Week 15

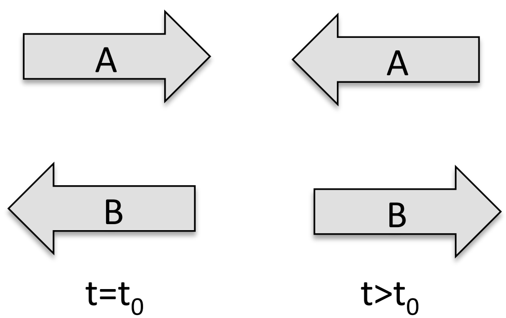
Review

Organic & Inorganic Semiconductors: What makes them different?

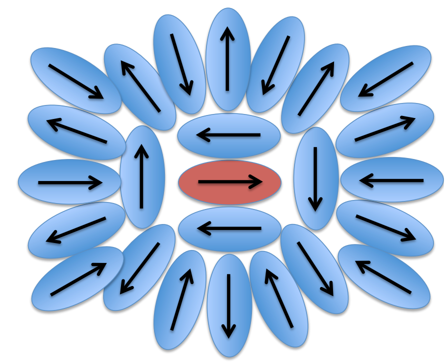
Property	Organics	Inorganics
Bonding	van der Waals	Covalent/Ionic
Charge Transport	Polaron Hopping	Band Transport
Mobility	~1 $cm^2/V \cdot s$	~1000 $cm^2/V \cdot s$
Absorption	10^5-10^6 cm^{-1}	10^4-10^5 cm^{-1}
Excitons	Frenkel	Wannier-Mott
Binding Energy	~500-800 meV	~10-100 meV
Exciton Radius	~10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

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

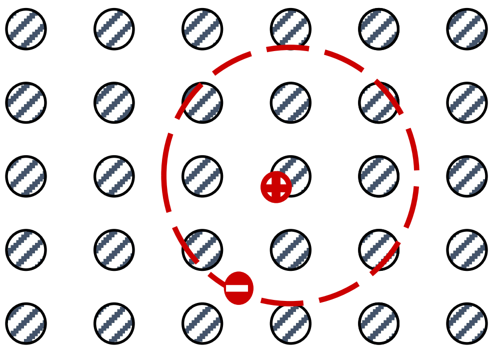
$$U(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$: Lennard-Jones 6-12 potential (includes core repulsion)

Organic Semiconductors are Excitonic Materials

Inorganics ⟷ **Organics**

Wannier exciton

Inorganic semiconductors

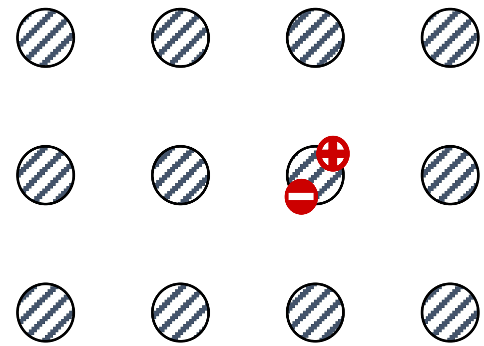


Charge Transfer (CT) Exciton

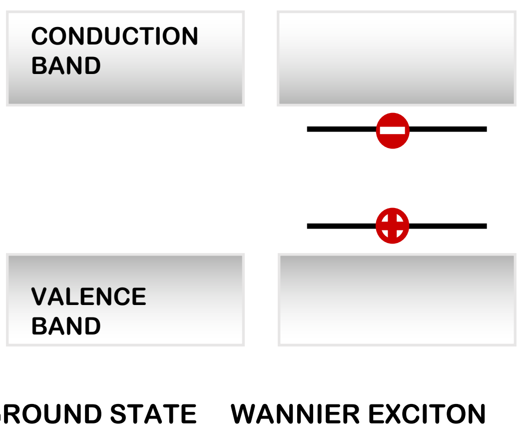
(bridge between W and F)

Frenkel exciton

Organic materials



SEMICONDUCTOR PICTURE

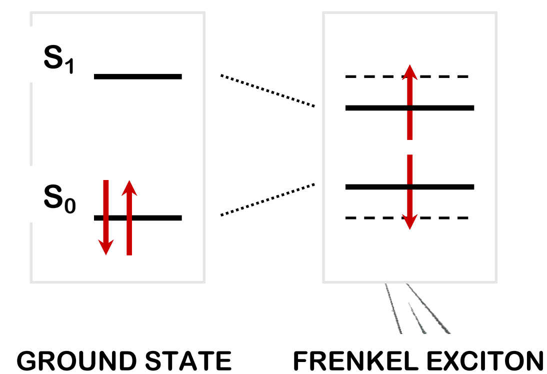


Dielectric constant ~15
binding energy ~10meV (unstable at RT)
radius ~100Å

treat excitons as chargeless particles capable of diffusion.

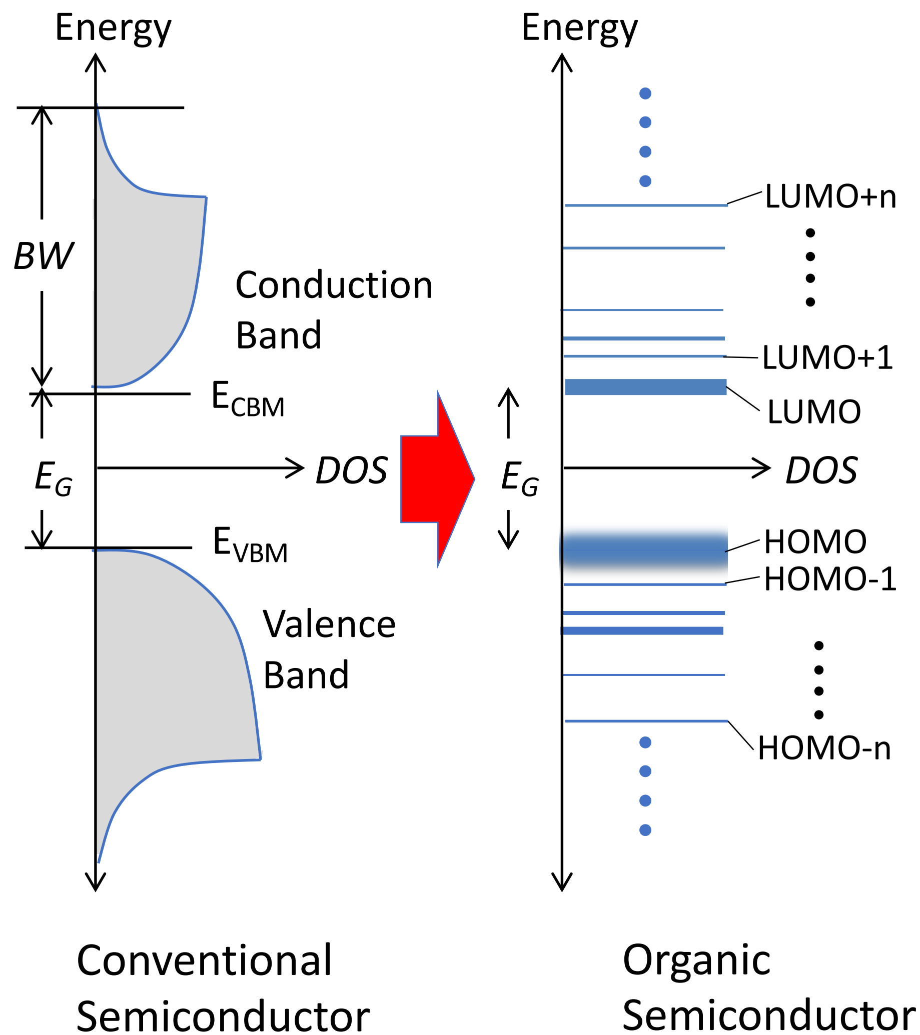
Transport of energy (not charge)

MOLECULAR PICTURE



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 <u>essential</u> 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

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

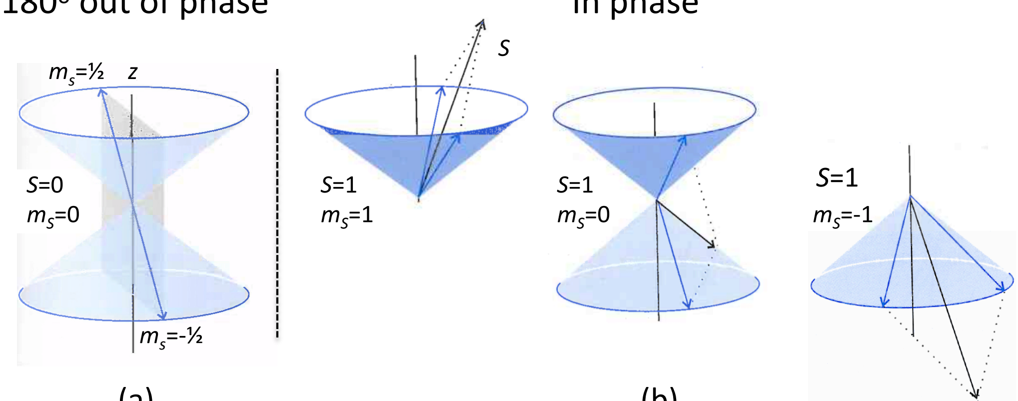
$$\psi(\mathbf{r}_1,\mathbf{r}_2;1,0)=\frac{1}{\sqrt{2}}\left(\phi_a(\mathbf{r}_1)\phi_b(\mathbf{r}_2)-\phi_a(\mathbf{r}_2)\phi_b(\mathbf{r}_1)\right)\left(\alpha_1\beta_2+\alpha_2\beta_1\right)$$

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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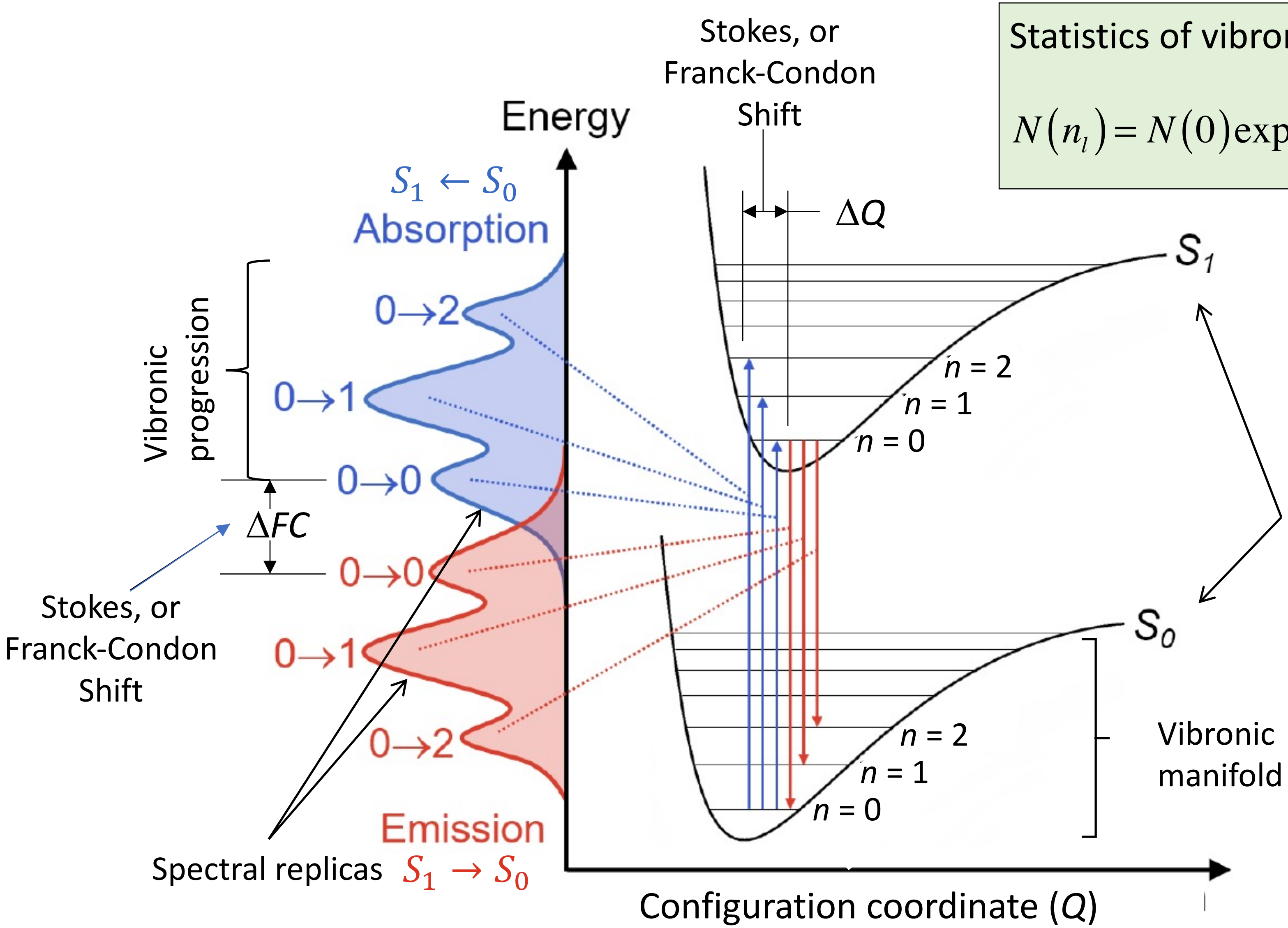
Pauli Exclusion Principle: Total wavefunctions must be antisymmetric

