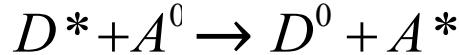
Getting to the excimer can
be a multi-step process



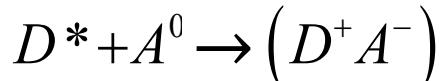
Exciplexes

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

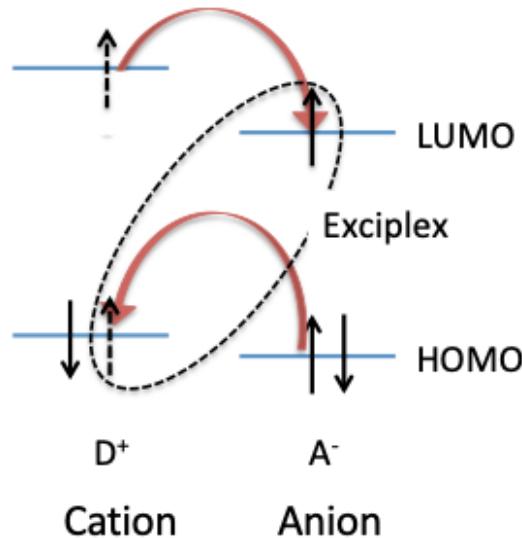
- An excitation moves from an excited donor (D^*) to a ground state acceptor (A^0)



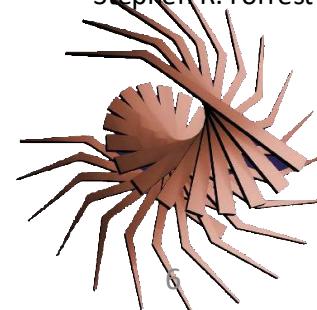
- Since there is an energy difference between D and A, an exciplex results in charge transfer (shared charge) between molecules:



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

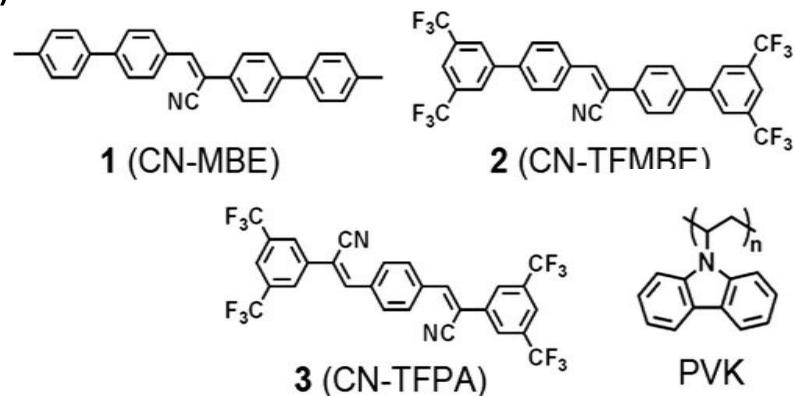


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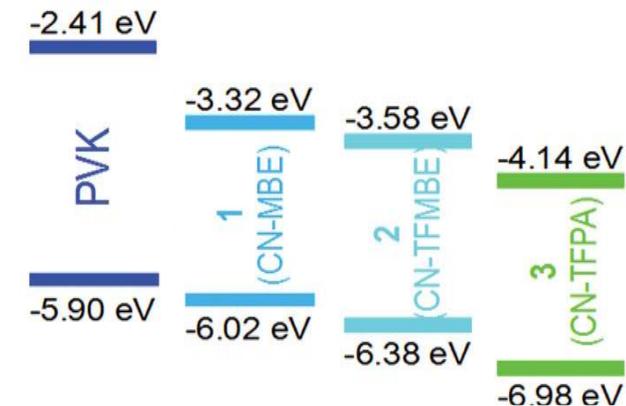


Example of an Exciplex

(a)

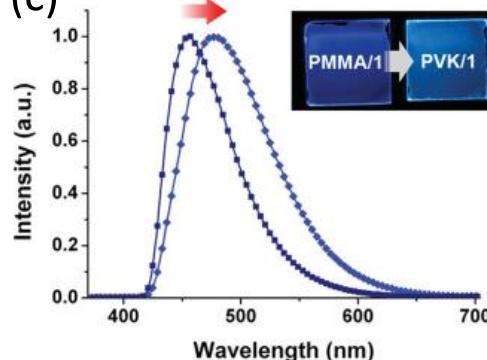


(b)

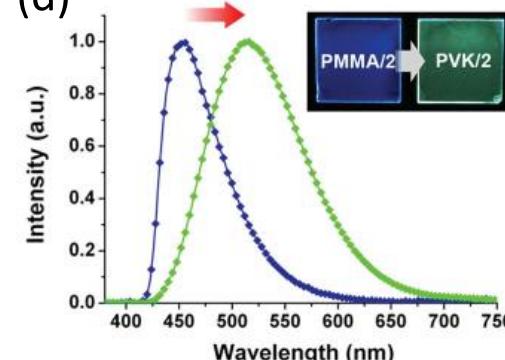


CF_3 groups are electron-withdrawing
⇒ more ‘stabilized’ HOMO w/o significant change in E_G

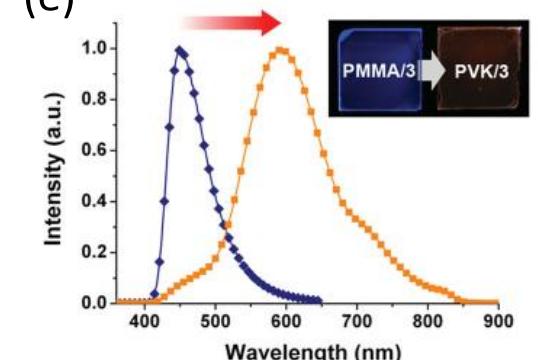
(c)



(d)

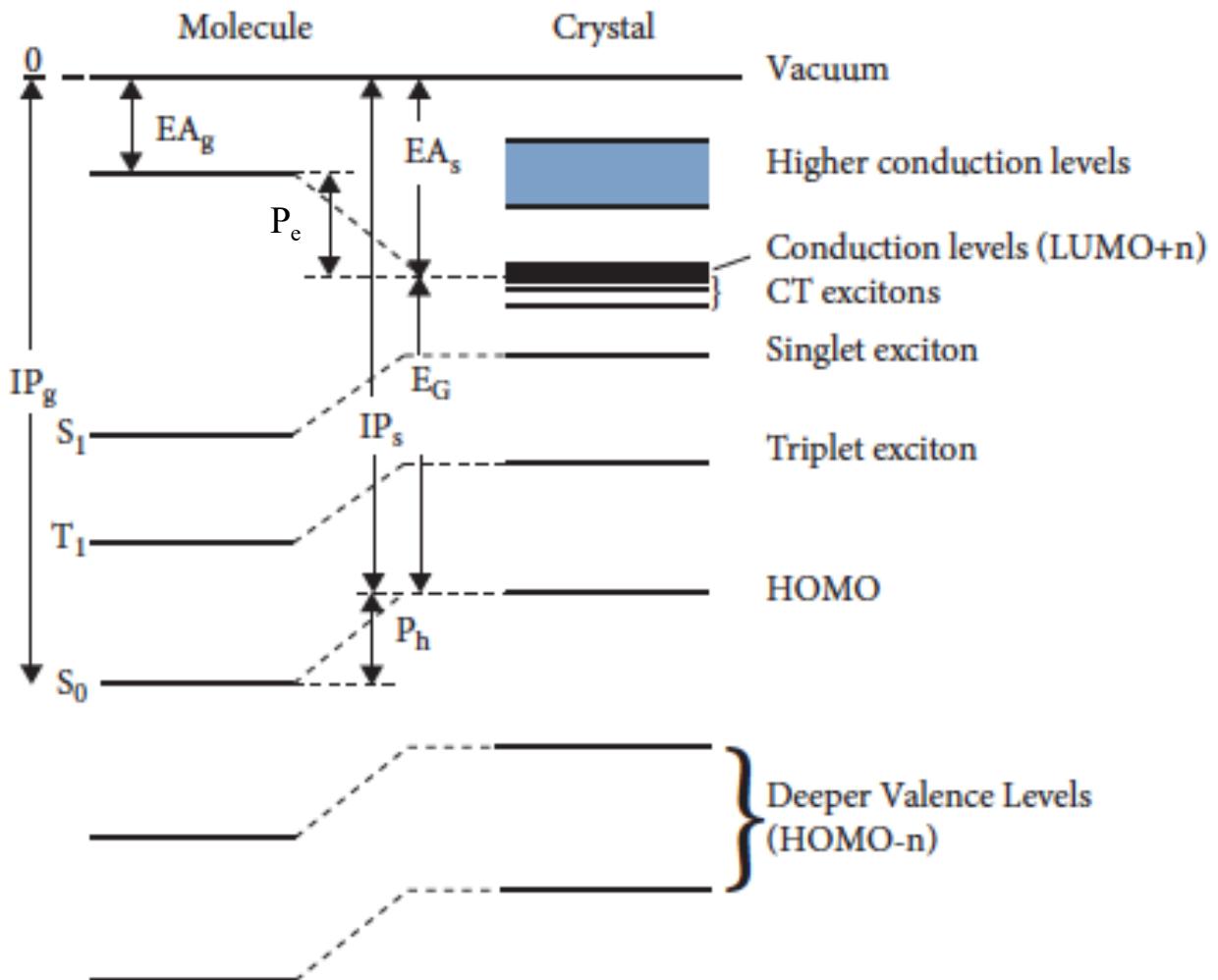


(e)



