# Week 1-15

## Review

# What organic electronics are good for

- Low cost
- Large area
- Flexible
- Conformable/Stretchable
- Light weight
- Optoelectronics

# This Chart Explains Why Organic Semiconductors are Unique

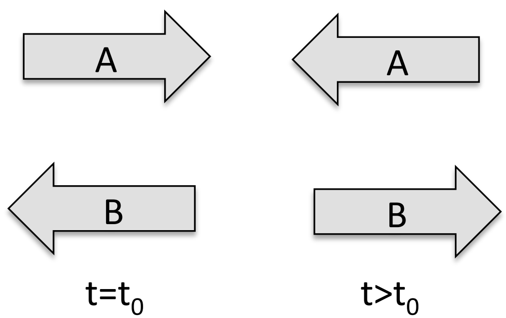
| Property | Organics | Inorganics |
|---|---|---|
| Bonding | van der Waals | Covalent/Ionic |
| Charge Transport | Polaron Hopping | Band Transport |
| Mobility | ~1 $cm^2/V \cdot s$ | ~1000 $cm^2/V \cdot s$ |
| Absorption | $10^5$-$10^6$ $cm^{-1}$ | $10^4$-$10^5$ $cm^{-1}$ |
| Excitons | Frenkel | Wannier-Mott |
| Binding Energy | ~500-800 meV | ~10-100 meV |
| Exciton Radius | ~10 Å | ~100 Å |

# Organic Materials are Interesting Because…

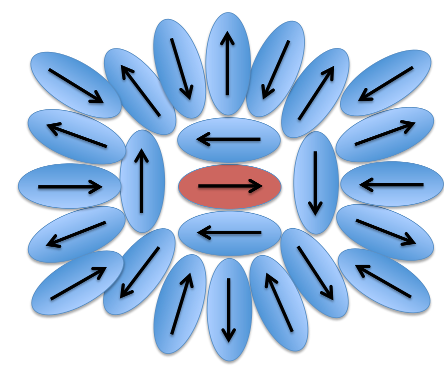
- They have properties that bridge between their individual molecular and collective (solid state) properties
- They provide deep insights into how the properties of molecules transform into band structure (via tight binding), conductivity and excitonic states
- Almost all physical properties result from electrostatic, van der Waals bonds (vs. chemical bonds) between molecules in the solid state
- Disorder governs characteristics in the solid state
- Their mechanical fragility leads to film growth and patterning that differ from more robust, inorganic semiconductors

# van der Waals bonding

- Purely electrostatic *instantaneous* induced dipole-induced dipole interaction between π-systems of nearby molecules.




Medium around the dipole is *polarized*



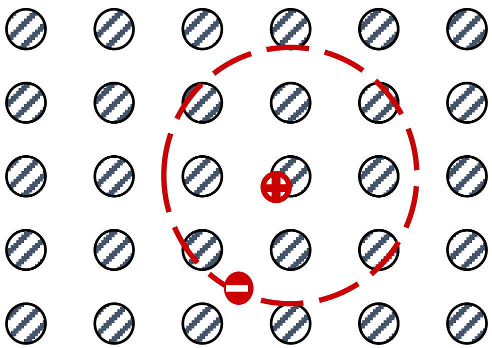
$$U(r_{12}) = -\frac{A_{disp}}{r_{12}^6}$$ : Dispersion interaction

$$U(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$ : Lennard-Jones 6-12 potential (includes core repulsion)

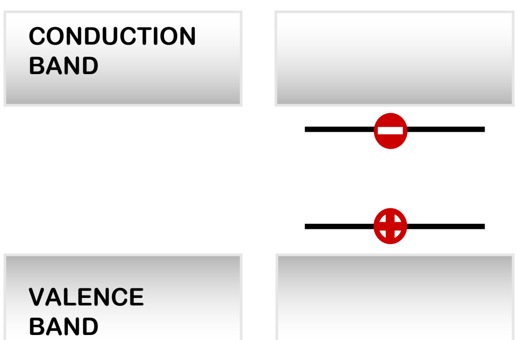
# Organic Semiconductors are Excitonic Materials

**Inorganics** ⟷ **Organics**

## Wannier exciton
Inorganic semiconductors



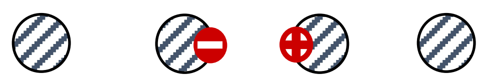
**SEMICONDUCTOR PICTURE**




GROUND STATE WANNIER EXCITON

Dielectric constant ~15
binding energy ~10meV (unstable at RT)
radius ~100Å

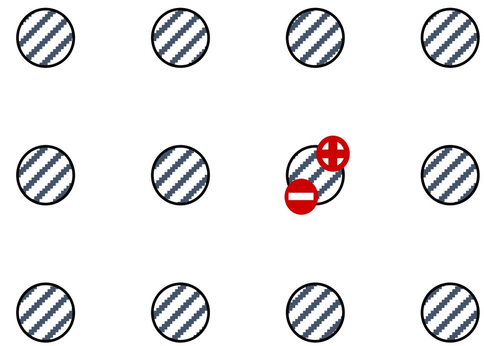
## Charge Transfer (CT) Exciton
(bridge between W and F)



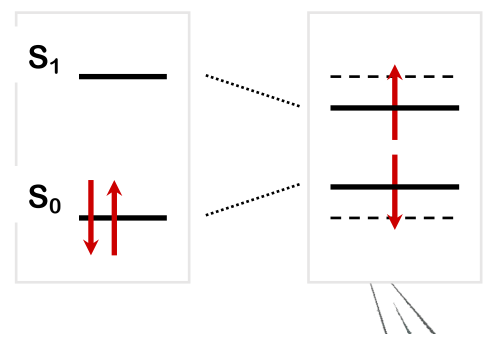
treat excitons as chargeless particles capable of diffusion.