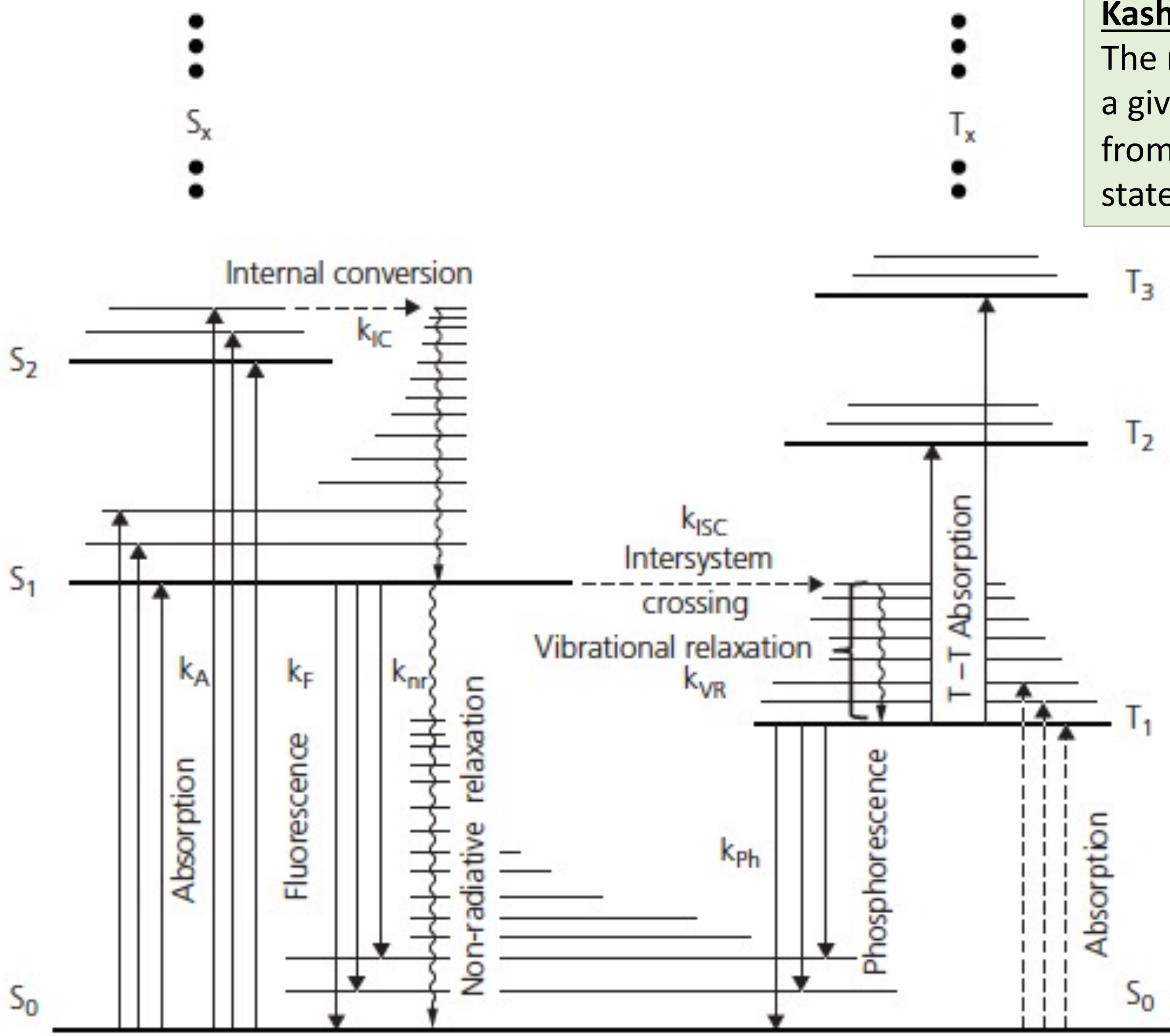
Understanding molecular spectra



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)

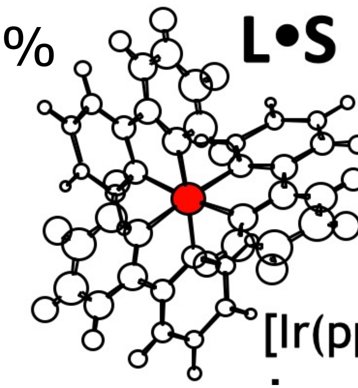
MOLECULAR EXCITED STATES
AFTER ELECTRICAL EXCITATION

Singlet 25%
spin anti-symmetric

75% **Triplet**
spin symmetric

100%

L•S



$[Ir(ppy)_3]$

Phosphorescence enhanced by mixing S+T eg: spin-orbit coupling via heavy metal atom

Relaxation disallowed
slow, inefficient
'Phosphorescence'

Relaxation allowed
fast, efficient
'**Fluorescence**'

Relaxation allowed
not so slow, efficient
'**Phosphorescence**'

GROUND STATE
spin anti-symmetric

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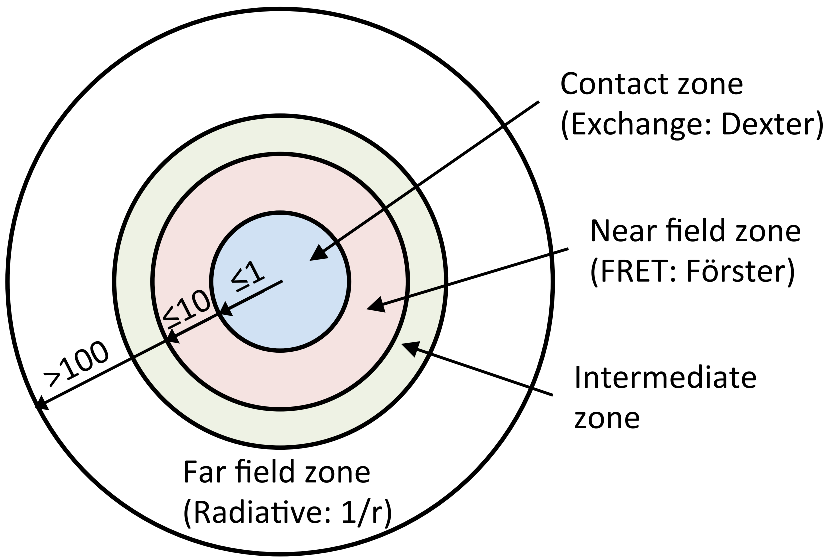
Energy Transfer

- 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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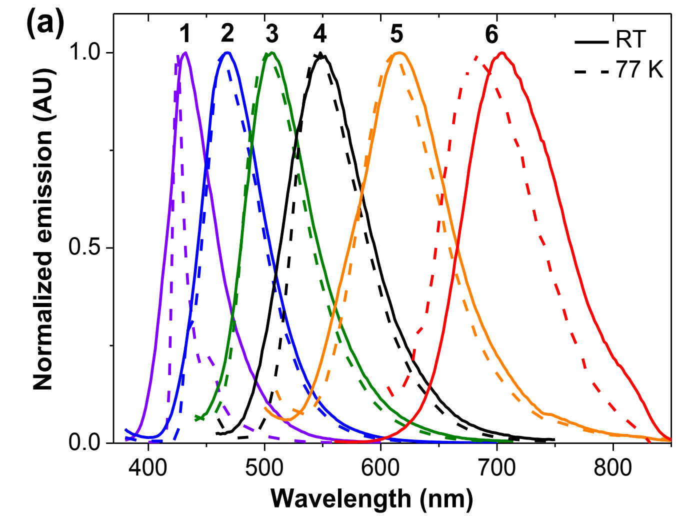
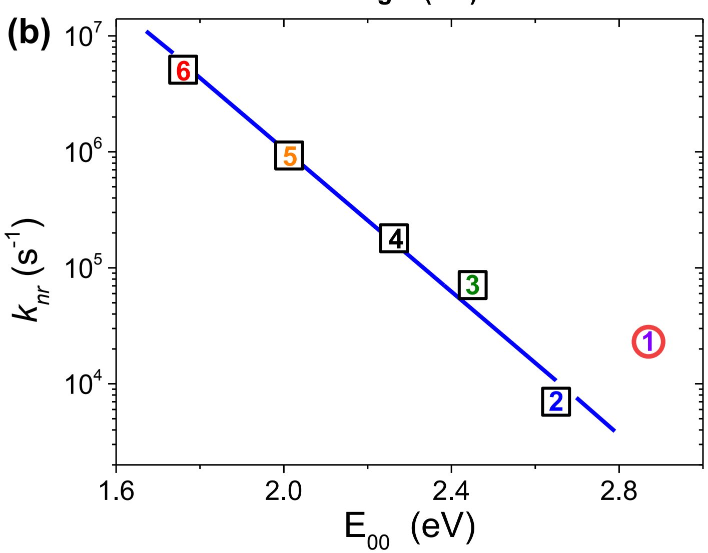
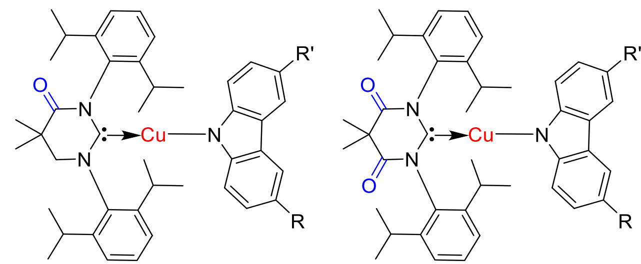
Energy Gap Law

- 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.