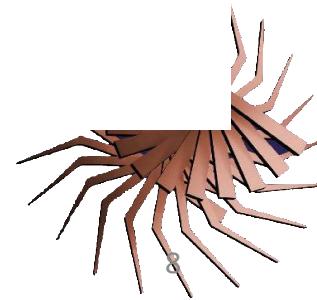
The correspondence between a molecule and a solid

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



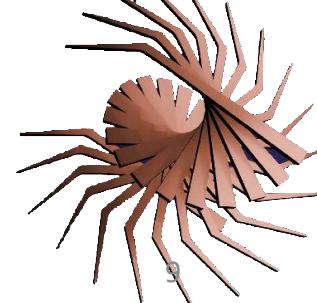
Lyons Model

tronics
Forrest

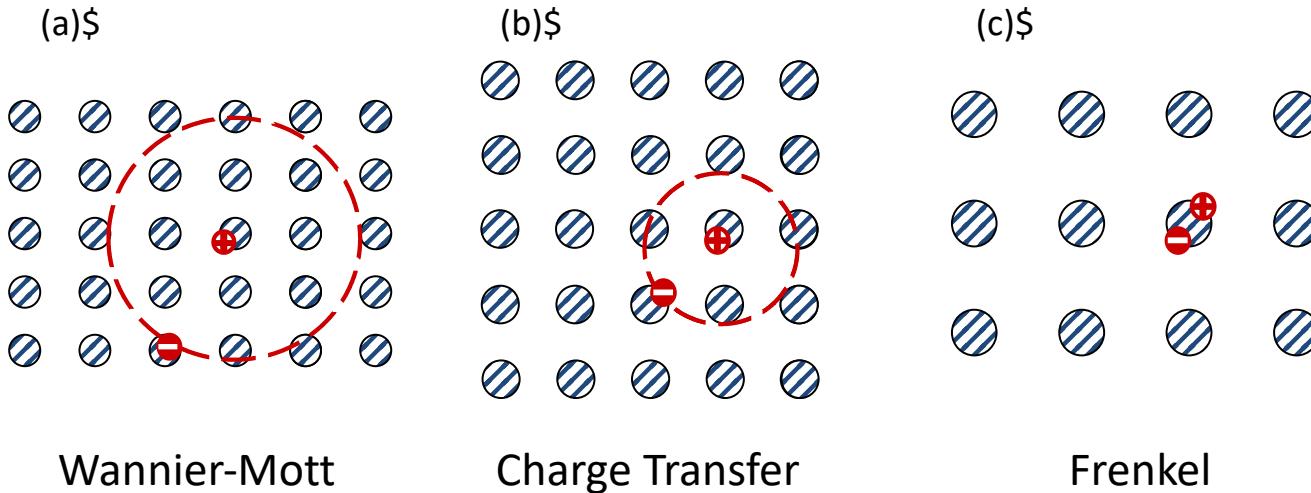


Excitons & Spin

- 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:

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

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

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

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 $|\mu_{if,e}|^2 F C_{if}$

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

Ave. emission freq.

Einstein spontan. abs.

Normalized lineshape

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

This leads to more practical expressions for the oscillator strength:

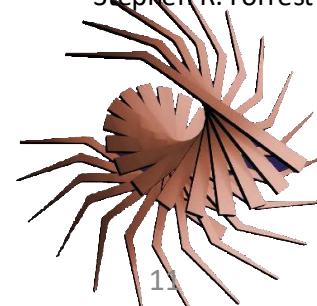
$$f_{in,fm} = \frac{2m_e \epsilon_0 c}{\pi q^2 n_r} \int \sigma(\omega) d\omega = \frac{2303 m_e c^2}{N_A \pi q^2 n_r} \int \epsilon(\tilde{v}) d\tilde{v} = \frac{4.39 \times 10^{-9}}{n_r} \int \epsilon(\tilde{v}) d\tilde{v}$$

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

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

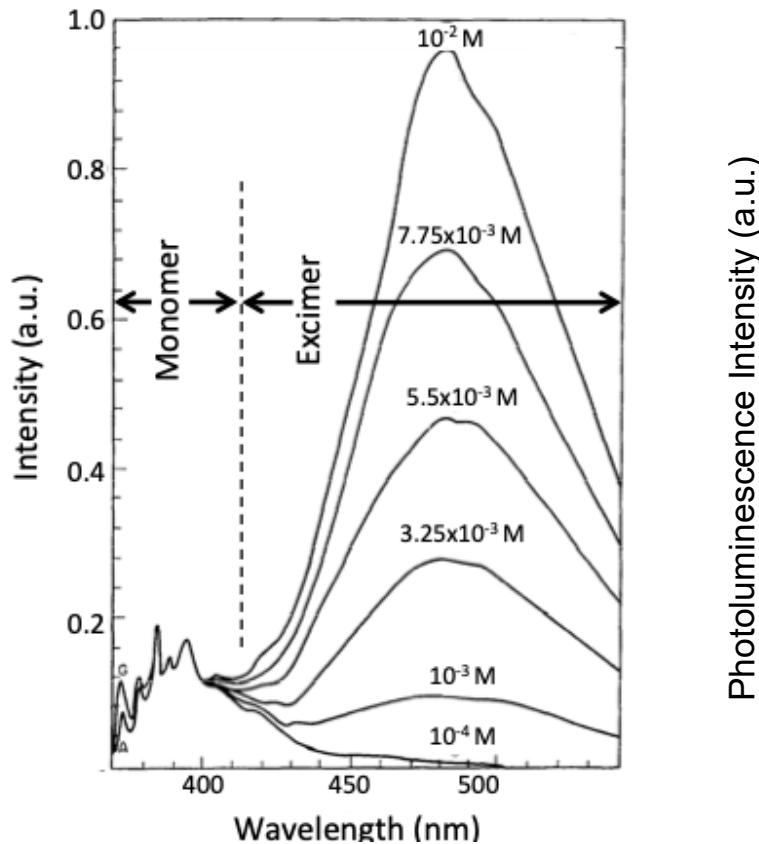
C=concentration [M/l]



Examples of Excimer Emission in Fluorophors and Phosphors

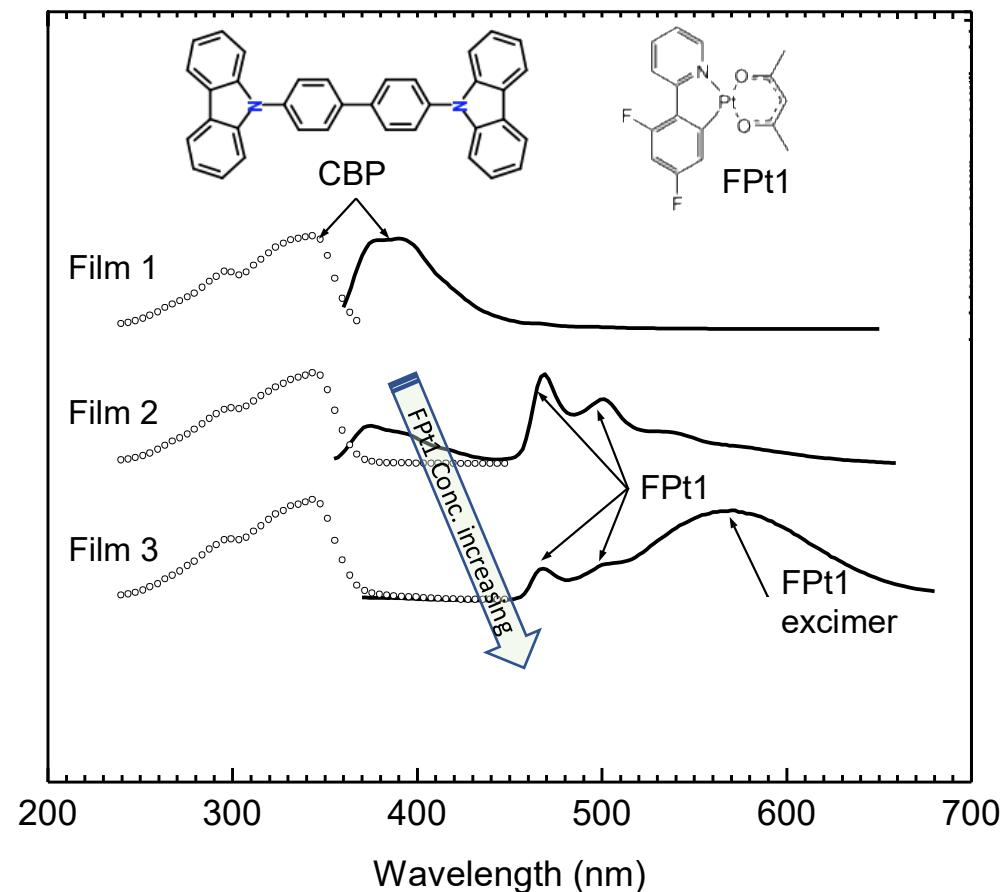
Excimer Fluorescence: Pyrene in solution