Transport of energy (not charge)

## Frenkel exciton
Organic materials



**MOLECULAR PICTURE**




GROUND STATE FRENKEL EXCITON

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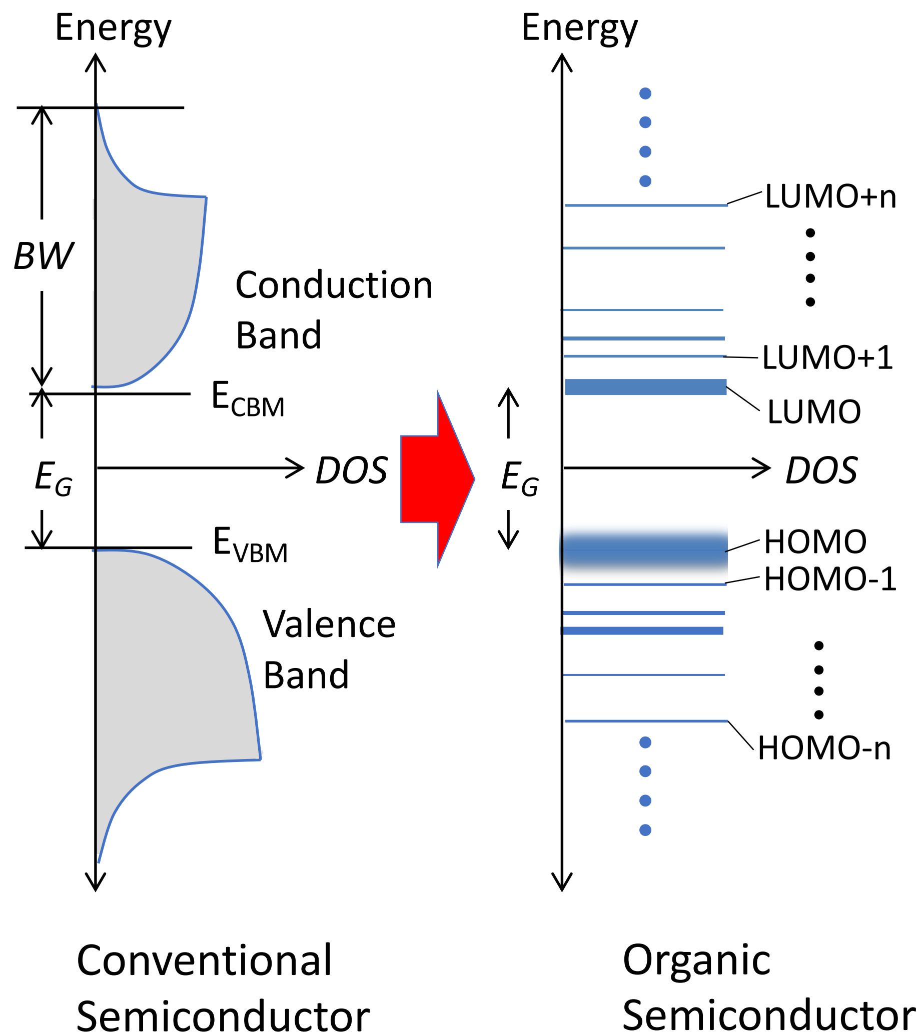
Dielectric constant ~2
binding energy ~1eV (stable at RT)
radius ~10Å

# Band Structure is Replaced by Energy Levels




LUMO: Lowest unoccupied molecular orbital

HOMO: Highest occupied molecular orbital



**It is essential to keep your terminology clear: Band gaps exist in inorganics, energy gaps without extended bands are the rule (but with important exceptions) in organics.**

# Singlet and triplet states

Spatially symm. Spin antisymm.

S m_S

$$\psi(\mathbf{r}_1,\mathbf{r}_2;0,0)=\frac{1}{\sqrt{2}}\left(\phi_a(\mathbf{r}_1)\phi_b(\mathbf{r}_2)+\phi_a(\mathbf{r}_2)\phi_b(\mathbf{r}_1)\right)\left(\alpha_1\beta_2-\alpha_2\beta_1\right)$$

**Singlet**
S=0
$m_s$= 0

$$\psi(\mathbf{r}_1,\mathbf{r}_2;1,1)=\frac{1}{\sqrt{2}}\left(\phi_a(\mathbf{r}_1)\phi_b(\mathbf{r}_2)-\phi_a(\mathbf{r}_2)\phi_b(\mathbf{r}_1)\right)\alpha_1\alpha_2$$

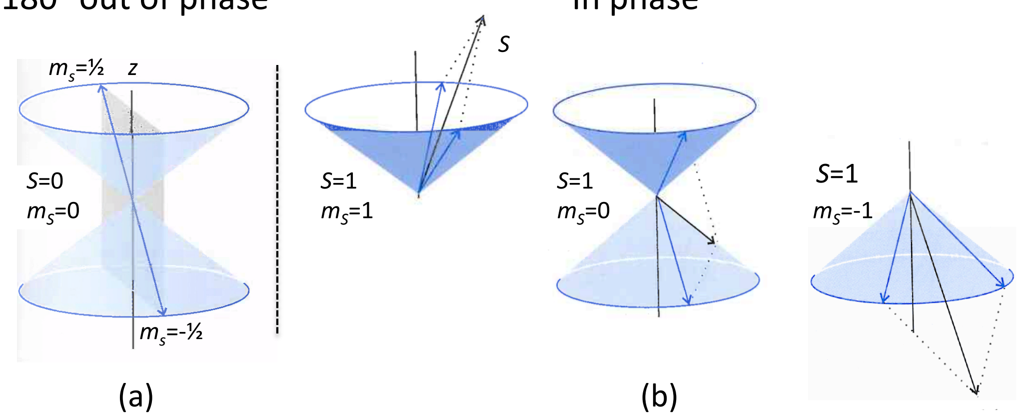
$$\psi(\mathbf{r}_1,\mathbf{r}_2;1,0)=\frac{1}{\sqrt{2}}\left(\phi_a(\mathbf{r}_1)\phi_b(\mathbf{r}_2)-\phi_a(\mathbf{r}_2)\phi_b(\mathbf{r}_1)\right)\left(\alpha_1\beta_2+\alpha_2\beta_1\right)$$

and

$$\psi(\mathbf{r}_1,\mathbf{r}_2;1,-1)=\frac{1}{\sqrt{2}}\left(\phi_a(\mathbf{r}_1)\phi_b(\mathbf{r}_2)-\phi_a(\mathbf{r}_2)\phi_b(\mathbf{r}_1)\right)\beta_1\beta_2$$

**Triplet**
S=1
$m_s$=±1, 0

180° out of phase In phase




(a) (b)