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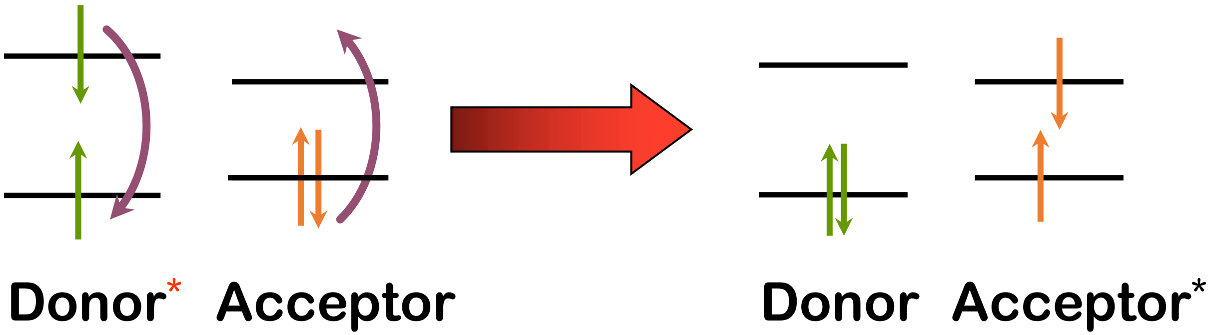
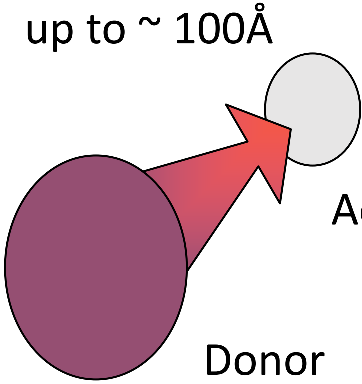
Shi, S., et al. 2019. *J. Am. Chem. Soc.*, *141*(8), pp.3576-3588.

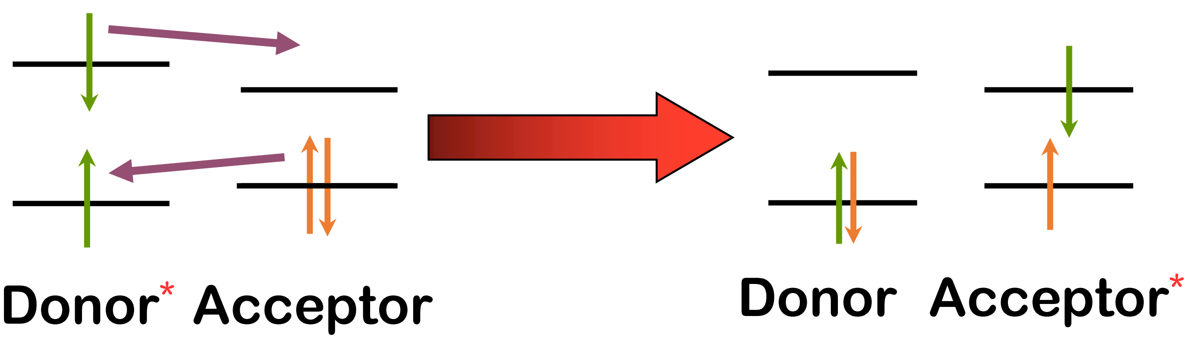
Energy Transfer from Host to Dopant: A Review

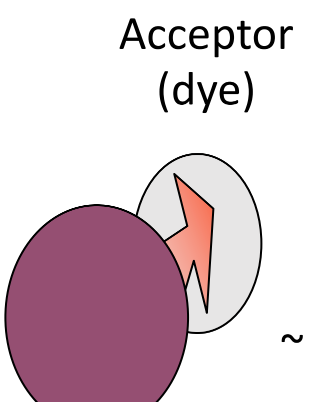
Förster:
- resonant dipole-dipole coupling
- donor and acceptor transitions must be allowed





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

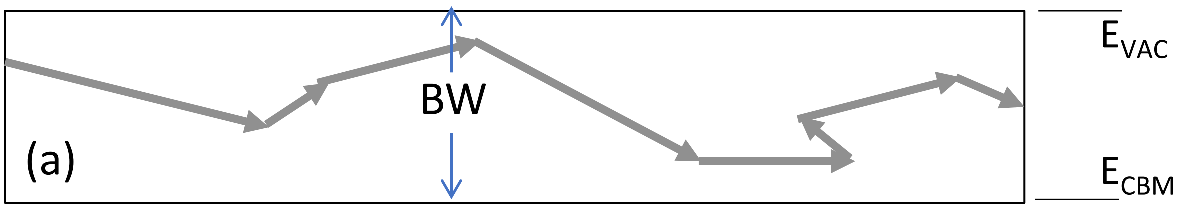




spin is conserved: e.g. singlet-singlet or triplet-triplet

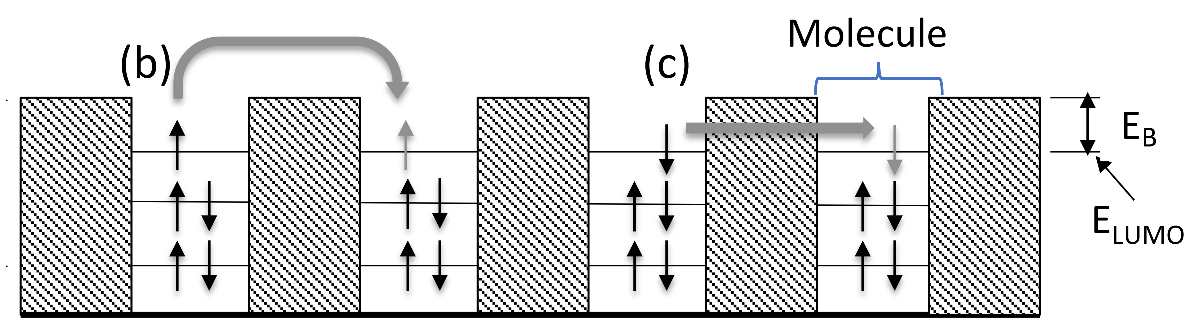
Modes of Conduction

Band transport



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

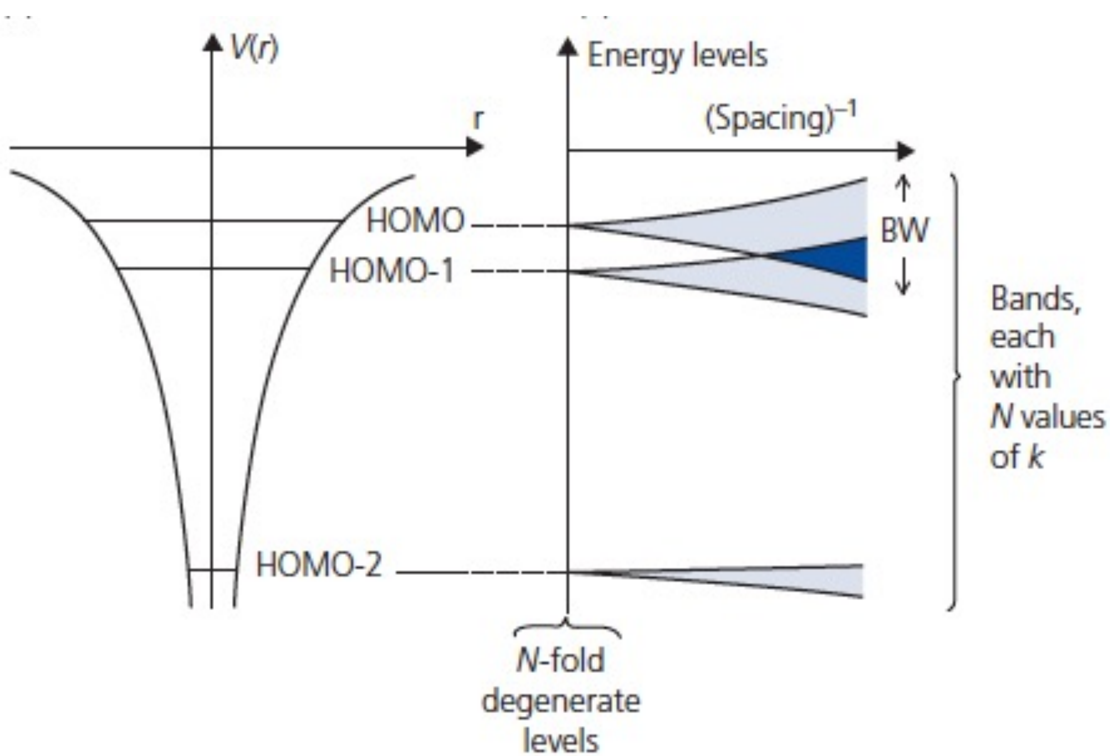
Hopping and tunneling transport



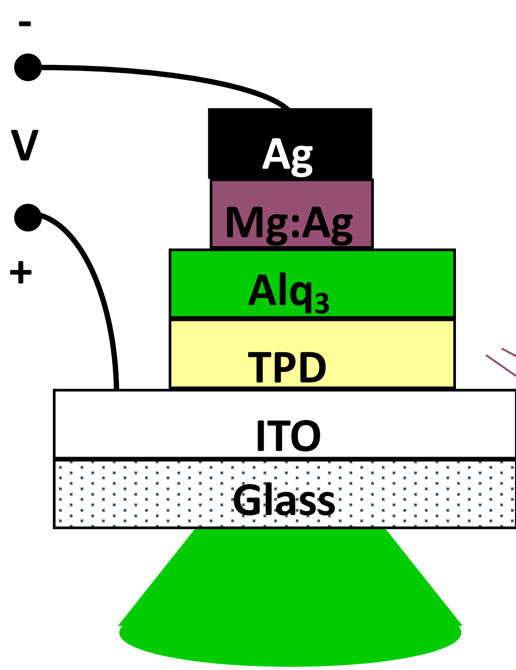
- Incoherent (each step independent of previous)
- Charge mean free path $\lambda \sim a$
- Tunneling between states of equal energy is band-like
- $BW < k_B T\, ,\, \hbar\omega_0$

Transport Bands in Organics

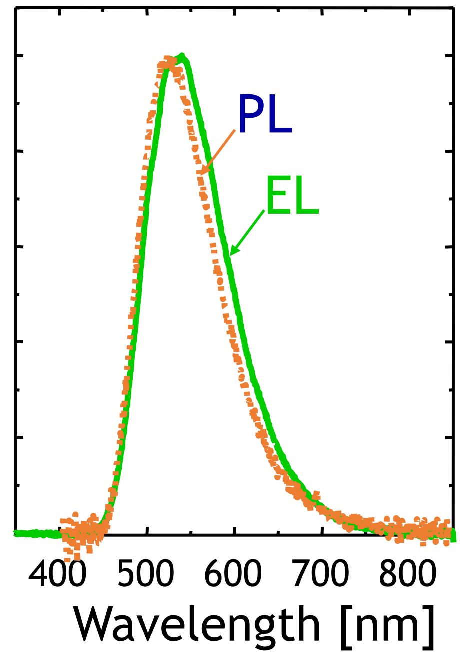
- **Tight binding** approximation is useful due to importance of only nearest neighbor interactions
- Recall case of dimers and larger aggregates on exciton spectrum. Close proximity of neighbors results in:
  - Coulomb repulsion
  - Pauli exclusion
  - ➢ Splitting leads to broadening of discrete energies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