Higher concentration=more excimer pairs



Excimer Phosphorescence

Coexistence of monomer and excimer emission = white light



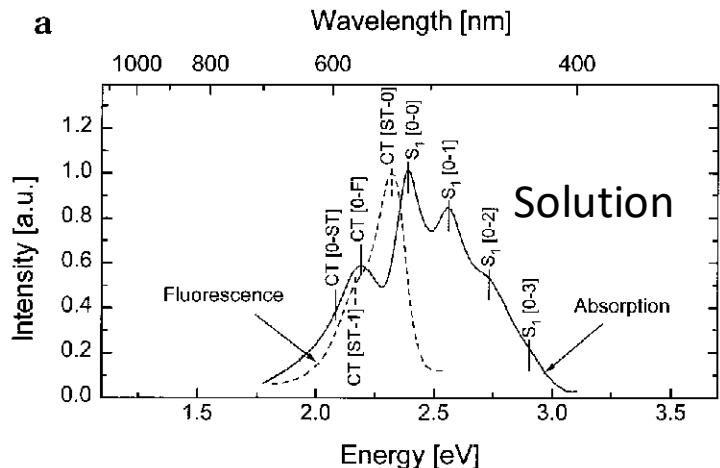
J. B. Birks and L. G. Christophorou, *Spectrochim. Acta*, **19**, 401, (1963).

B. W. D'Andrade, et al. *Adv. Mater.*, **14**, 1032 (2002).

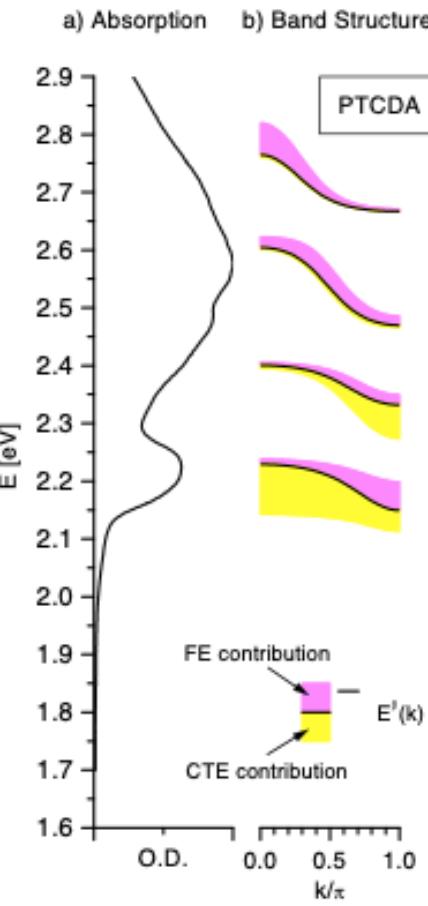
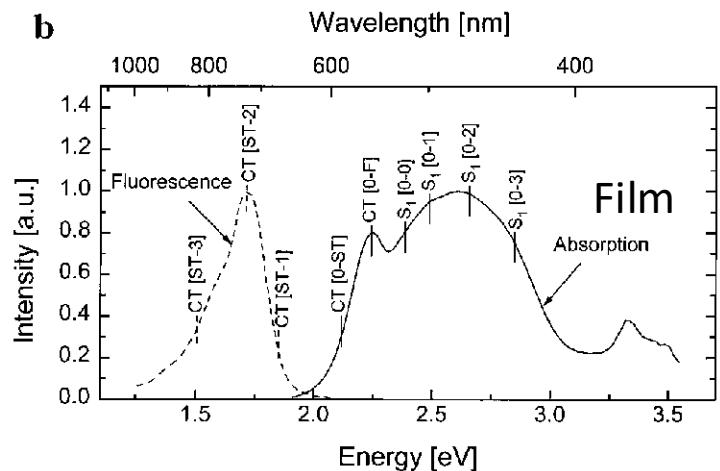
Charge Transfer States: Intermediates between molecule and solid

Tight packing in PTCDA leads to strong CT oscillator strength

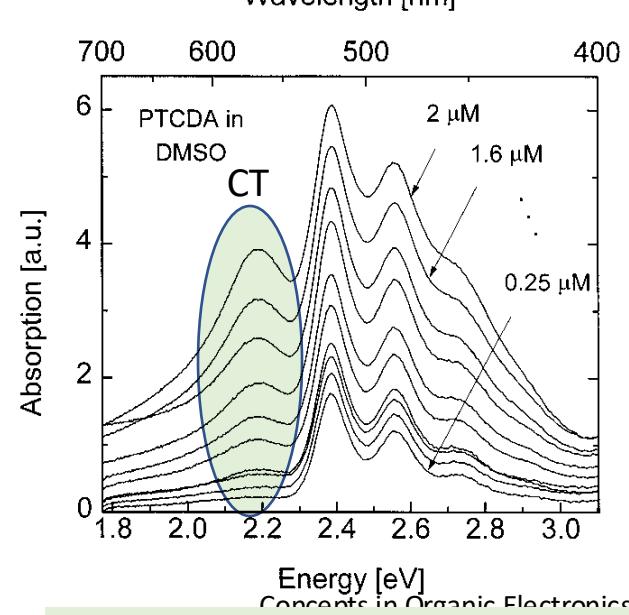
a



b



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



CT state intensity drops much
faster than Frenkel intensity
with dilution due to their
collective nature

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

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

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

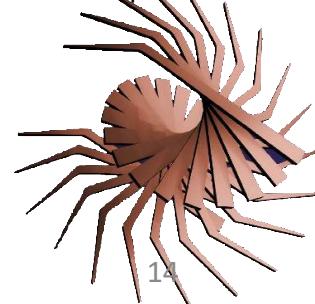
Exciton Spin

- 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

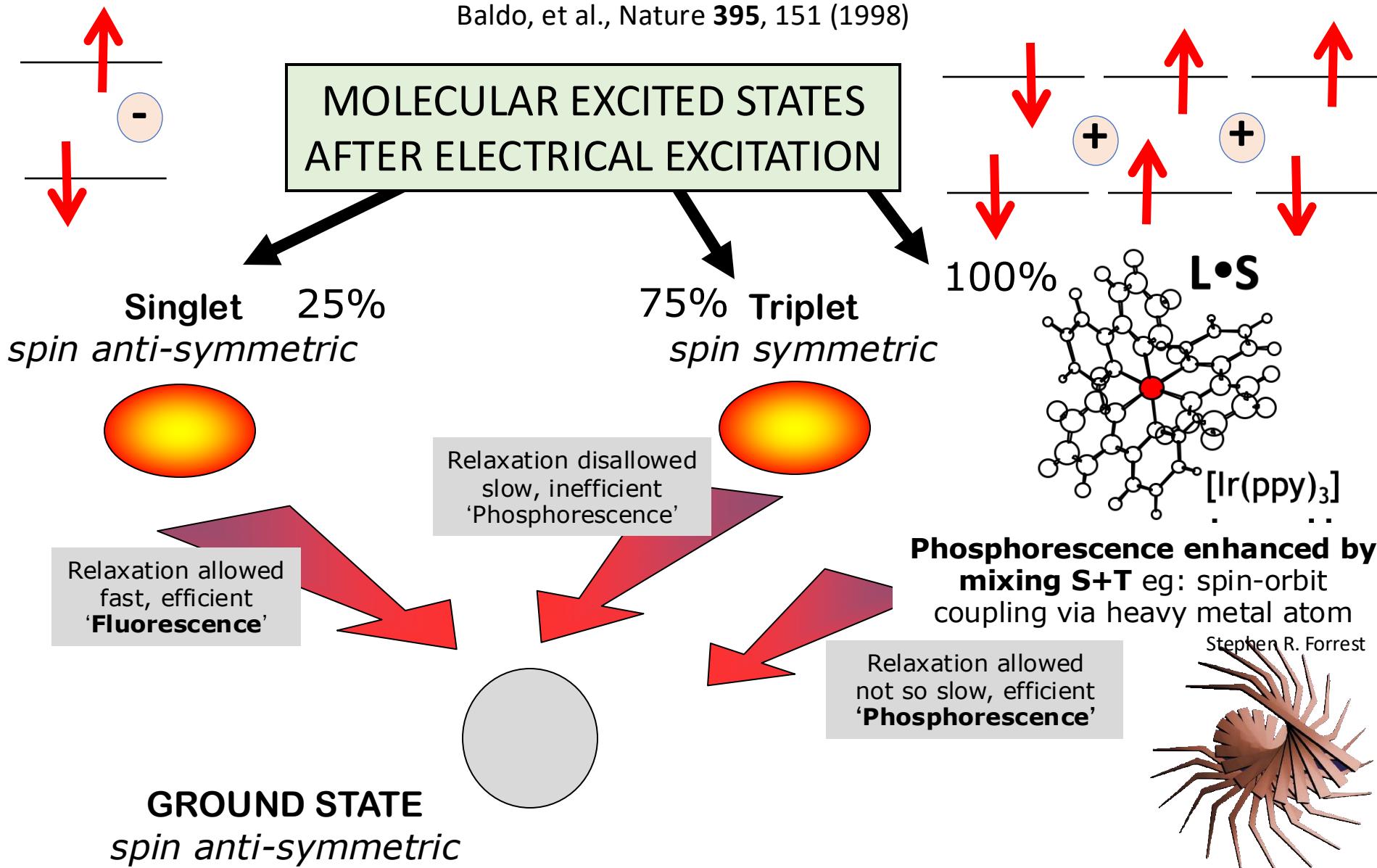
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100% Internal Efficiency via Spin-Orbit Coupling