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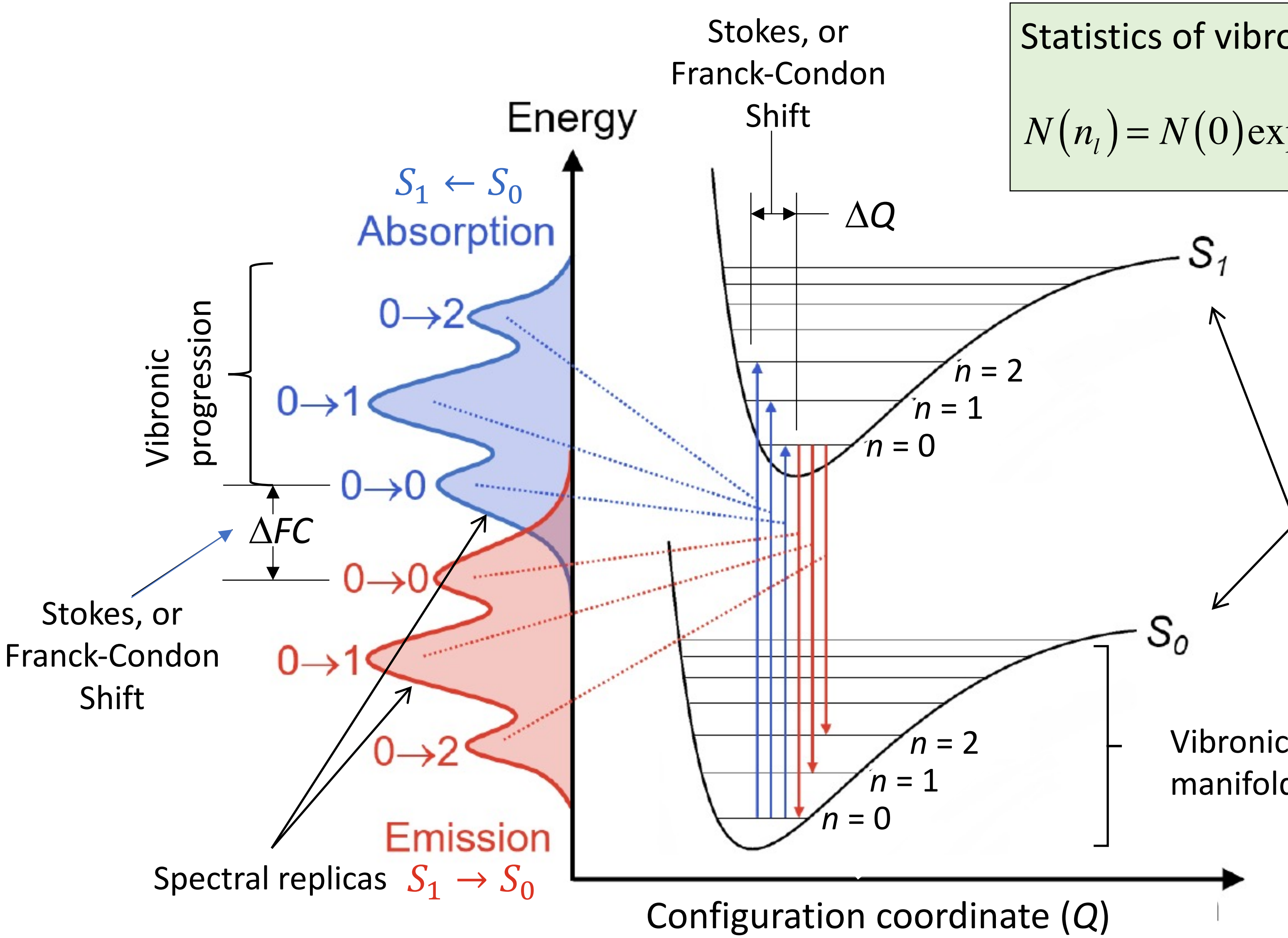
**Pauli Exclusion Principle: Total wavefunctions must be antisymmetric**

# Understanding molecular spectra

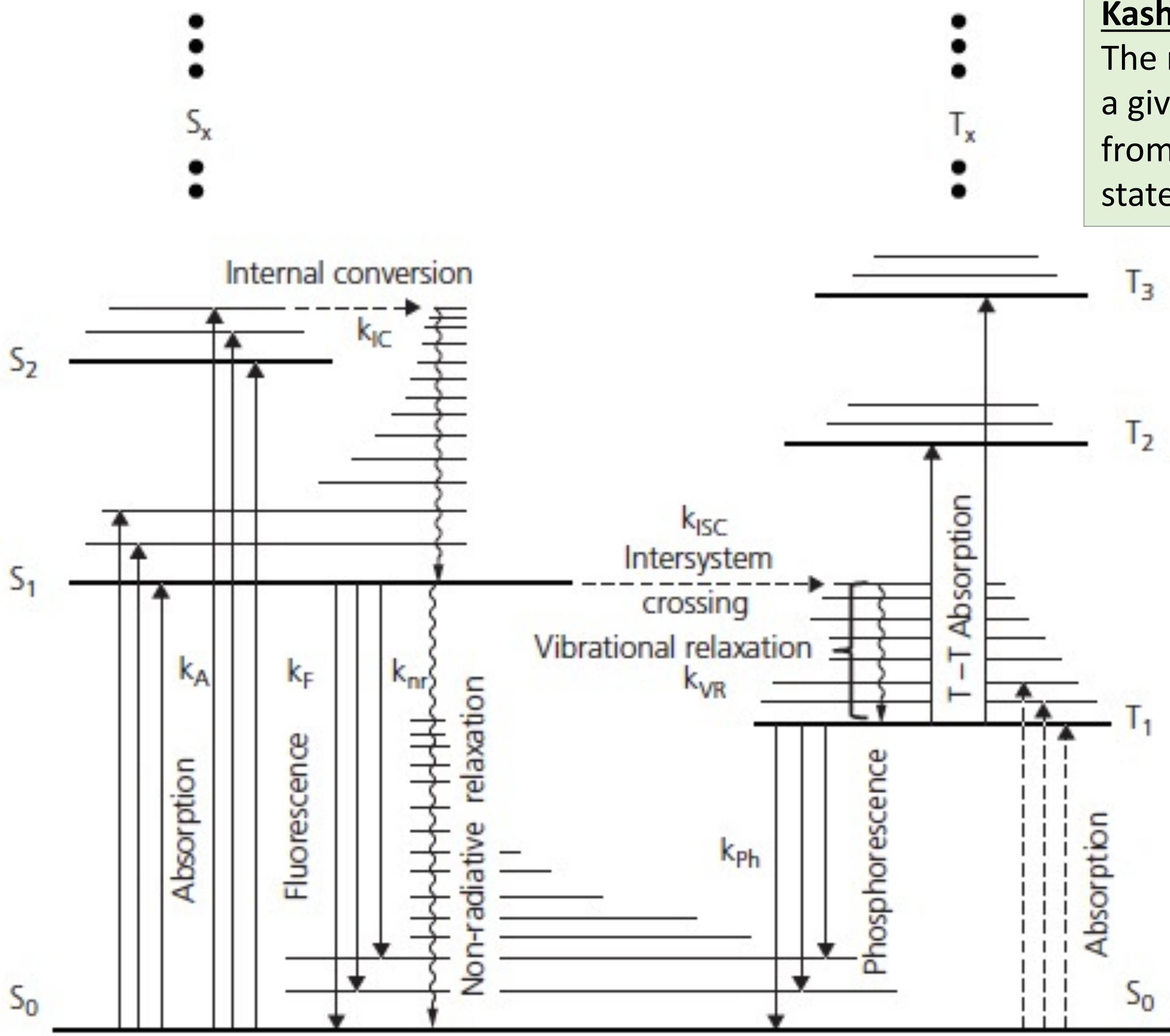



Statistics of vibronic state filling:

$$N(n_l) = N(0)\exp(-n_l \hbar\omega_l / k_B T)$$

# Jablonski Diagrams:
## Life Histories of Excitons

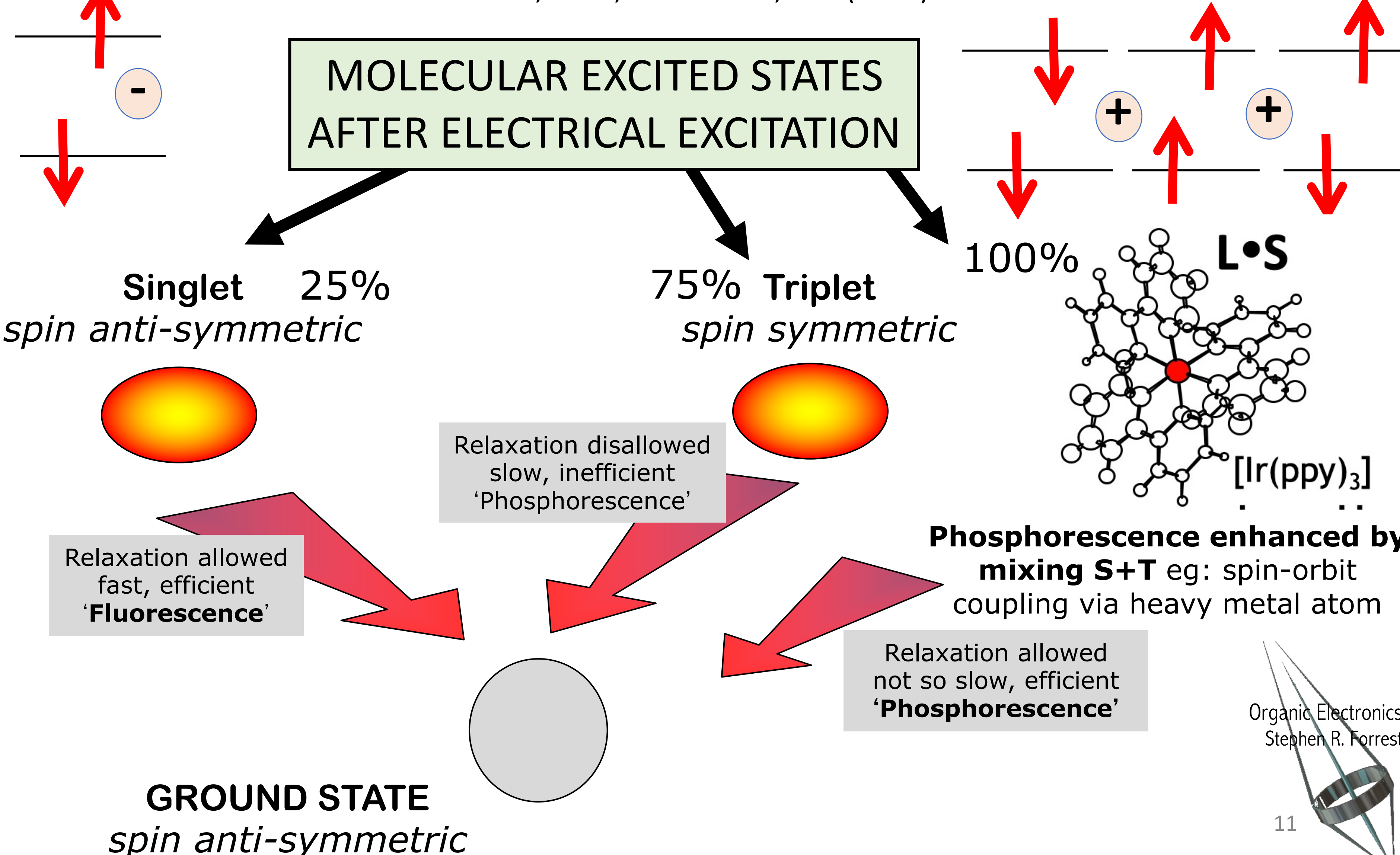
**Kasha's rule**
The radiative transition from a given spin manifold occurs from the lowest excited state.



# 100% Internal Efficiency via Spin-Orbit Coupling

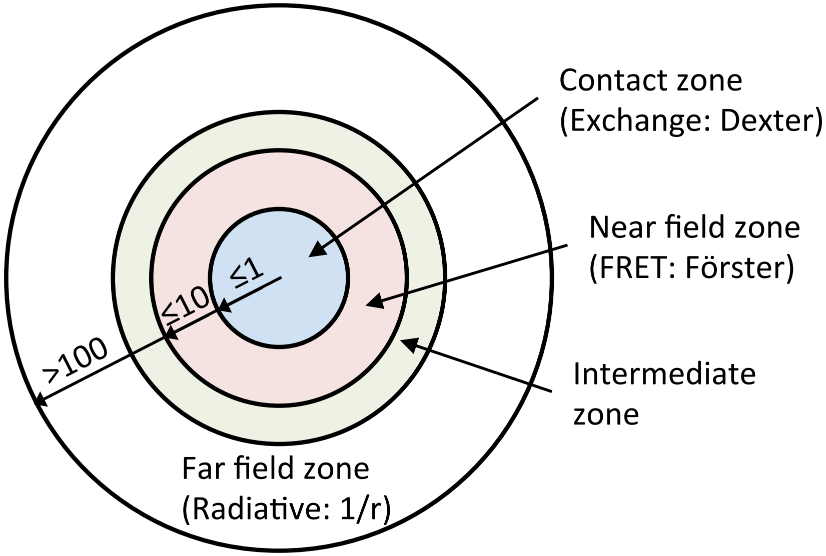
## Heavy metal induced electrophosphorescence ~100% QE

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



# Energy Transfer

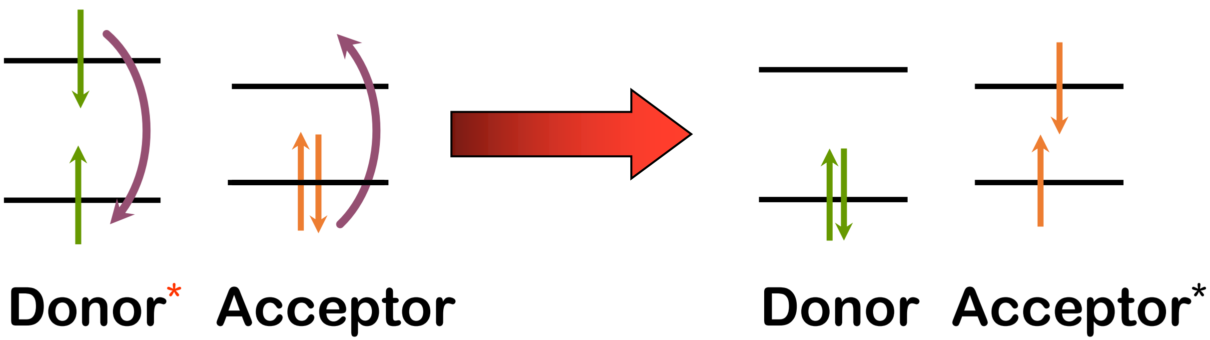
- If excitons are mobile in the solid, they must move from molecule to molecule
  - ✧ The microscopic "hopping" between neighboring molecules = energy transfer