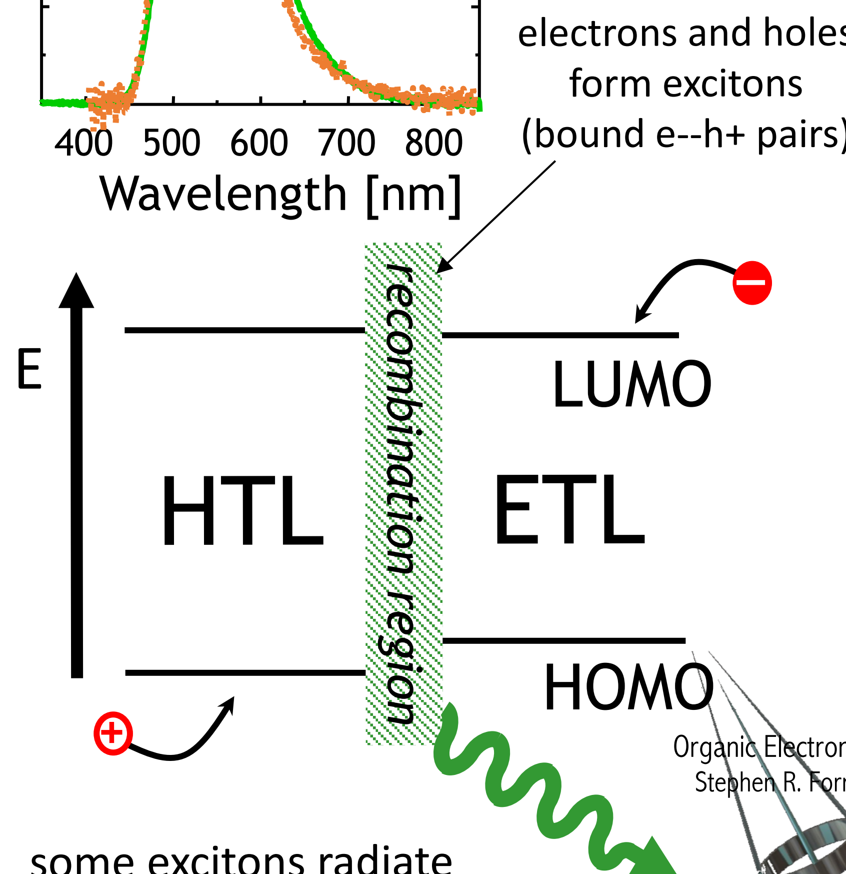


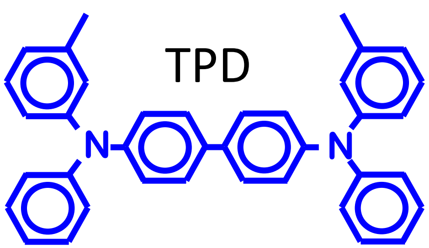
Organic Light Emitting Diode (OLED)

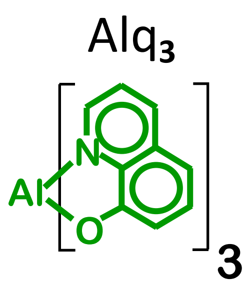


η_{EQE} = 1%



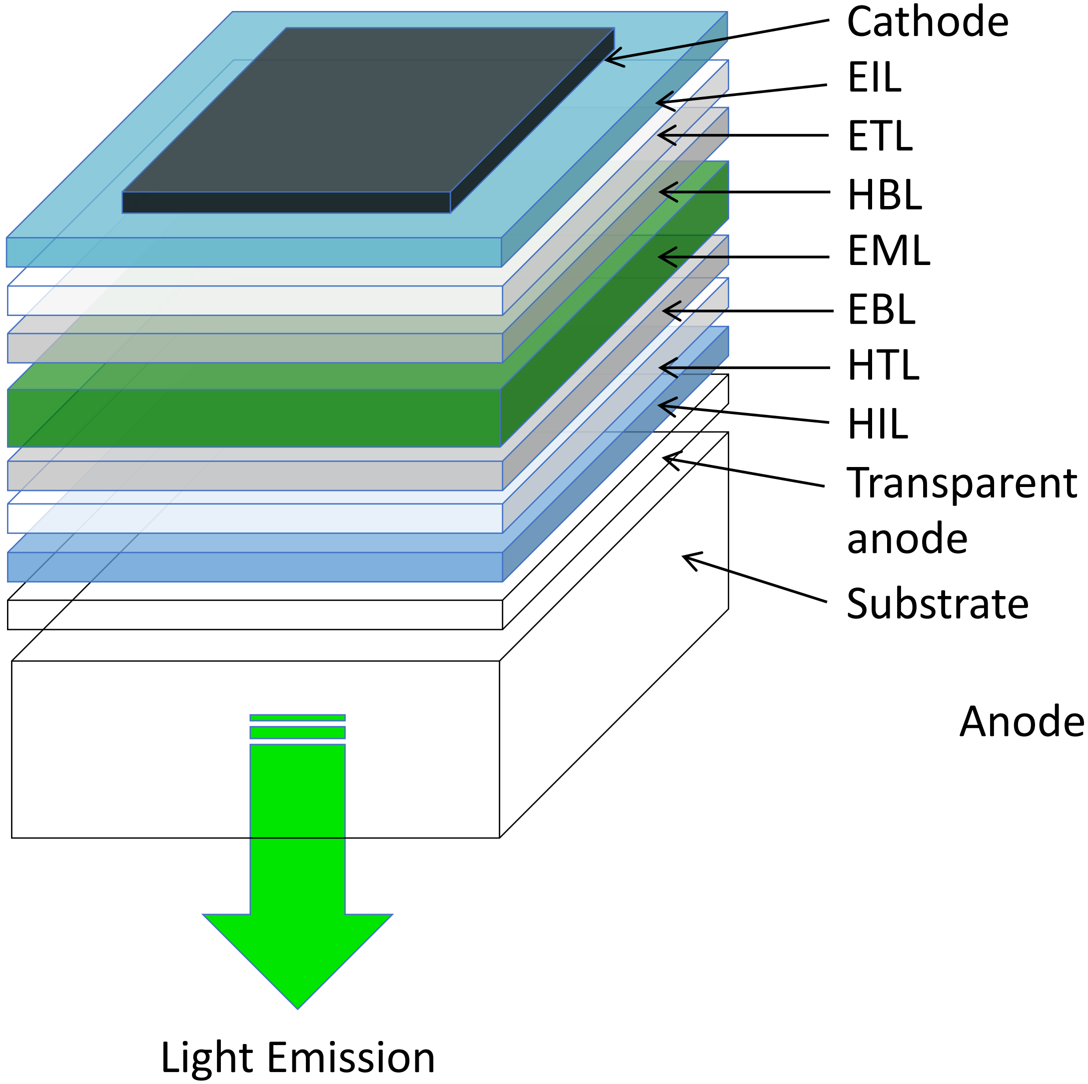


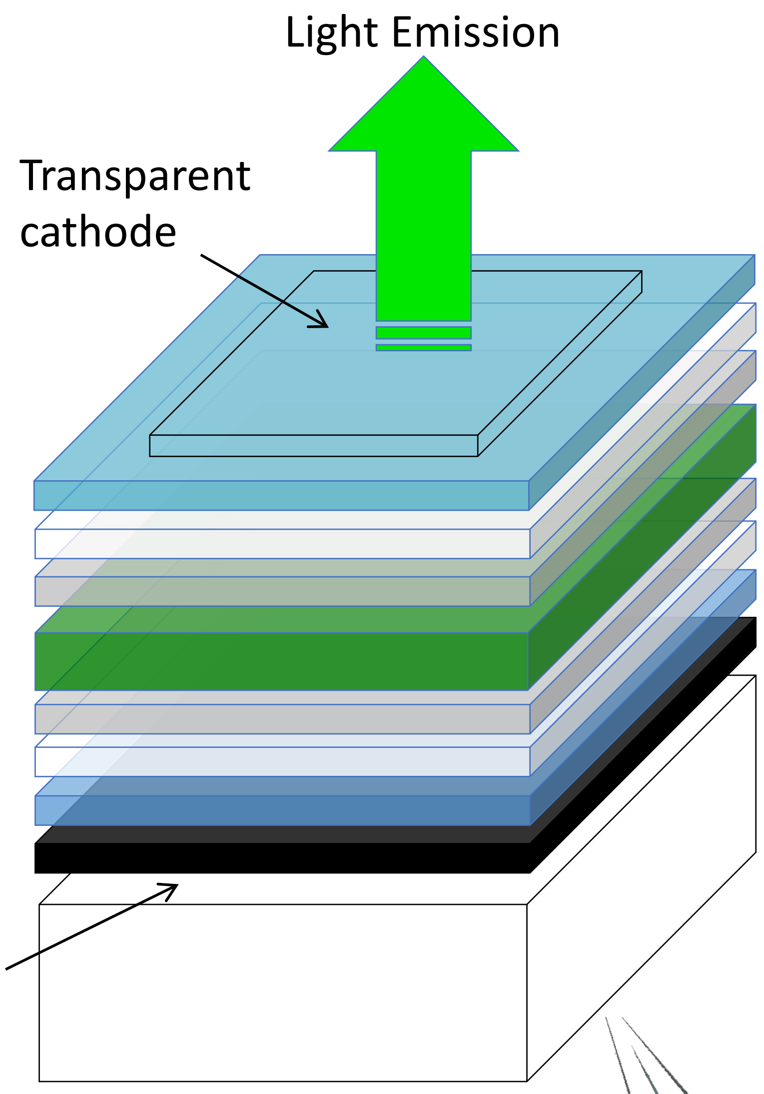




Tang & van Slyke, Appl. Phys. Lett., **51**, 913 (1987)

Today's OLEDs Are Not So Simple





OLED efficiency

$$\eta_{ext} = \eta_{\text{int}}\eta_{out} = \gamma\chi_r\phi_p\eta_{out}$$

~100% (for γ) ? (for χ_r) ~100% (for ϕ_p) ~20% (for η_{out})

γ: charge carrier balance factor
ratio of e/h

χ_r: luminescent exciton production

ϕ_p: quantum efficiency of fluorescence

η_{out}: light out-coupling efficiency

1. Fluorescence is restricted to singlet excitons χ_r ~ 25%

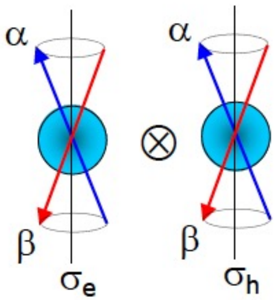
Singlet $\quad \frac{1}{\sqrt{2}}\left(\alpha(\sigma_e)\otimes\beta(\sigma_h)-\alpha(\sigma_h)\otimes\beta(\sigma_e)\right)$

Triplet

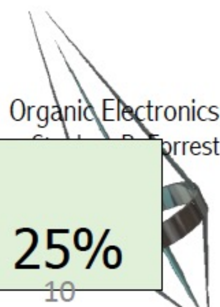
$$\alpha(\sigma_e)\otimes\alpha(\sigma_h)$$

$$\beta(\sigma_e)\otimes\beta(\sigma_h)$$

$$\frac{1}{\sqrt{2}}\left(\alpha(\sigma_e)\otimes\beta(\sigma_h)+\alpha(\sigma_h)\otimes\beta(\sigma_e)\right)$$