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

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

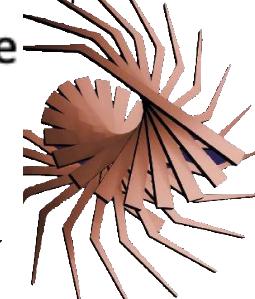
Orbital angular momentum is given by: $\mathbf{l} = \mathbf{r} \times m_e \mathbf{v}$

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

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

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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: $\xi(r) = -\frac{Zq^2}{8\pi\epsilon_0 m_e^2 c^2} \frac{1}{r^3}$

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

$$\Rightarrow \text{the expectation value: } E_{SO} \propto \langle nl | \frac{1}{r^3} | nl \rangle = \langle R_{nl} | \frac{1}{r^3} | R_{nl} \rangle \Rightarrow E_{SO} = \frac{2\pi\alpha^2 R_\infty Z^4 c}{n^3 l(l+\frac{1}{2})(l+1)\hbar} \langle \mathbf{l} \cdot \mathbf{s} \rangle$$

Fine structure Rydberg

Electrophosphorescence: 100% IQE Achieved

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

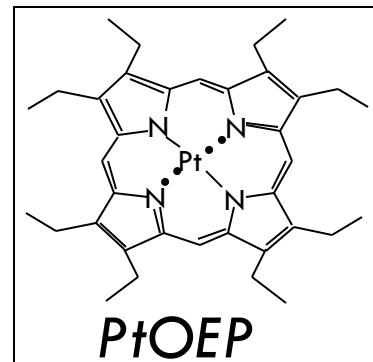
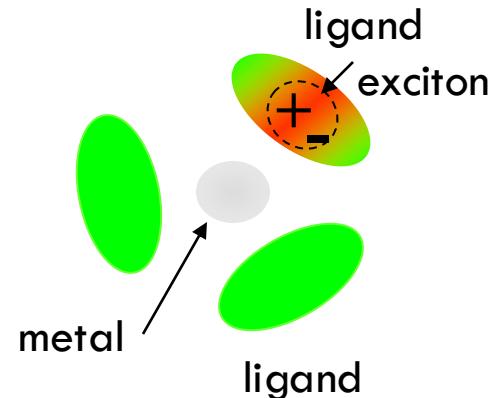
Use metal-organic complexes with heavy transition metals



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

Type I phosphor

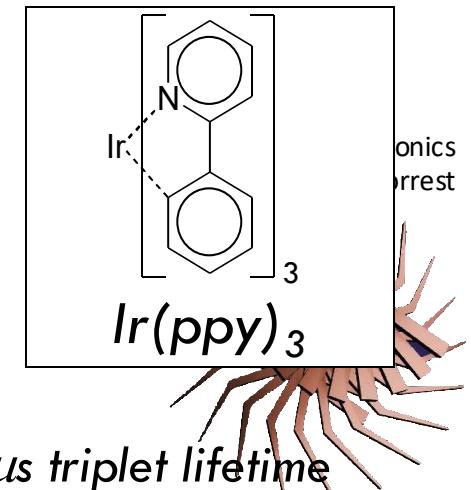
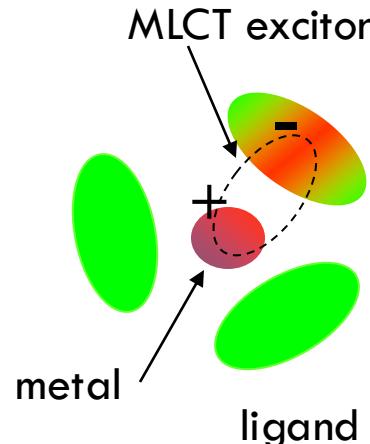
Exciton localized on organic



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

Type II phosphor

Metal-ligand charge transfer exciton

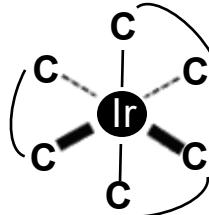


most mixing $\sim 1 \mu\text{s}$ triplet lifetime

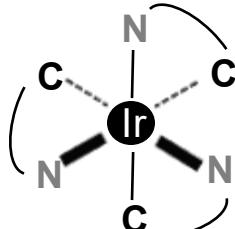
Differences between Type I and Type II Phosphors

N-Heterocyclic carbene (NHC) ligand for blue

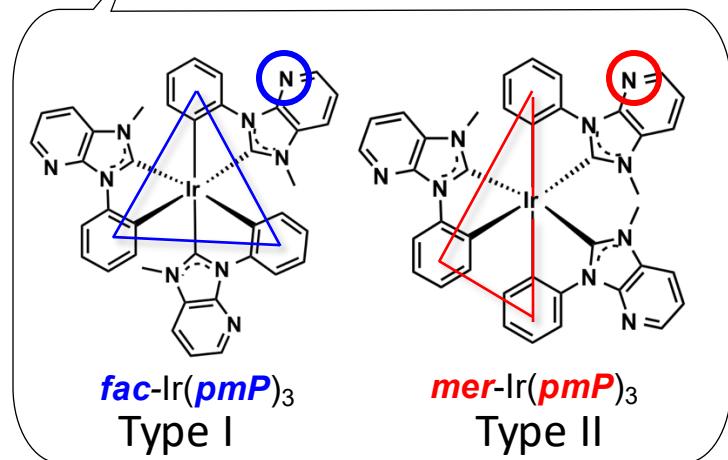
NHC Ir (III) complex = $\text{Ir}(\text{C}^{\wedge}\text{C}:)_3$



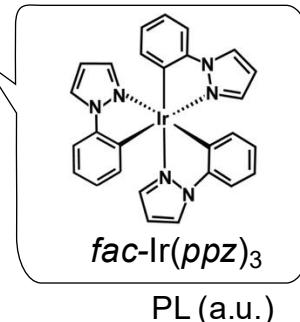
Conventional design = $\text{Ir}(\text{C}^{\wedge}\text{N})_3$



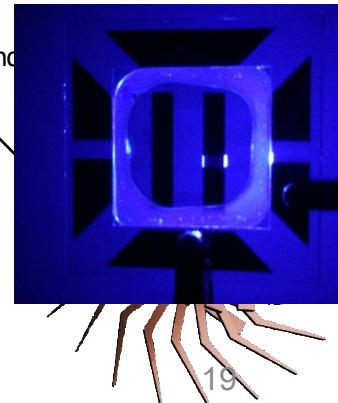
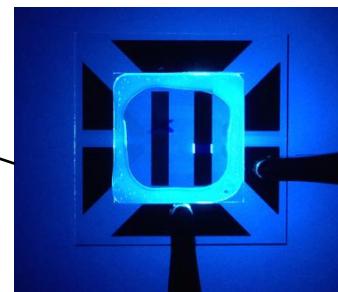
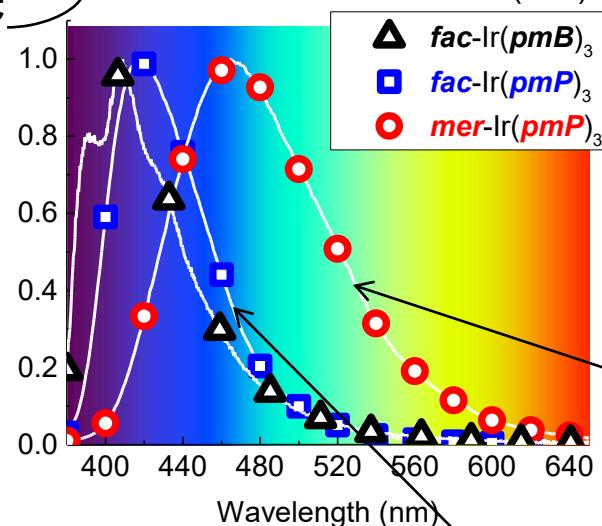
vs.