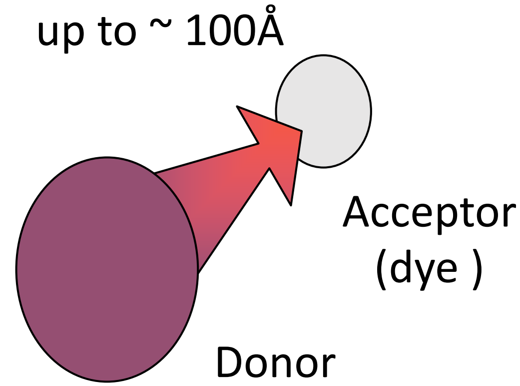



Different transfer ranges accessed by different processes

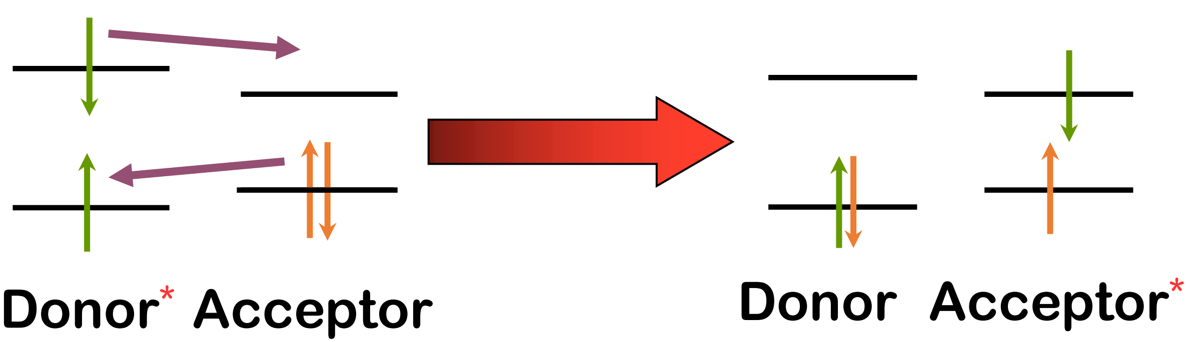
# Energy Transfer from Host to Dopant: A Review

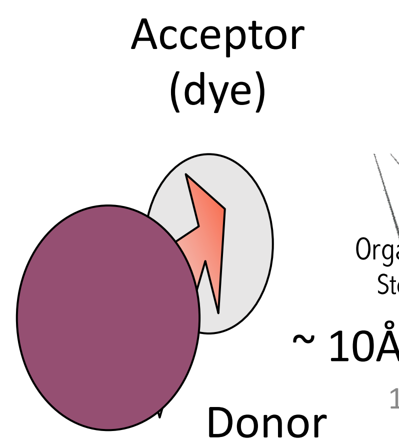
Förster:
- resonant dipole-dipole coupling
- donor and acceptor transitions must be allowed



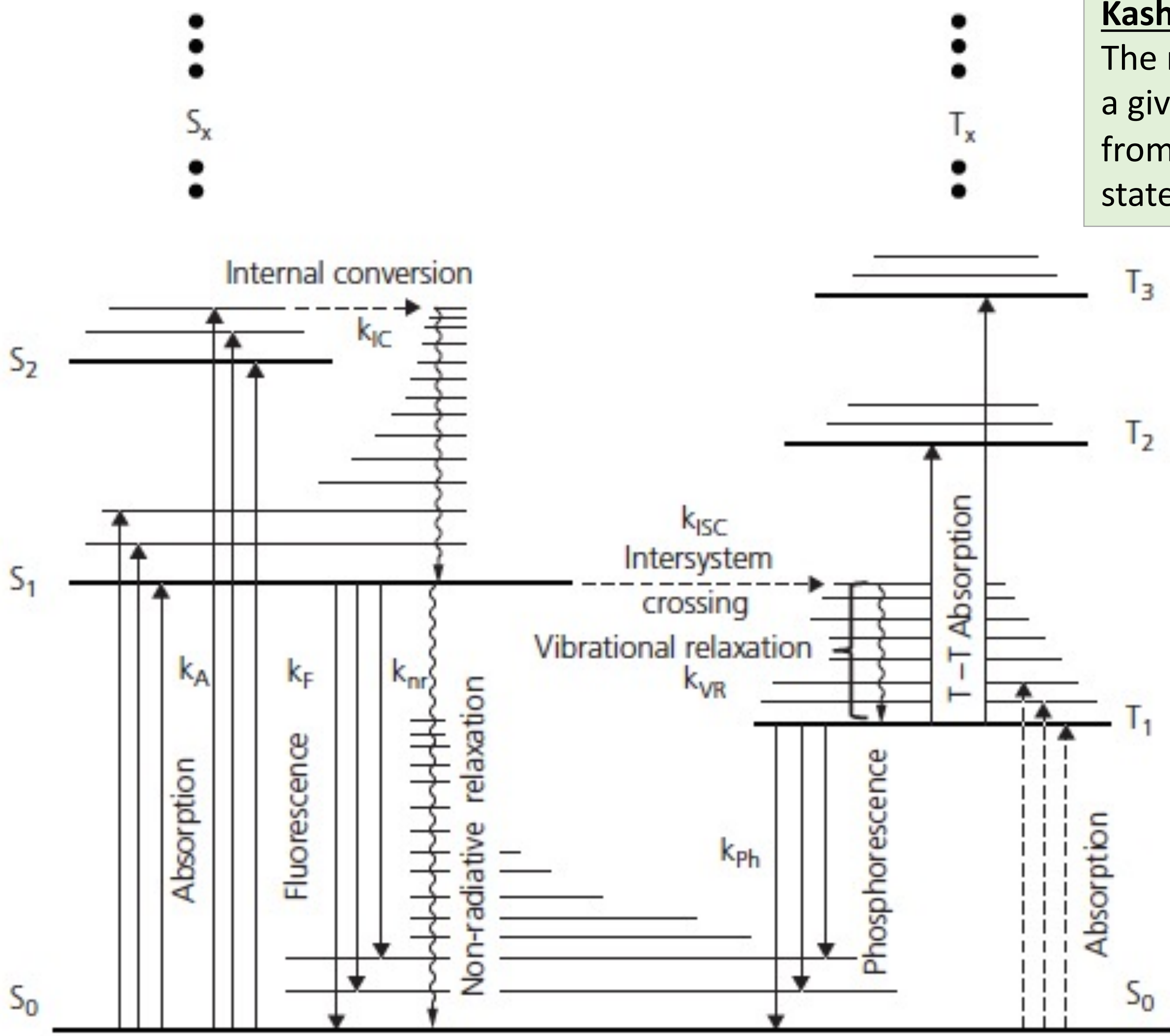

Electron Exchange (Dexter):
- diffusion of excitons from donor to acceptor by simultaneous charge exchange: short range