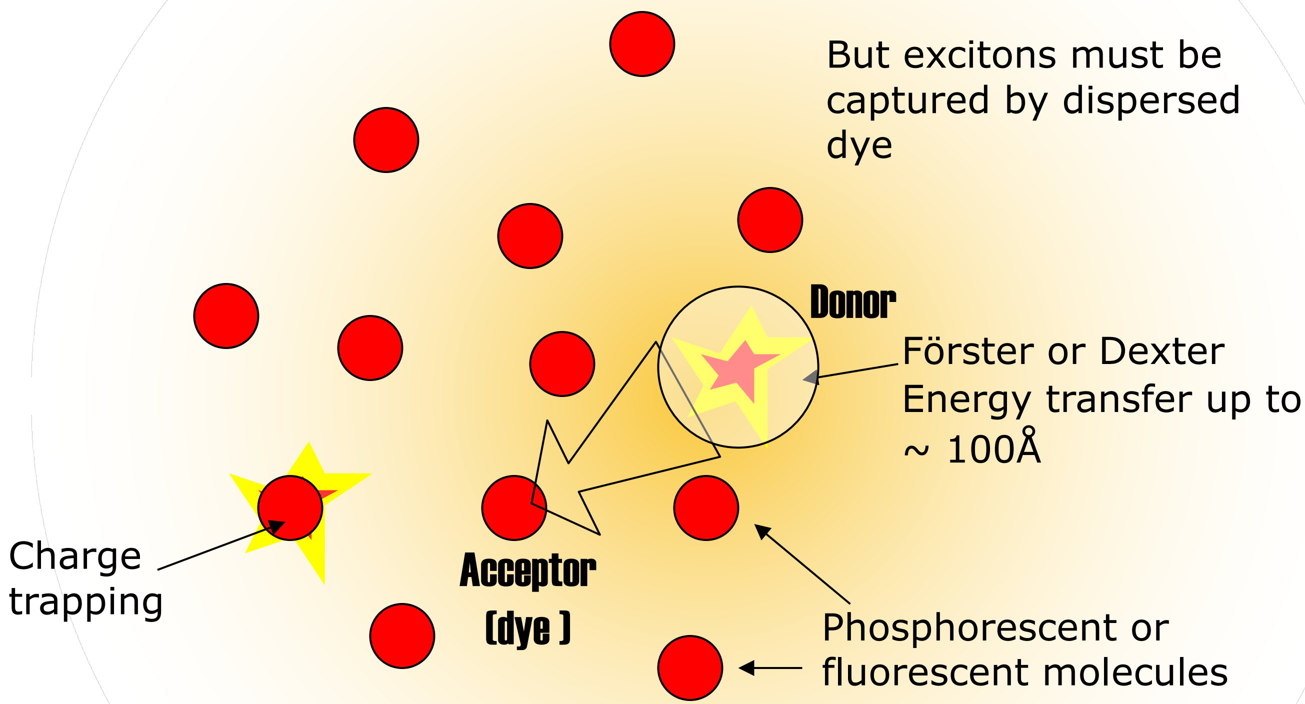


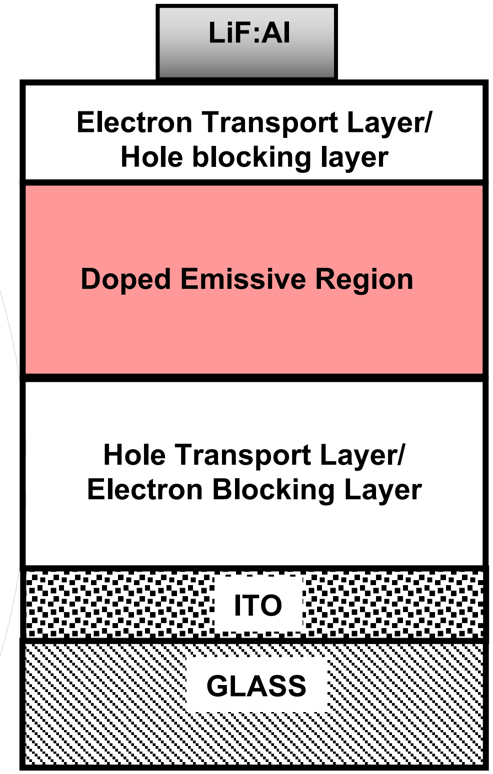
2. Only ~ 20% of photons are coupled out of OLED devices due to TIR



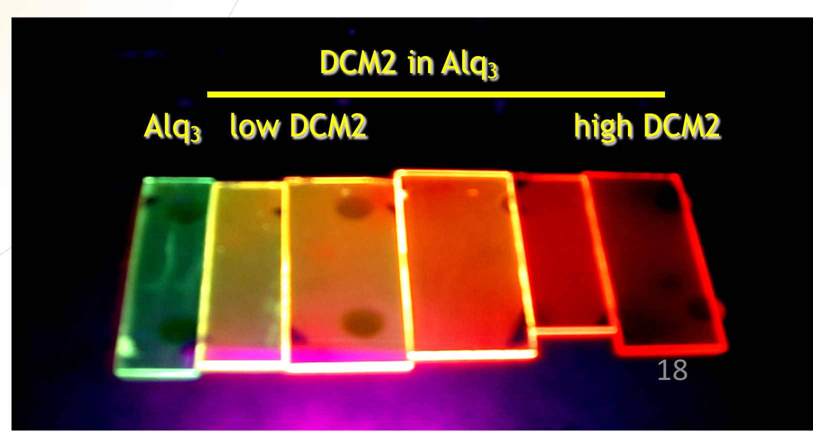
Maximum Fluorescence External Quantum Efficiency on Glass ~ 5%
Maximum Phosphorescence External Quantum Efficiency on Glass ~ 25%

Efficiency Improves if Dopant Dispersed in Host





1. Charges trapped on dye molecules
2. Energy transferred from host
3. Effect used to increase color range and efficiency of OLEDs



C. W. Tang, et al. 1989. *J. Appl. Phys.*, 65, 3610.

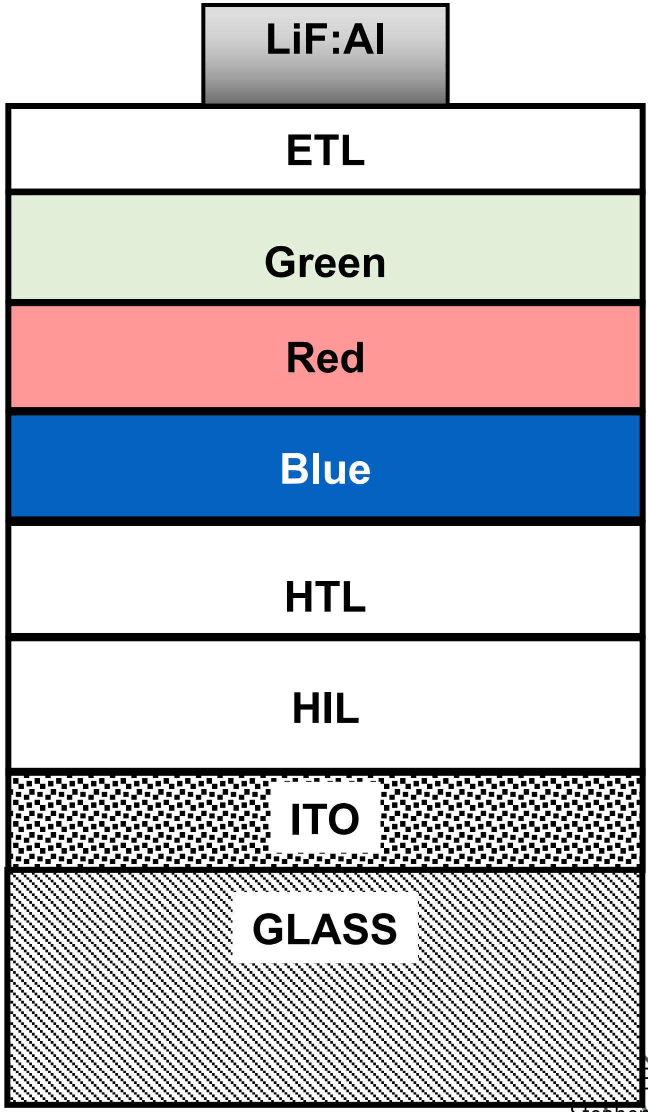
Lighting Comparisons

	Incandescent	Fluorescent	LEDs	OLEDs
Efficacy	17 lm/W	100 lm/W	80-90 lm/W – White 65 lm/W – warm white 240 lm/W-lab demo	150 lm/W Lab demos
CRI	100	80-85	80 – white 90 – warm white	Up to 95
Form Factor	Heat generating	Long or compact gas filled glass tube	Point source high intensity lamp	Large area thin diffuse source. Flexible, transparent
Safety concerns	Very hot	Contains mercury	Very hot in operation	None to date
LT70 (K hours)	1	20	50	30
Dimmable	Yes, but much lower efficacy	Yes, efficiency decreases	Yes, efficiency increases	Yes, efficiency increases
Noise	No	Yes	No	No
Switching lifetime	Poor	Poor	Excellent	Excellent
Color Tunable	No	No	Yes	Yes

OLEDs for White Light Generation

Separating dopants into bands

- Prevents energy transfer between dopants.
- Control relative emission intensity of dopants by:
  - ✓ Varying doping concentrations
  - ✓ Adjusting the thickness of bands
  - ✓ Inserting blocking layers
  - ✓ Adjusting the position of the dopants relative to the HTL

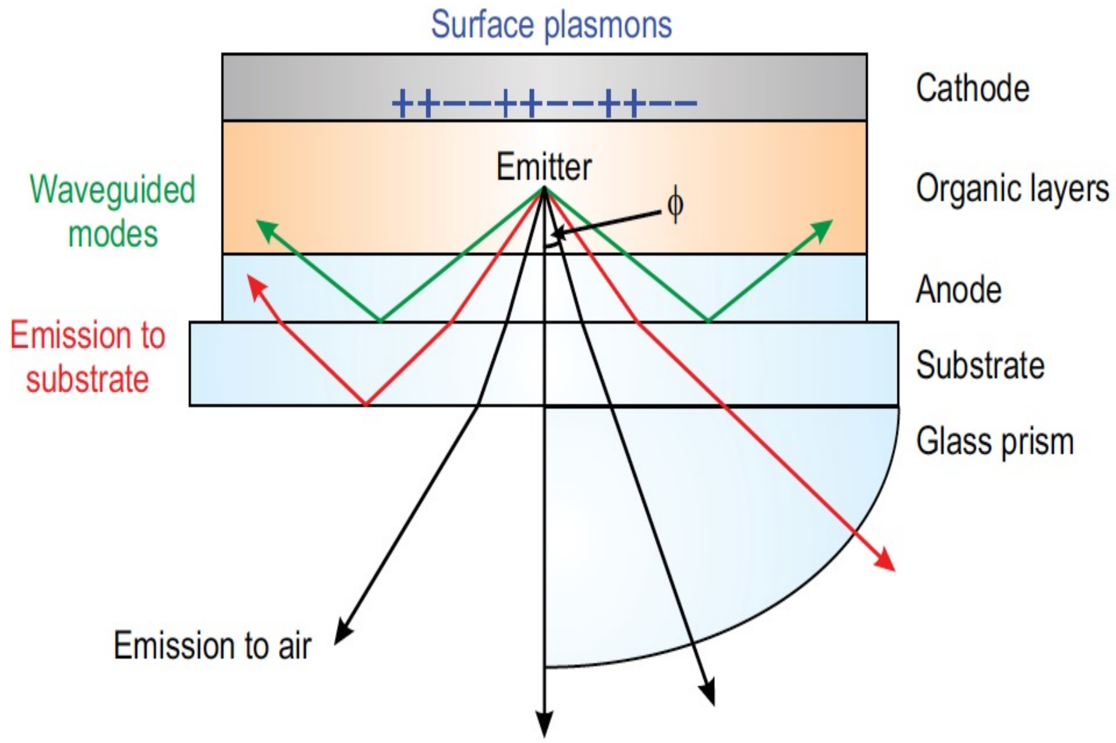


Why does it work?