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

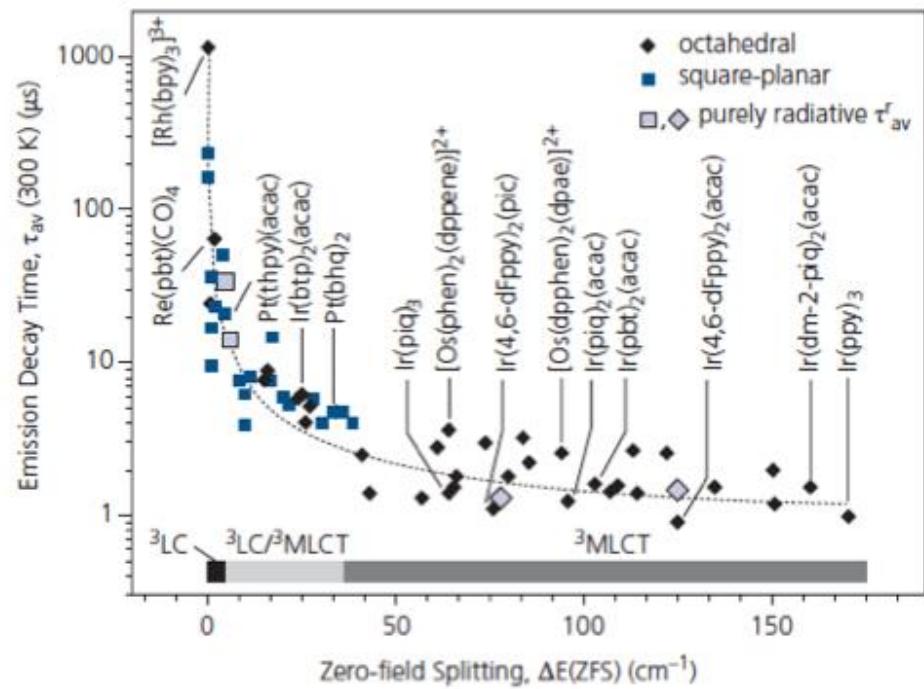
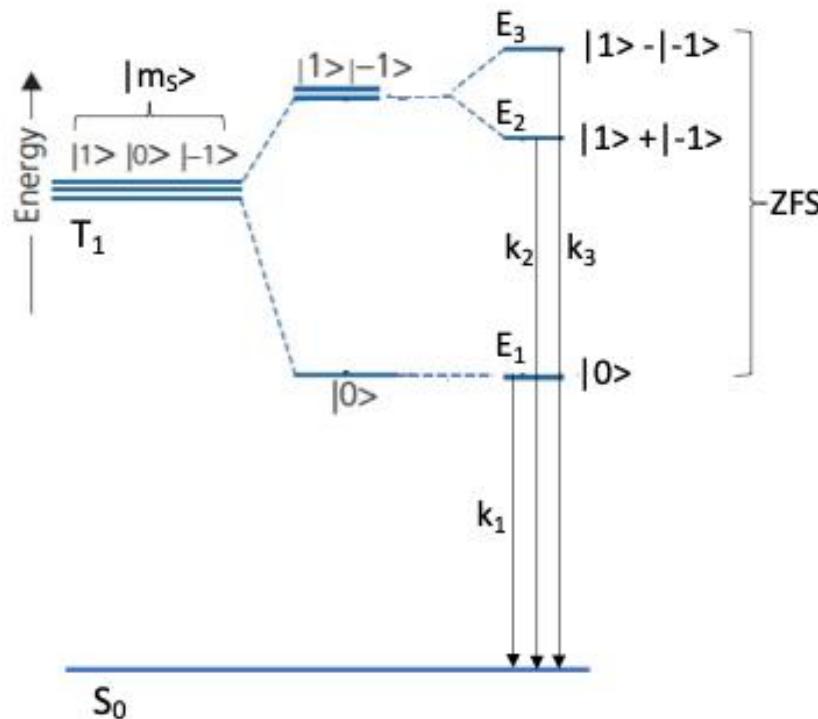


PL (a.u.)

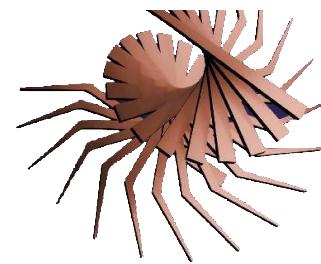


Property	fac-$\text{Ir}(pmP)_3$	mer-$\text{Ir}(pmP)_3$
Emission energy	3.0 eV	2.7 eV
Solvatochromism (in DCM)	-0.19 eV	-0.33 eV
Rigidochromic shift (300 → 77K)	+0.19 eV	+0.34 eV
FWHM change (300 → 77K)	58 → 30 nm	93 → 55 nm
Excited state dipole	Small (localized)	Large (extended)

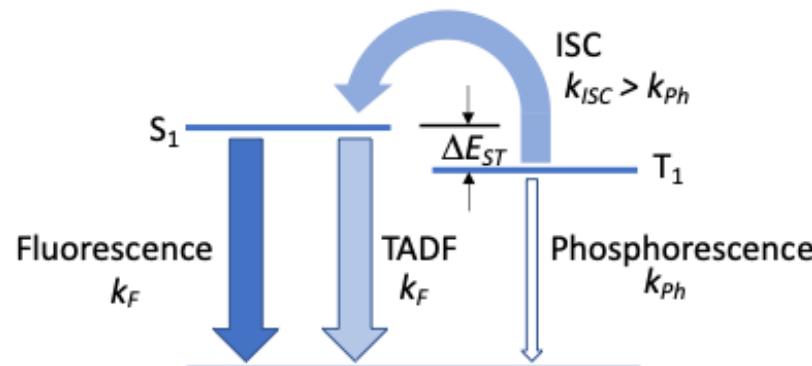
Zero field splitting and triplet lifetime



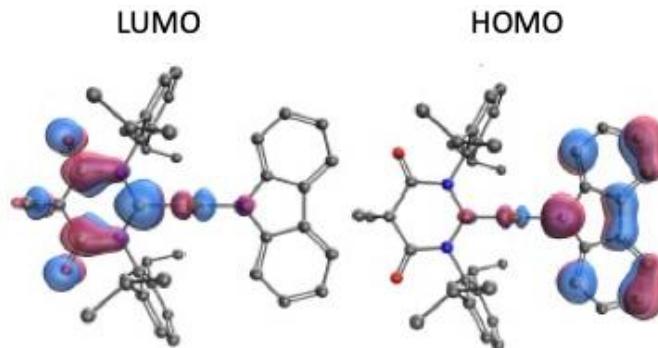
H. Yersin, H., et al. (2011). Coordination Chem. Rev., **255**, 2622.



Thermally activated delayed fluorescence (TADF): Another route to 100% IQE



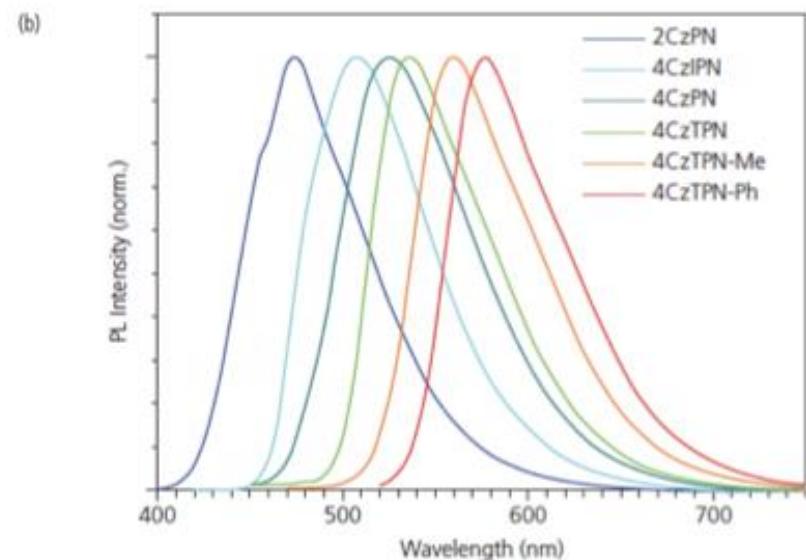
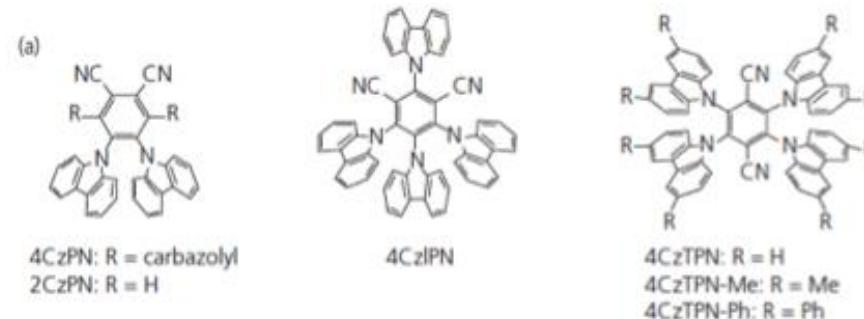
Small exchange energy (ΔE_{ST}) allows rapid equilibrium between T_1 and S_1