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

# Jablonski Diagrams

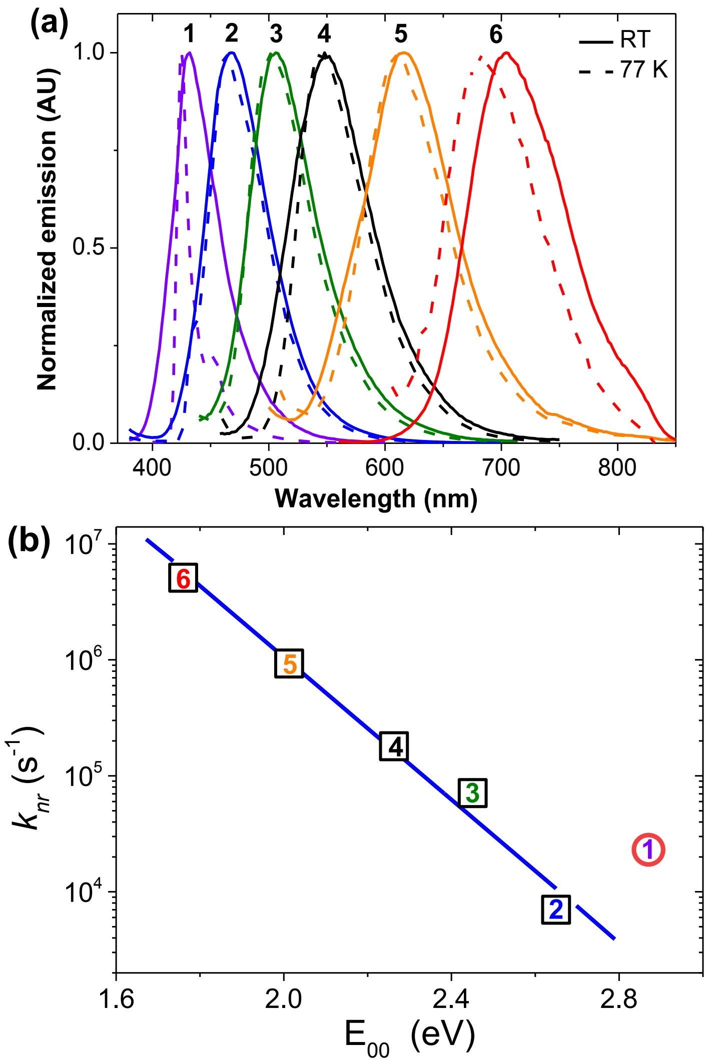


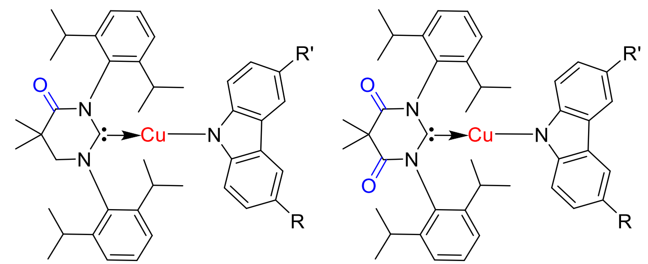

**Kasha's rule**
The radiative transition from a given spin manifold occurs from the lowest excited state.

# 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**)

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

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

Ω= number of modes contributing to the maximum phonon energy,
= ½ the Stokes shift.

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Shi, S., et al. 2019. *J. Am. Chem. Soc.*, *141*(8), pp.3576-3588.

# Bad things happen to good excitons

$$S+T \overset{k_{STA}}{\rightarrow} T^n + S_0 \overset{k_{Tn}}{\rightarrow} T + S_0 \qquad \text{(STA)}$$

$$S+P \overset{k_{SPA}}{\rightarrow} P^n + S_0 \overset{k_{Pn}}{\rightarrow} P + S_0 \qquad \text{(SPA)}$$

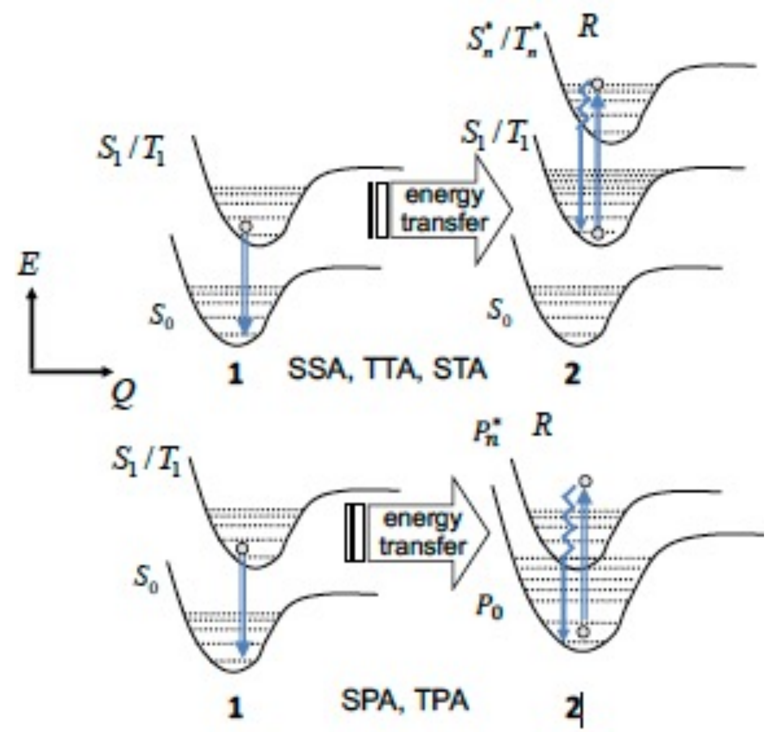
$$S+S \overset{k_{SSA}}{\rightarrow} S^n + S_0 \overset{k_{Sn}}{\rightarrow} S + S_0 \qquad \text{(SSA)}$$