- Triplets can diffuse much further than singlets (measured ~1000Å)
- Good control over diffusion of excitons using blocking layers and layer thickness

OLEDs: Not All Light Goes to the Viewer

- Optical paths outcoupled with hemispherical lens

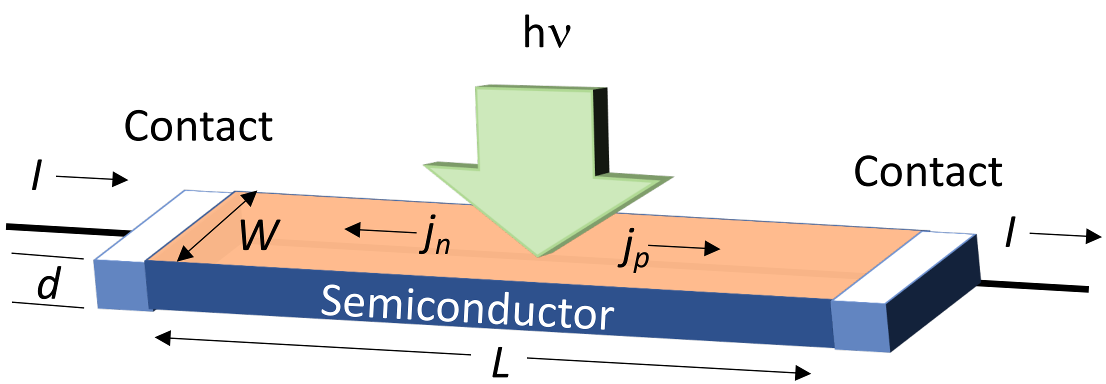


Photodetectors

- Transducers that convert light to another energy form (in our case, electricity)
- Types
  - Photoconductors
  - Photodiodes
    - These are operated in the reverse-biased (photodetection) or photovoltaic mode
- Properties
  - Sensitivity & Efficiency
  - Spectral range
  - Bandwidth
  - Dynamic range

Photoconductors

- Earliest organic electronic devices
- Simplest (no HJs needed)



When illuminated, conductivity changes

$$\sigma = q\left(\mu_n n + \mu_p p\right) \quad \begin{cases} p = p_{ph} + p_0 \\ n = n_{ph} + n_0 \end{cases}$$

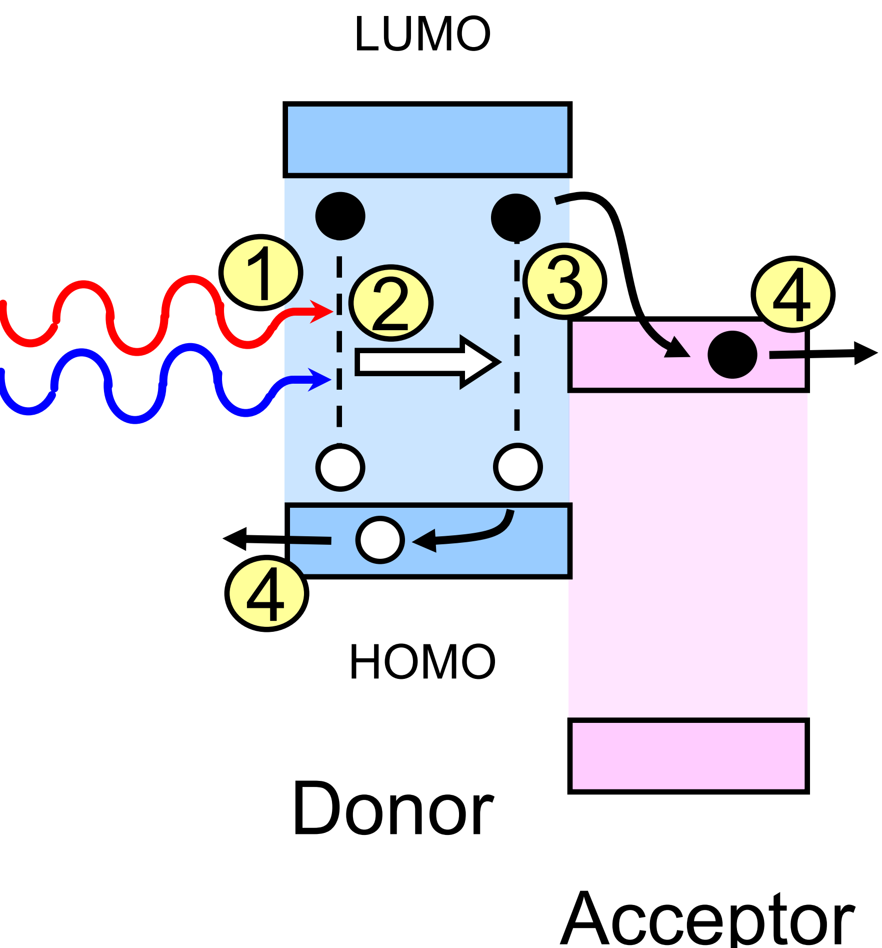
$n_{ph} = p_{ph}$

Without background doping: $n_0 = p_0 = n_i$

Photoinduced Charge-Transfer at a Type II HJ

The Basis of OPV Operation

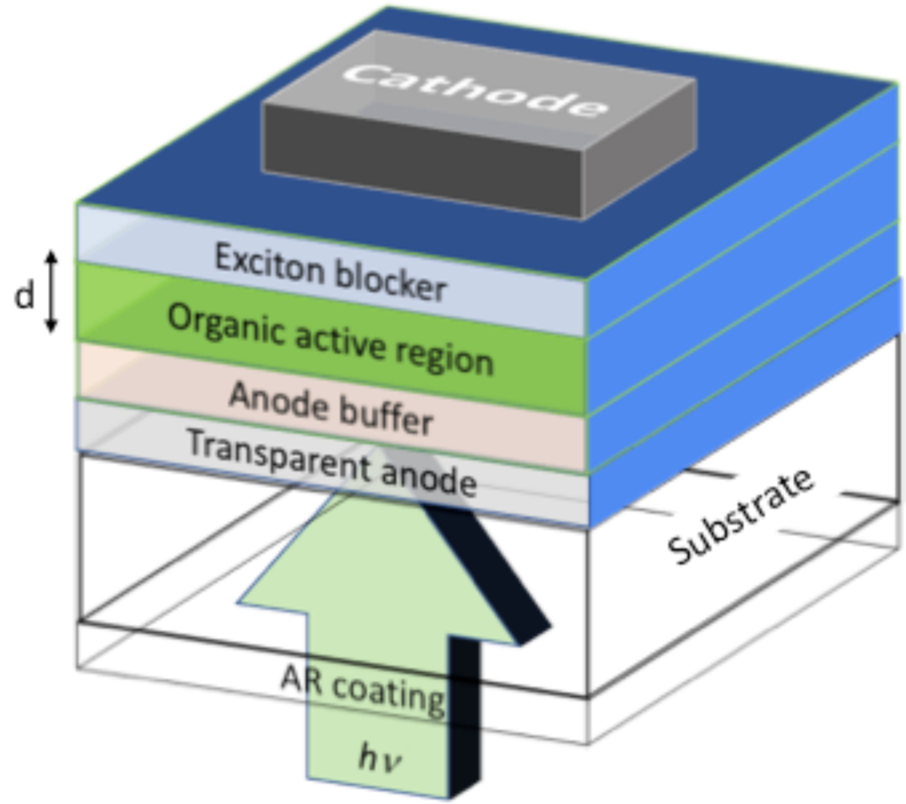
Processes occuring at a Donor-Acceptor heterojunction



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

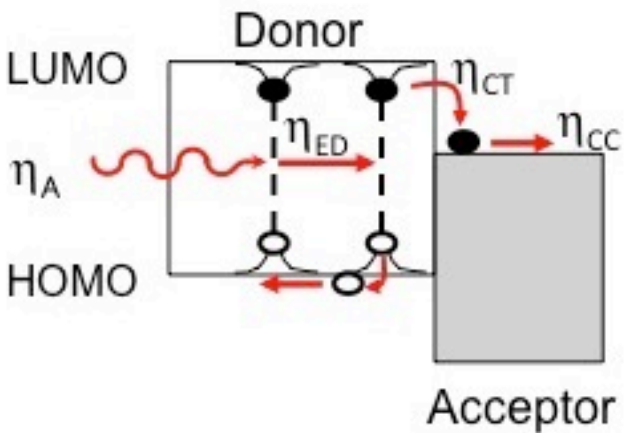
Typically: $L_D << 1/\alpha$

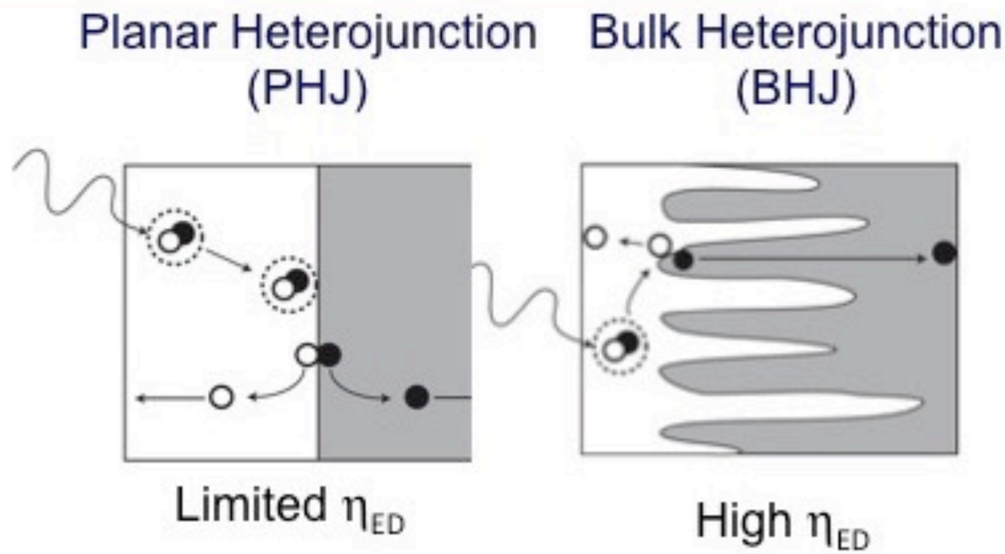
Basic OPD/OPV structure

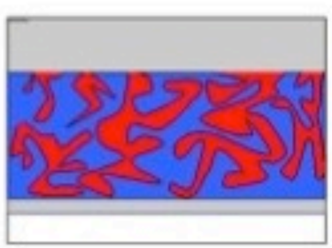


Heterojunction Morphologies

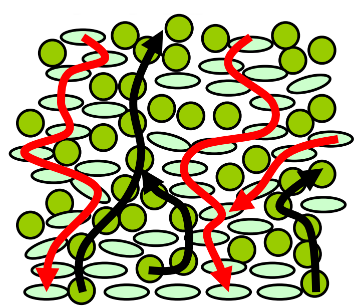
Breaking the tradeoff between L_D and α with BHJs