Metal-organic TADF molecules (MAC-Cu-Cz) separates HOMO and LUMO \Rightarrow small ΔE_{ST}

H. Uoyama, et al. (2012). Nature, **492**, 234.

Organic TADF uses orthogonal D and A groups

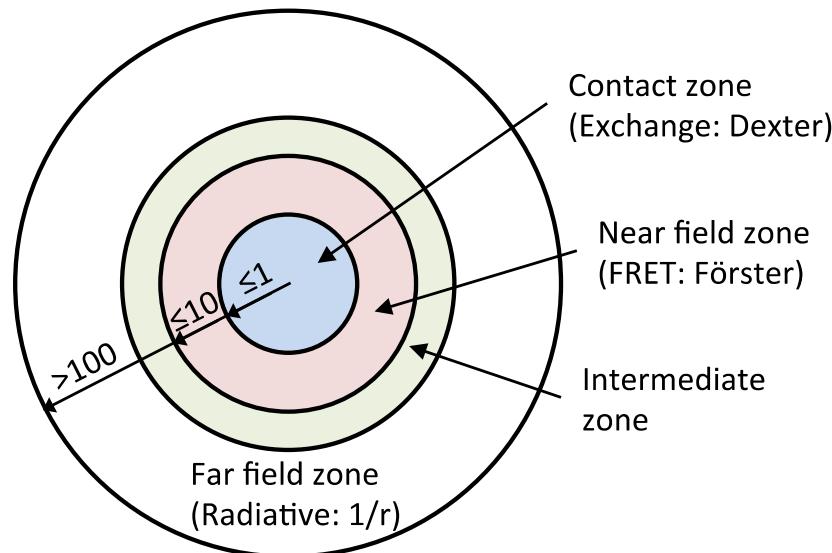


S. Shi, et al. (2019). JACS, **141**, 3576



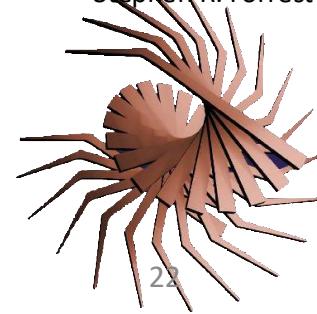
Energy Transfer

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



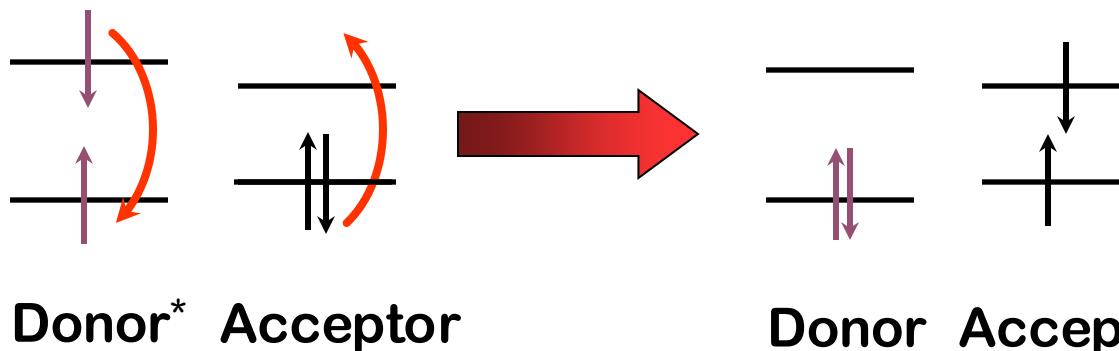
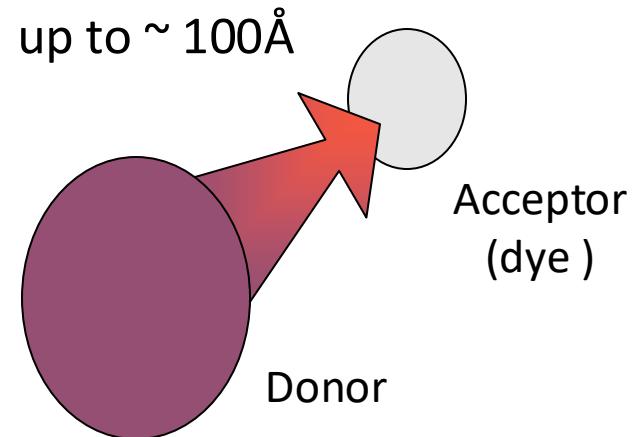
Different transfer ranges accessed by different processes

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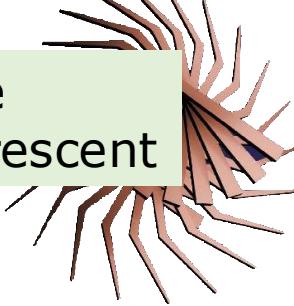
Förster Resonant Energy Transfer (FRET)

- 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

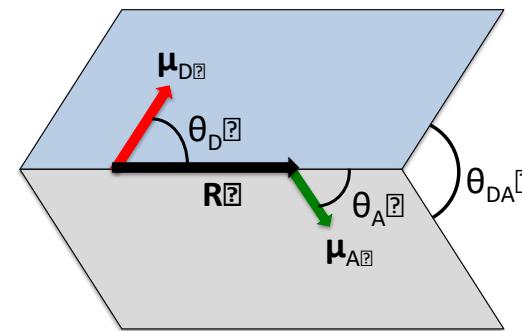
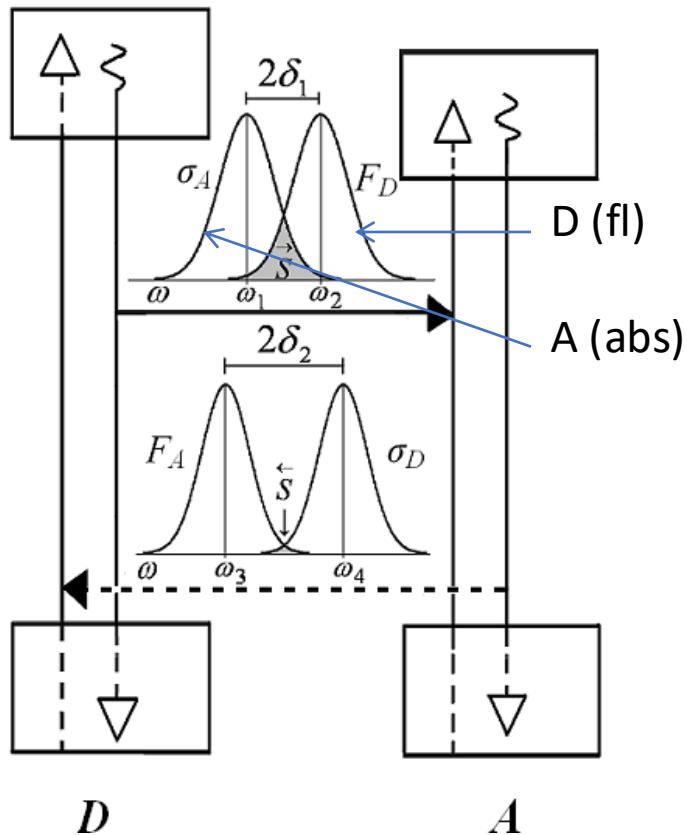
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Transfer occurs via electric dipole interactions

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

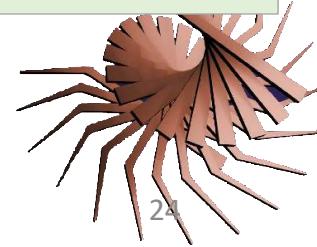
Relative orientation of *excited state* donor and *ground state* acceptor dipoles determines coupling strength (i.e. its efficiency):



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!

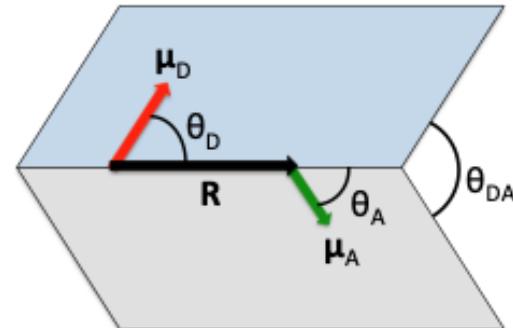


Calculating FRET

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

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!

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

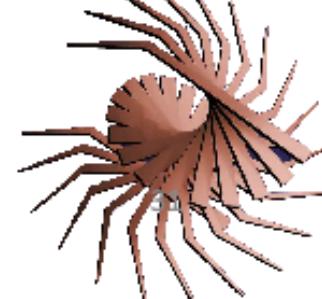
Fluorescence quantum yield of donor

Donor natural lifetime

Normalized fluorescence spectrum of donor

Molar mass/mass density of acceptor

Absorption coeff't of
acceptor
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What FRET Implies

Simply put:

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

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.