Delayed fluorescence
Triplet fusion

$$T+T \overset{k_{TTA-S}}{\rightarrow} S^n + S_0 \overset{k_{Sn}}{\rightarrow} S + S_0 \qquad \text{(TTA-S)}$$

$$T+T \overset{k_{TTA-T}}{\rightarrow} T^n + S_0 \overset{k_{Tn}}{\rightarrow} T + S_0 \qquad \text{(TTA-T)}$$

$$T+P \overset{k_{TPA}}{\rightarrow} P^n + S_0 \overset{k_{Pn}}{\rightarrow} P + S_0 \qquad \text{(TPA)}$$

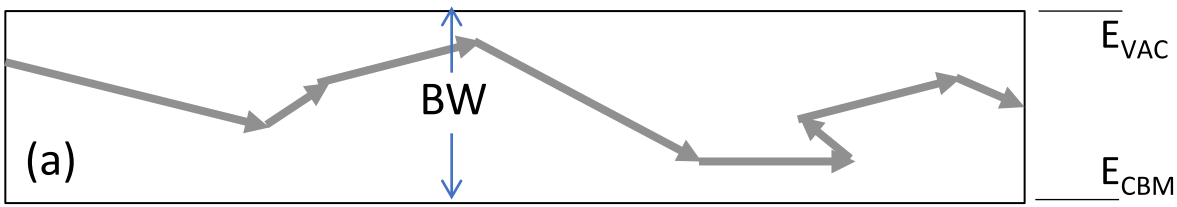



Singlet fission when $E_S \geq 2E_T$

$$S \rightarrow 2T$$

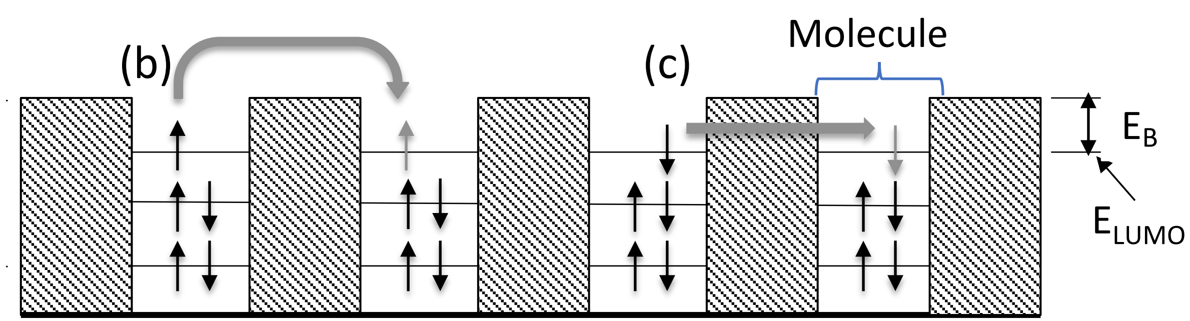
# Modes of Conduction

**Band transport**




- Coherent
- Charge mean free path $\lambda >> a$
- $BW > k_B T,\ \hbar\omega_0$

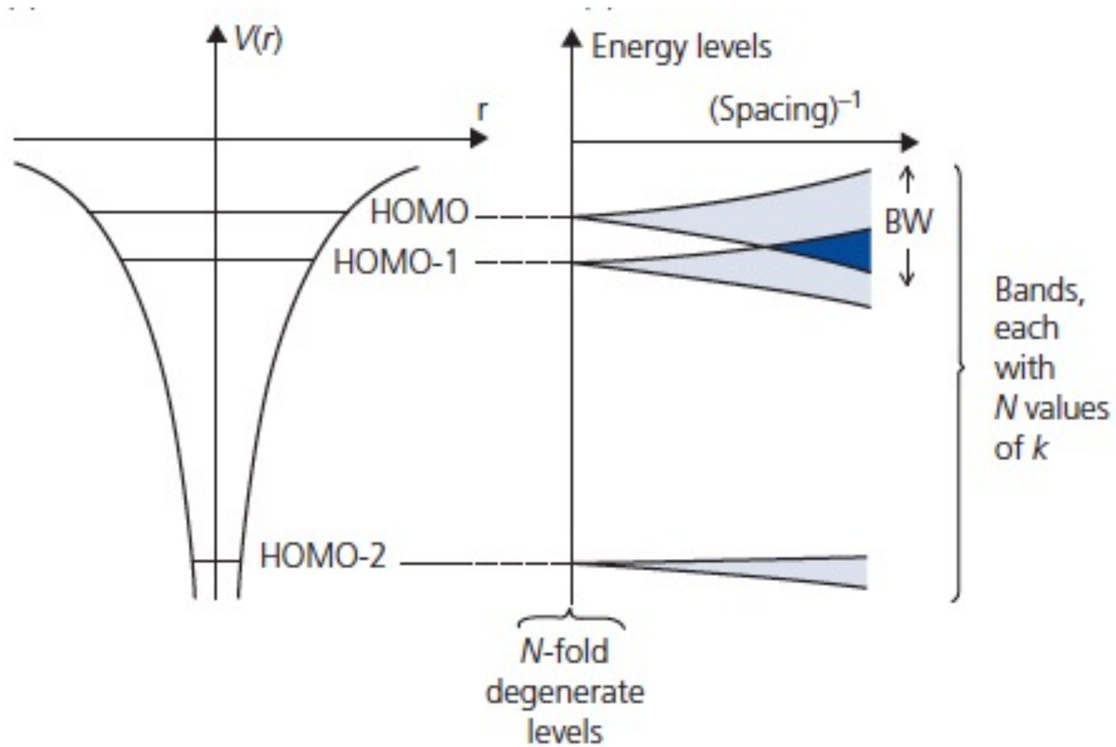
**Hopping and tunneling transport**




- Incoherent (each step independent of previous)
- Charge mean free path $\lambda \sim a$
- Tunneling between states of equal energy <u>is</u> band-like
- $BW < k_B T,\ \hbar\omega_0$