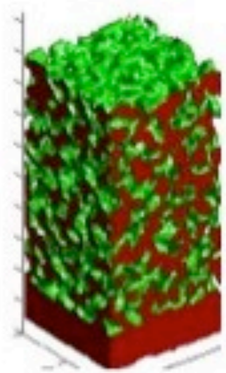




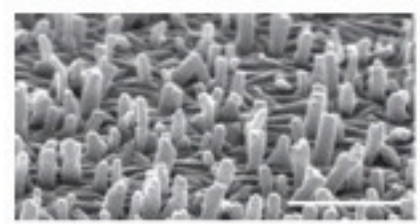
Bulk HJ



Mixed HJ



Annealed BHJ

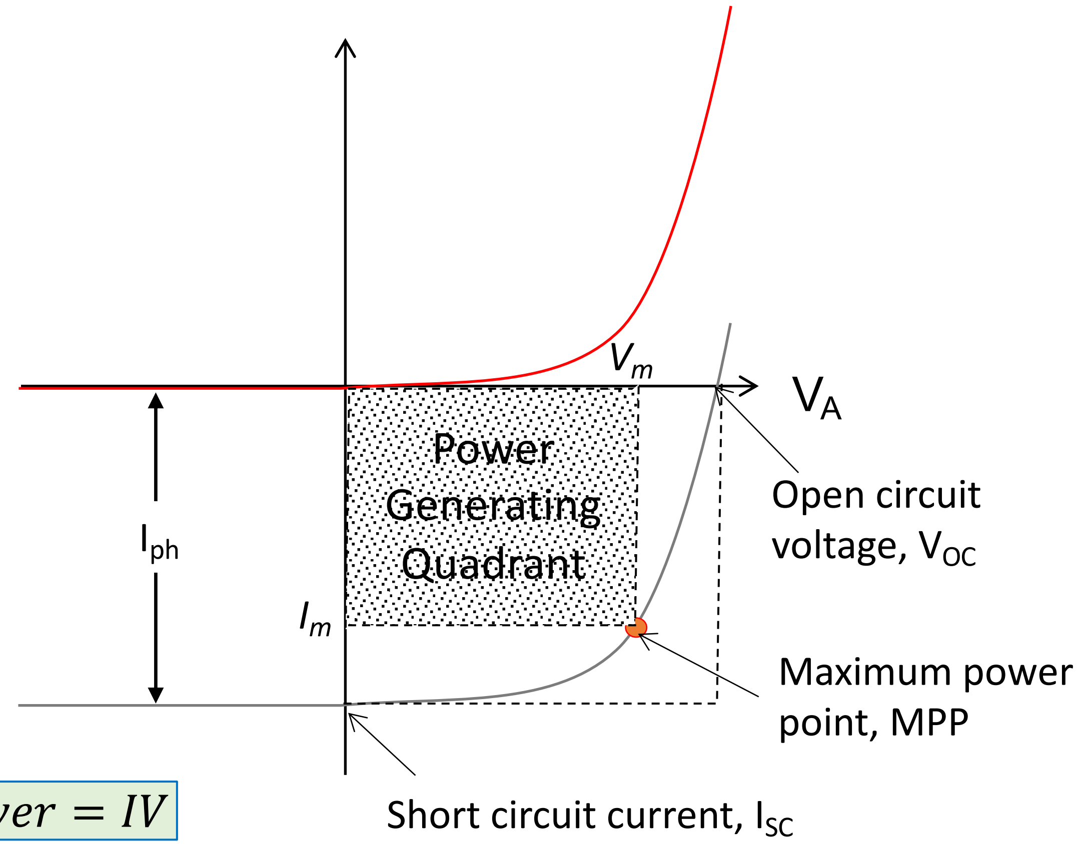


Controlled BHJ

Solar Cell Basics

Power Conversion Efficiency, η_P:

- $I_{SC} \propto$ number of photons absorbed
- V_{OC} determined by material
- Fill factor (FF) related to device resistance



$$Power = IV$$

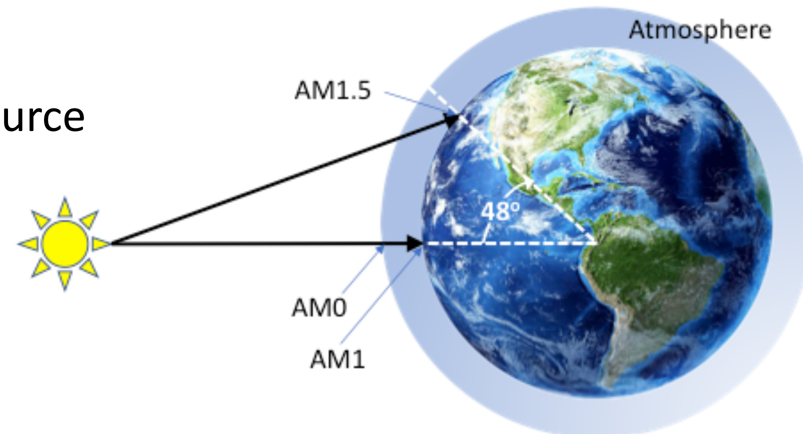
Maximum power generated: $P_m = I_m V_m = FF I_{SC} V_{OC}$

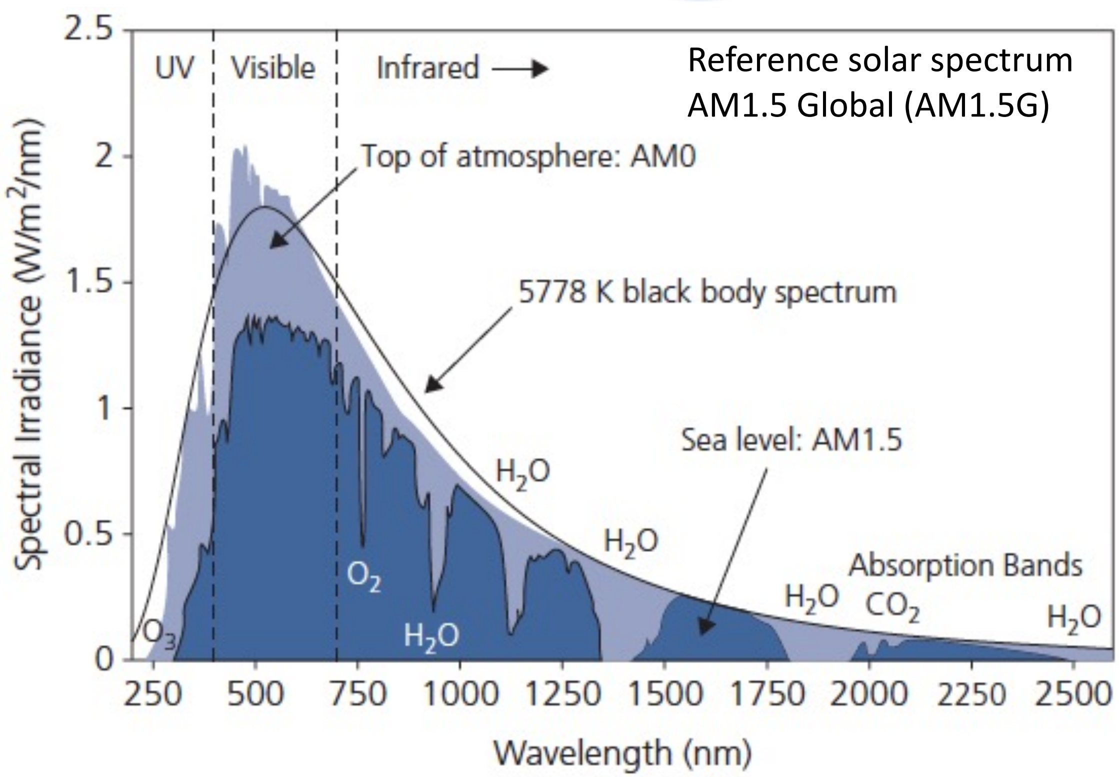
Fill Factor: $FF = \dfrac{V_m I_m}{V_{OC} I_{SC}}$

$$\eta_P = \frac{FF \cdot I_{SC} \cdot V_{OC}}{P_{inc}}$$

Understanding Solar Cell Efficiency Limits

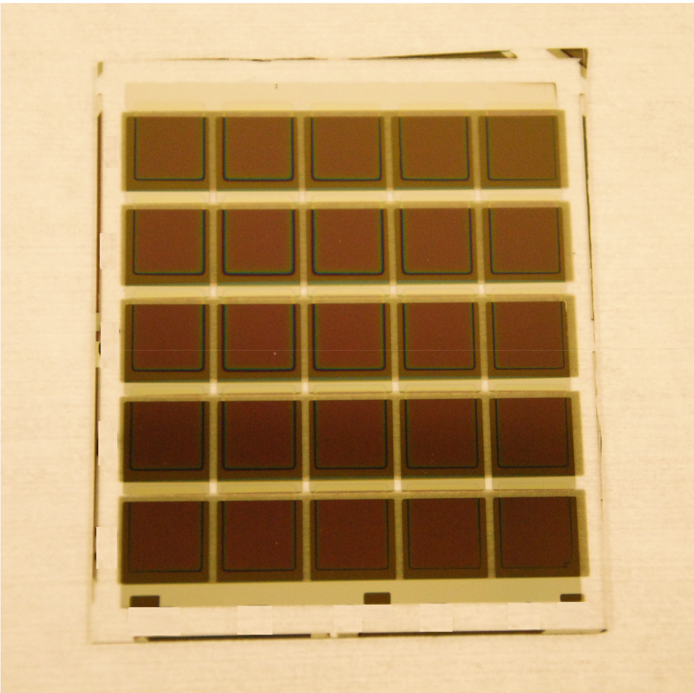
Consider the Source

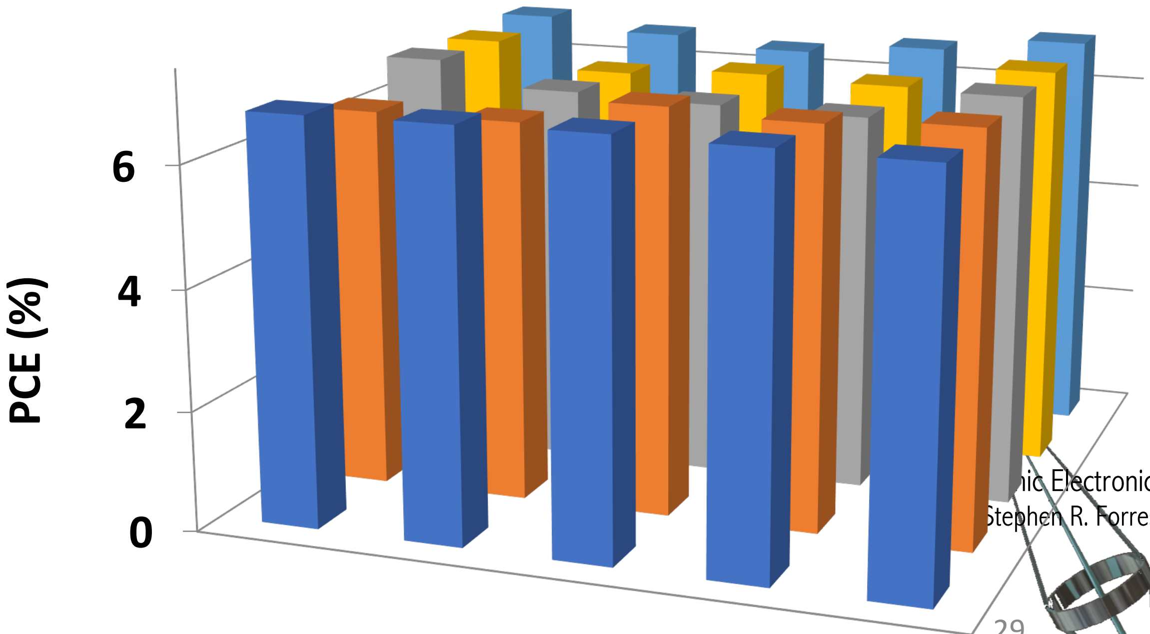




Organic Solar Cell Challenges

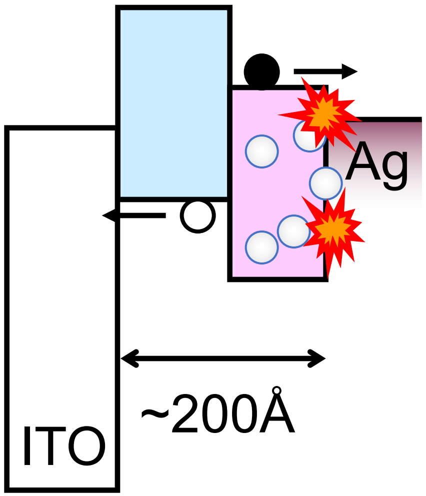
- High efficiency (>17%)
- Large Module Size
- High Reliability (>20 years)
- Low Production Cost (<$0.50/Watt)