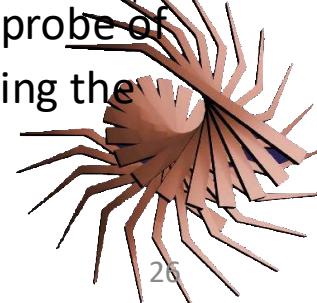
That is, when $R_0 = R_{DA}$, then $k_{ET} = 1/\tau_D$, the natural radiative lifetime. Thus, the transfer efficiency is:

$$\eta_{ET} = \frac{\tau_D}{\tau_{ET} + \tau_D} \rightarrow \frac{1}{2} \quad \left(\frac{1}{\tau_D} = \frac{1}{\tau_F} + \frac{1}{\tau_{NR}} \right)$$

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

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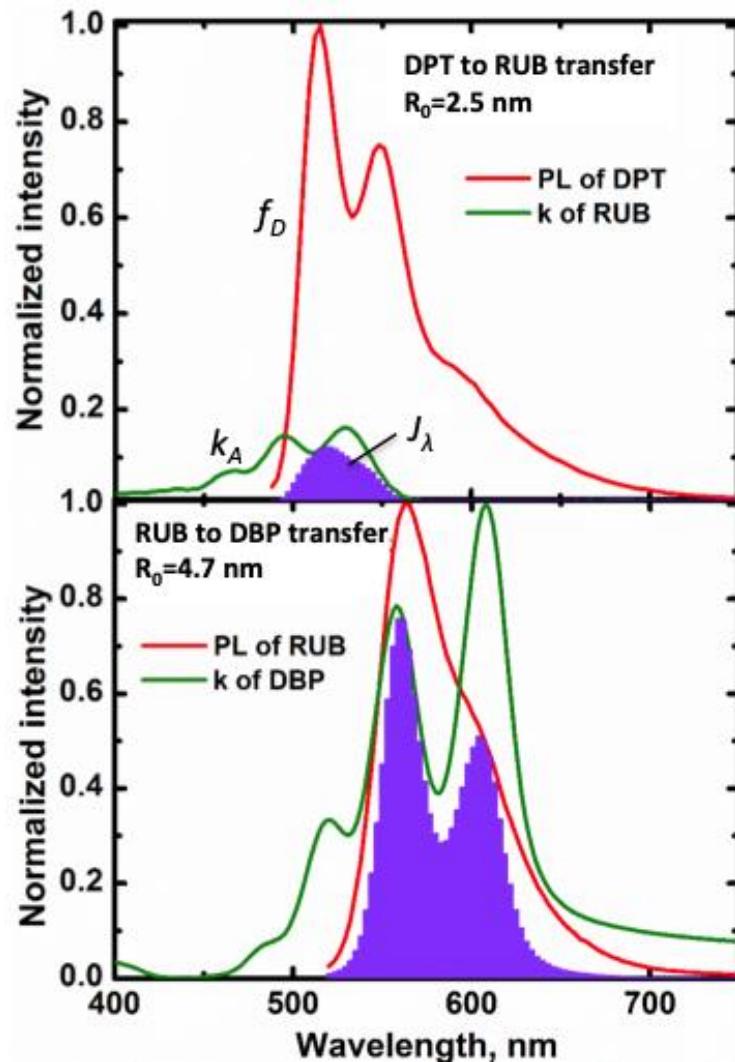
- Keep in mind that **FRET is orientation dependent** : this makes it a probe of molecular orientation by using polarized input light, and determining the polarization of the light emitted from the acceptors
- **FRET transfer time ~ radiative emission time**: $k_{ET} \sim 1-10$ ns.
- Primary route to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



A FRET Example

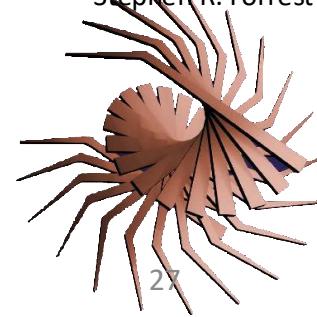
FRET is important in OLEDs, OPVs, biology,....

Typical molecules used in OPVs and OLEDs



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

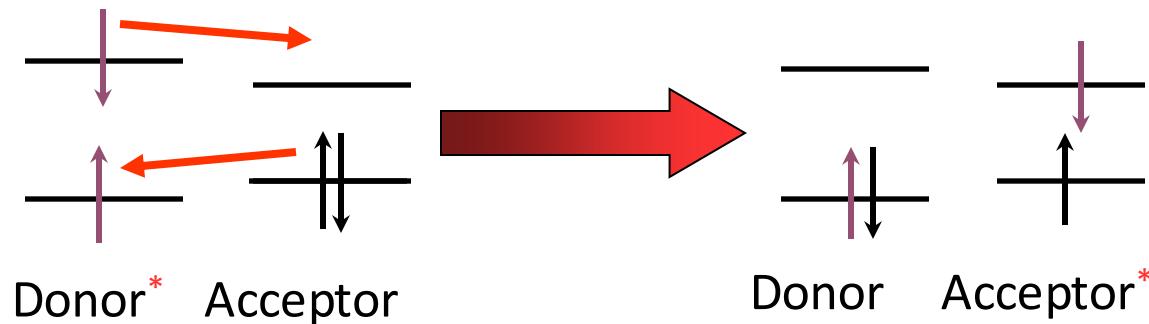
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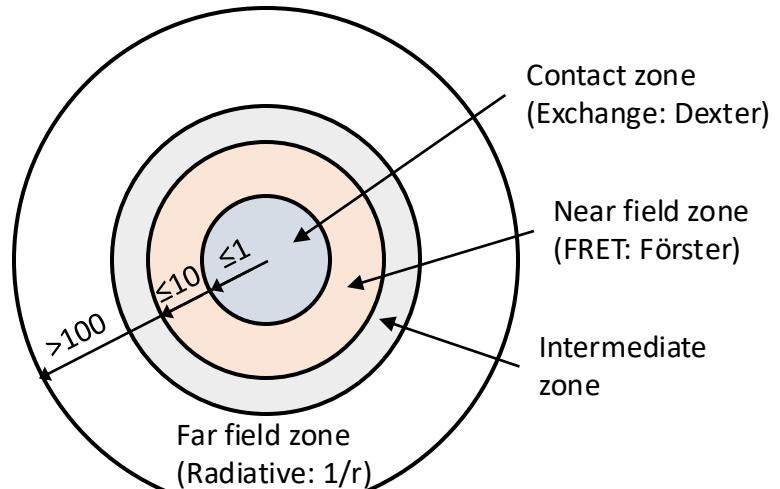
Exchange Energy Transfer

- 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

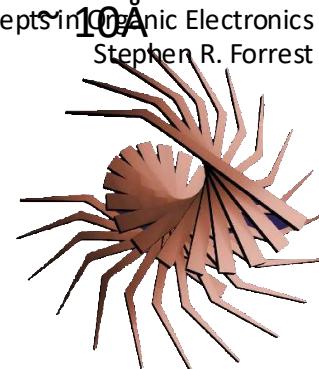
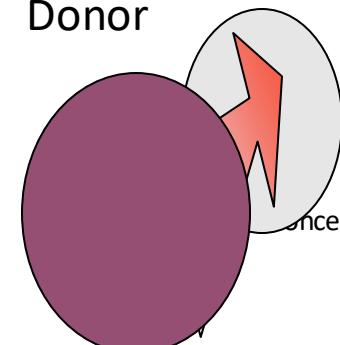


Dexter, L. A Theory of Sensitized Luminescence in Solids. *J. Chem. Phys.*, **21**, 836 (1953).