# Transport Bands in Organics

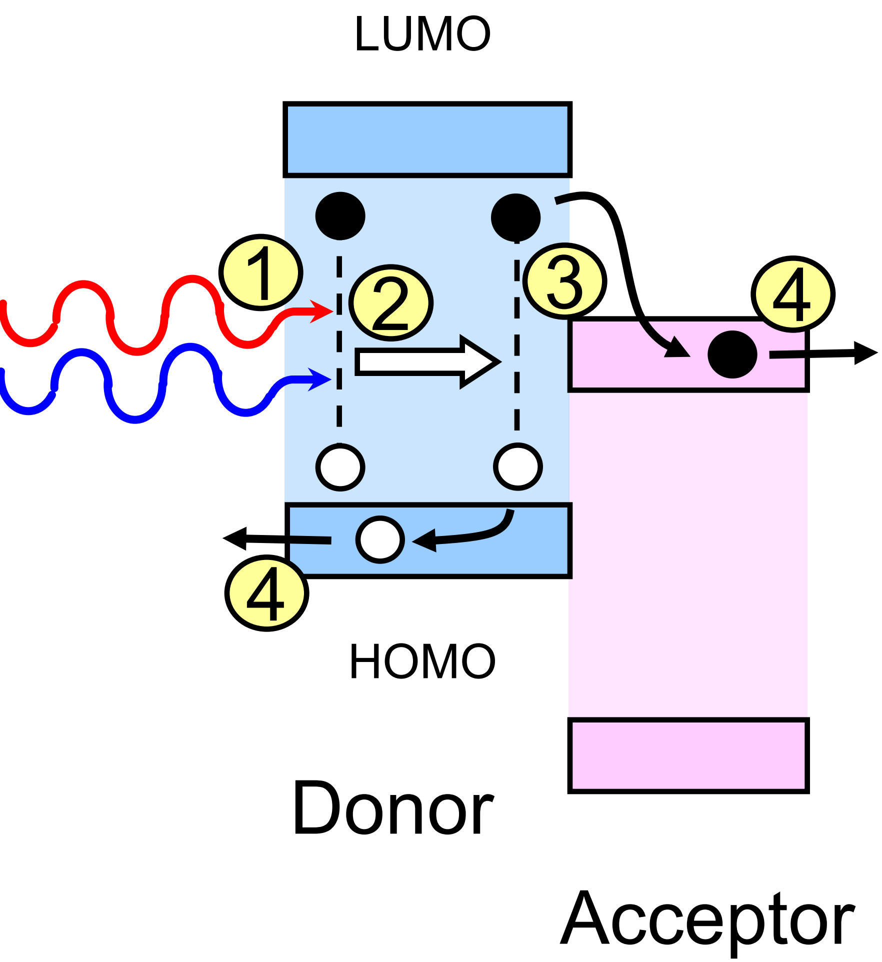
- **Tight binding** approximation is useful due to importance of only nearest neighbor interactions
- Recall case of dimers and larger aggregates on exciton spectrum. Close proximity of neighbors results in:
  - Coulomb repulsion
  - Pauli exclusion
  - ➢ Splitting leads to broadening of discrete energies into bands



# Photoinduced Charge-Transfer at a Type II HJ

## The Basis of OPV Operation

Processes occuring at a Donor-Acceptor heterojunction

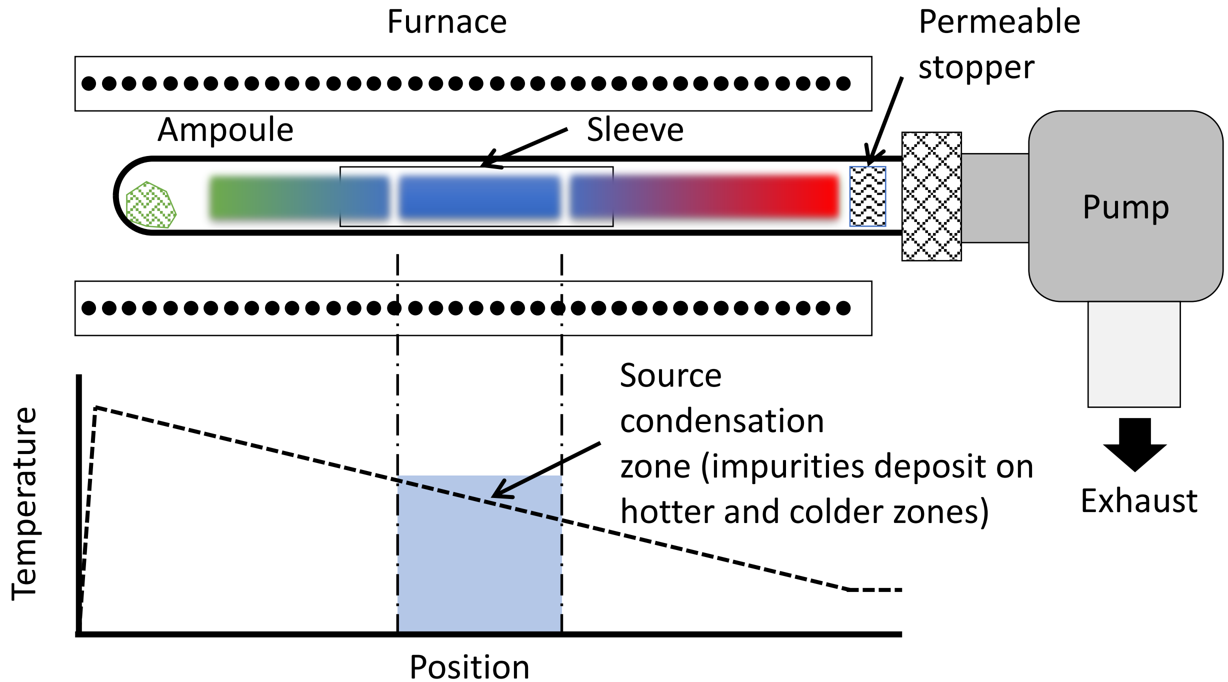


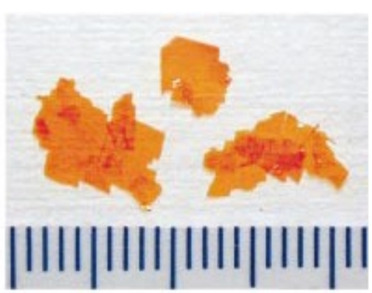

1. Exciton generation by absorption of light ($1/\alpha$)
2. Exciton diffusion over $\sim L_D$
3. Exciton dissociation by rapid and efficient charge transfer
4. Charge extraction by the internal electric field

Typically: $L_D \ll 1/\alpha$

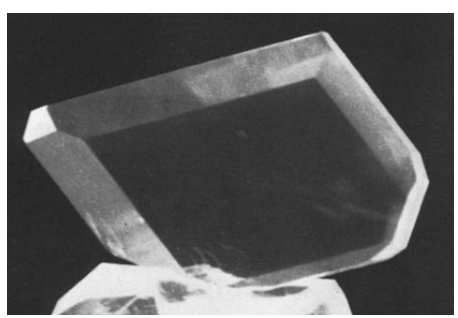
# Purification by Thermal Gradient Sublimation

Useful for obtaining very high purity small molecule materials



Tetracene after sublimation



Pyrene

- Reasonably fast and simple
- Material must be sublimable
- Multiple cycles result in higher purity
- Can occur in vacuum or under inert gas flow
- Small crystal growth on chamber walls possible

# Film Deposition

## Vacuum Thermal Evaporation (VTE)

- Most common method to date
- Simple
- Precise
- Multilayer structures possible
- Small molecules, not polymers
- Wasteful of materials
- High vacuum: $10^{-7}$ torr
- Oil-free pumps