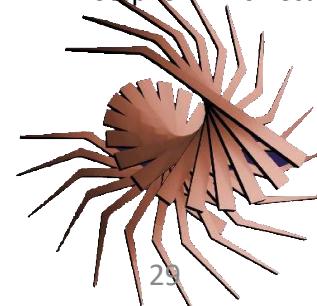
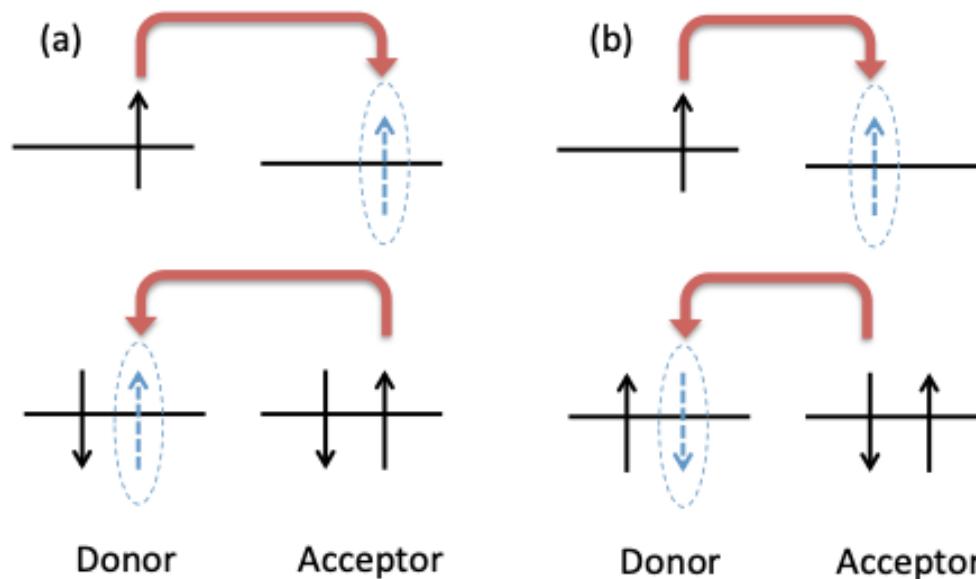
Acceptor
(e.g. phosphorescent dye)

Donor



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Spin conserving exchange interactions



Dexter Also Requires Resonance between D* and A⁰

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

Overlap, φ , 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

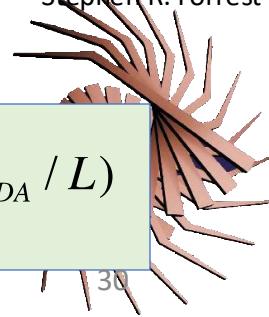
$$\Gamma^2 \propto \frac{q^2}{(4\pi\epsilon_0)^2 n_r R_{DA}^2} \exp(-2R_{DA}/L)$$

Very rapidly decreasing
“tunneling” between nearest
neighbors

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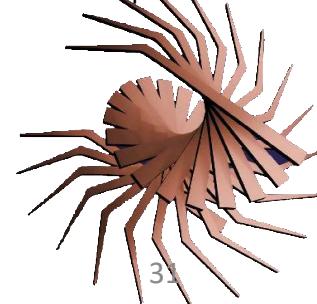
Finally resulting in the Dexter transfer equation:

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



Important facts about Dexter exchange

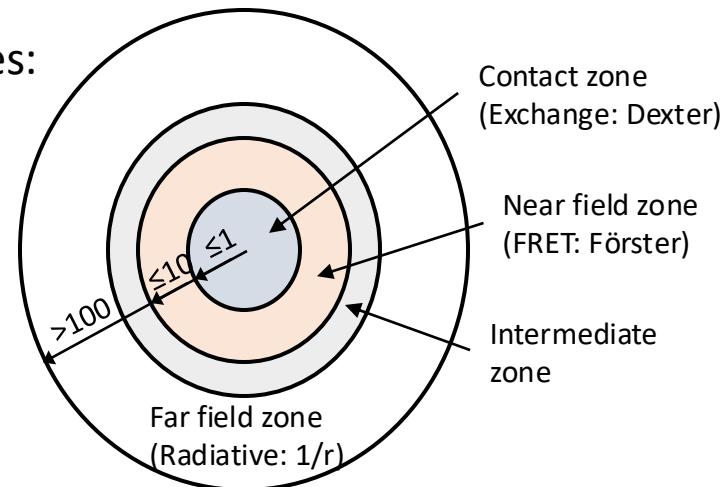
- **Spin of the donor and acceptor can change during exchange**
 - Spin of the excited and ground states cannot change
 - Effective in transfer of non-radiative triplet states (FRET is not since triplets are *generally* non-radiative)
- **Transfer is in the contact zone, only between nearest neighbors**
 - Range determined by vdW radius of the molecules
- **To first order (s-like states), there is no dependence on orientation**
 - κ 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

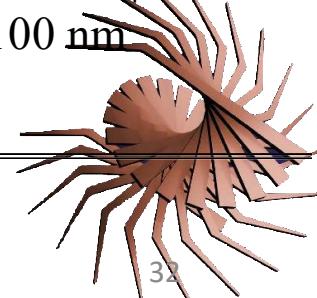
The total rate is equal to the sum of the individual rates:

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



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

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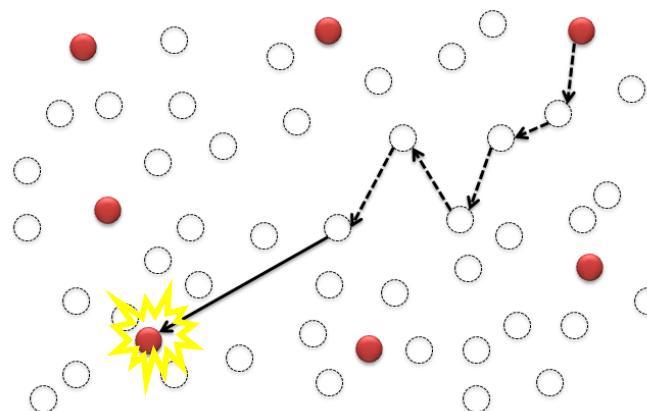


Annihilation!

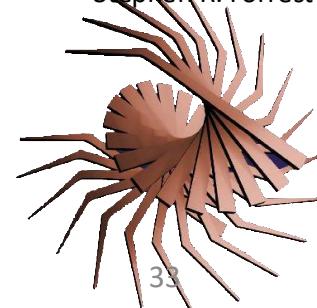
When excitons collide at a single molecular site, they can combine to form a single exciton and a ground state molecule: Exciton-exciton annihilation

Spin multiplicity can determine annihilation efficiency (Dexter vs FRET). Annihilation leads to losses, and phenomena like delayed fluorescence.

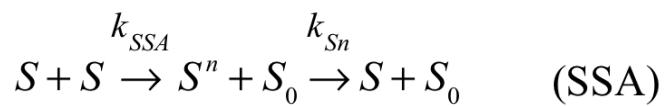
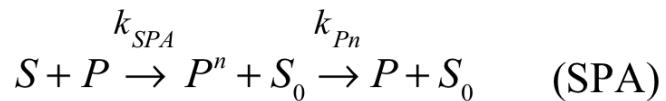
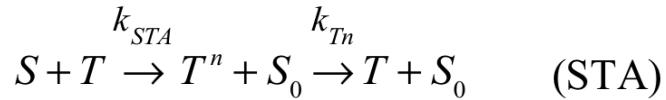
When excitons collide with charges, the charge can be excited, losing the exciton: Exciton-polaron annihilation



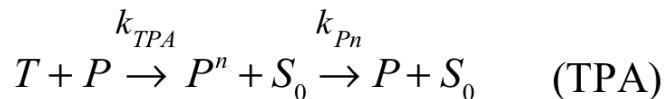
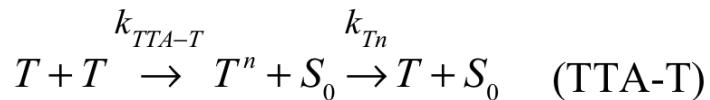
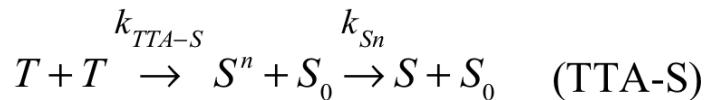
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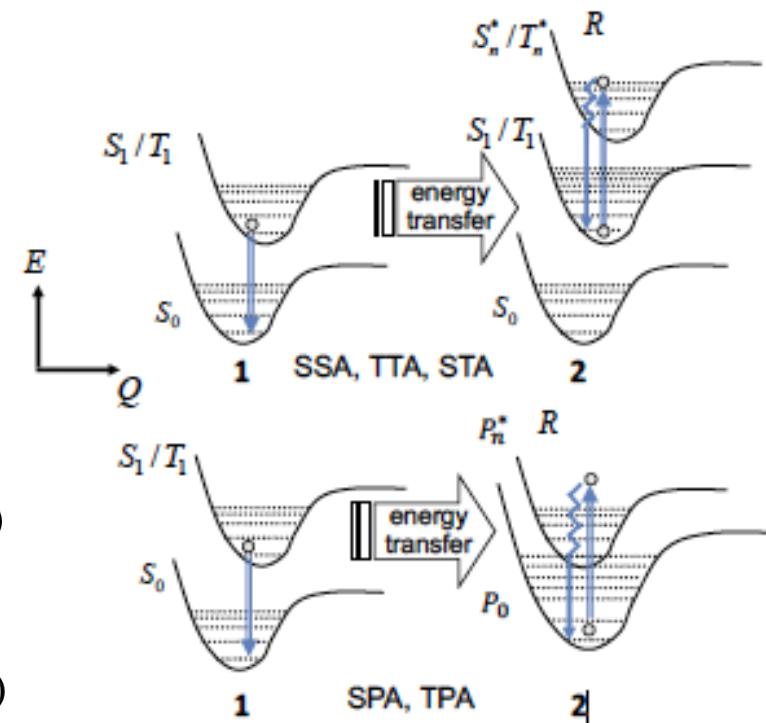
Bad things happen to good excitons



Delayed fluorescence
Triplet fusion



Singlet fission when
 $E_S \geq 2E_T$



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