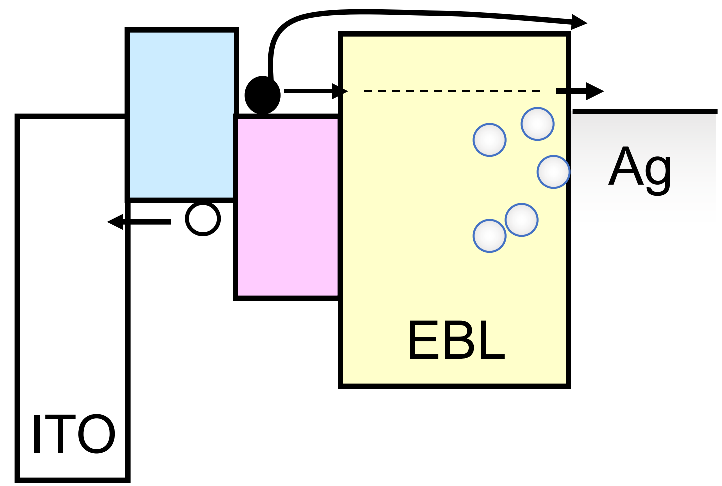
Getting to High Efficiency: The Double Heterojunction

Problem	Solution



(Tang cell: 1%)

- cathode metal diffusion
- deposition damage
- exciton quenching
- vanishing optical field
- electrical shorts



Introduce ‘Exciton Blocking Layer’ (EBL) to:

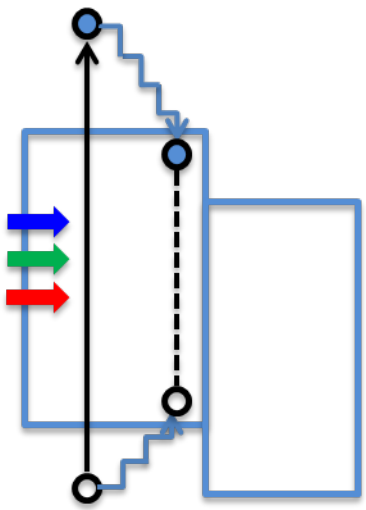
- confine excitons to active region
- separates active layer from metal
- act as a buffer to damage
- EBL thickness determined by depth of damage (if too thick, EBL is insulating)

Multijunction OPV cells: The Most Effective Way to Increase Efficiency

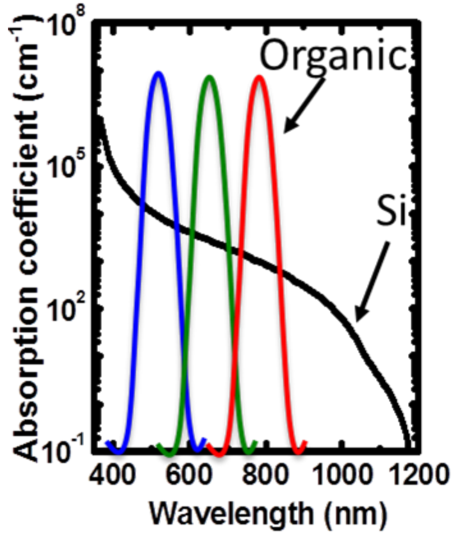
Can significantly exceed the thermodynamic limit of single junction cells

Major issues of single junction OPV:

(a) Thermalization loss

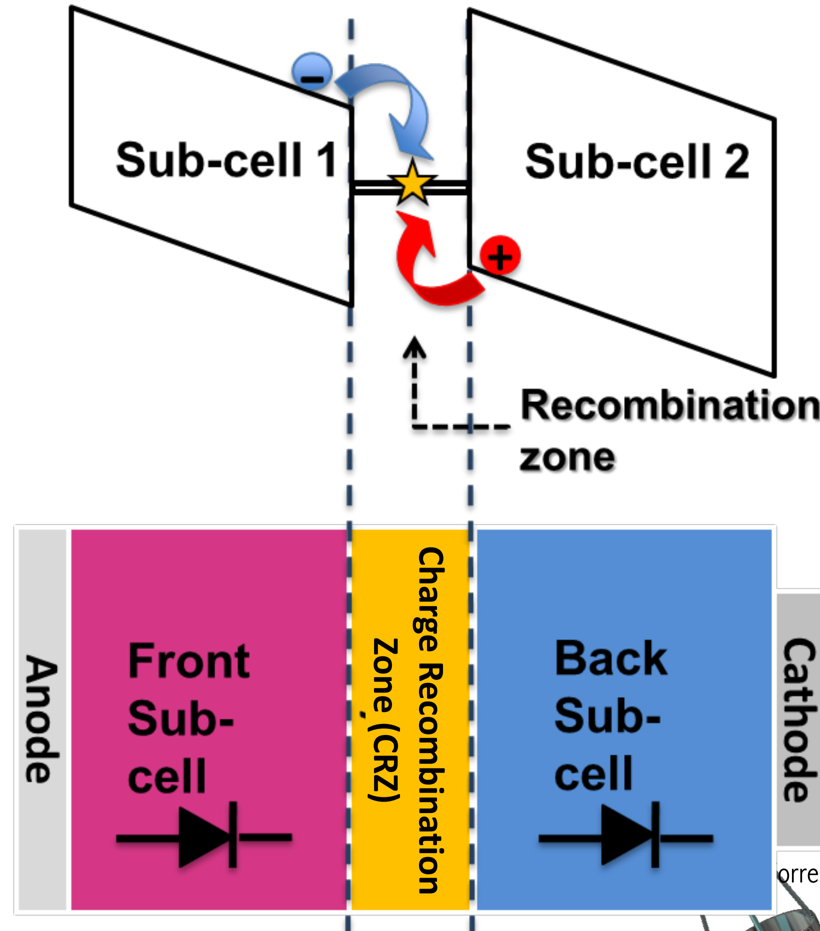


(b) Narrow absorption range

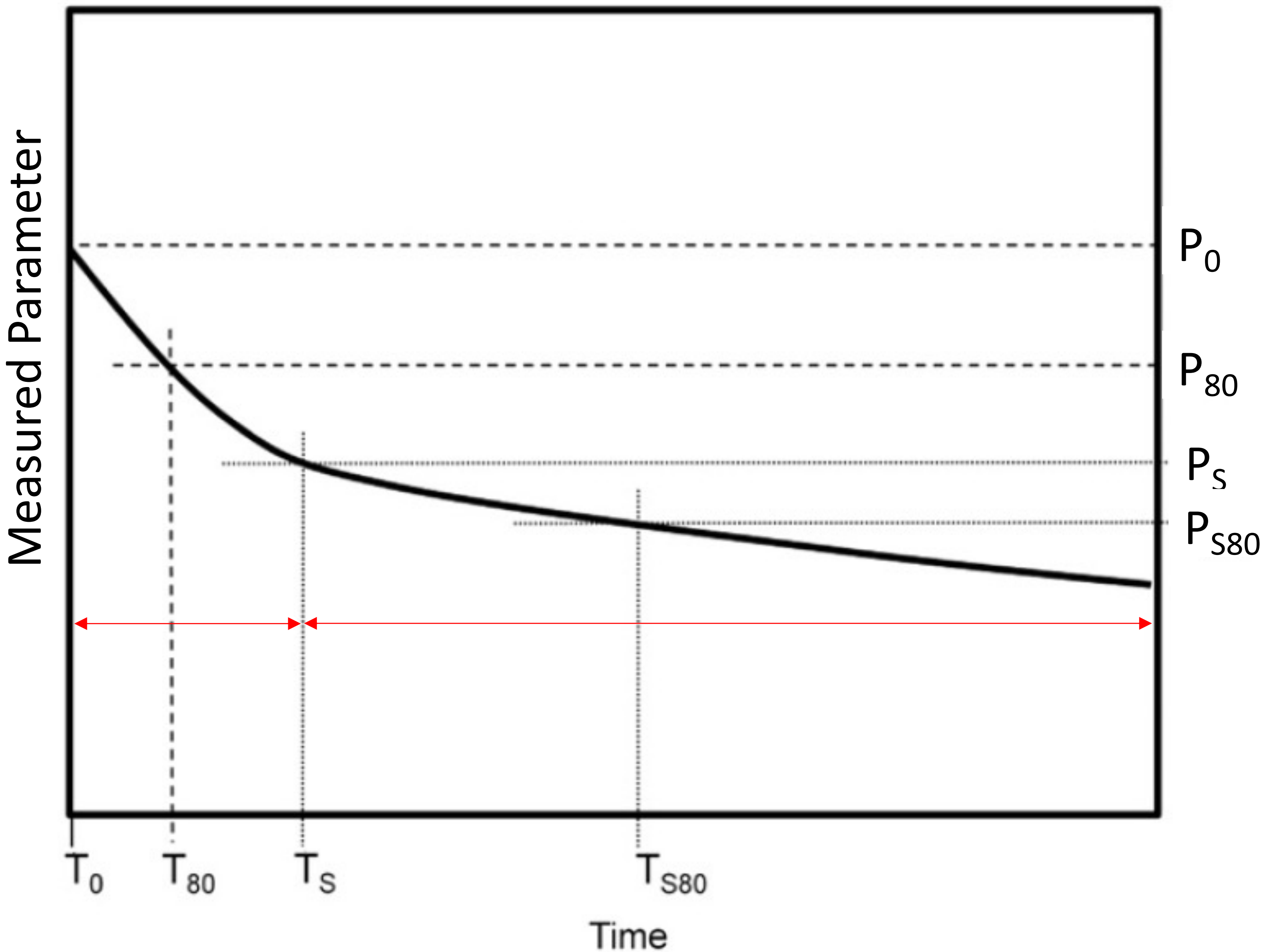


Advantages of multijunction cells:

- Decrease thermalization losses
- Cover a broad spectral range

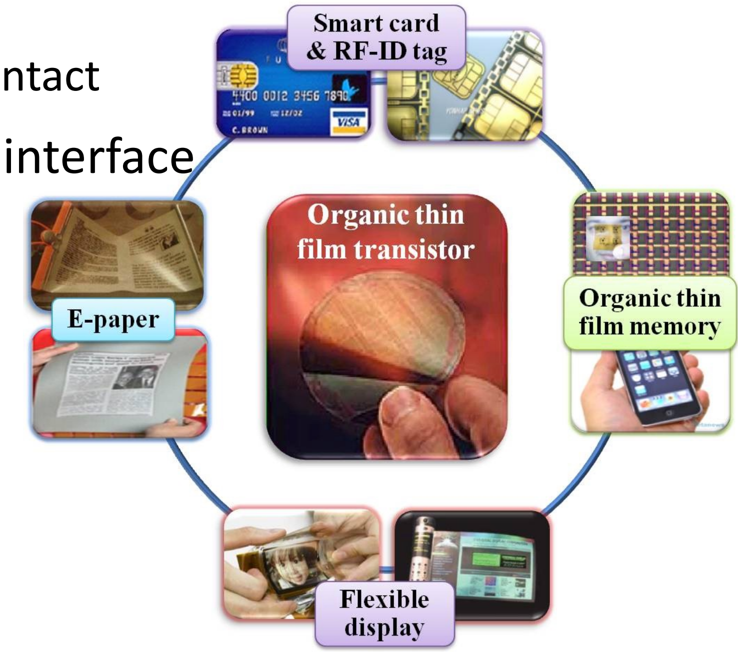


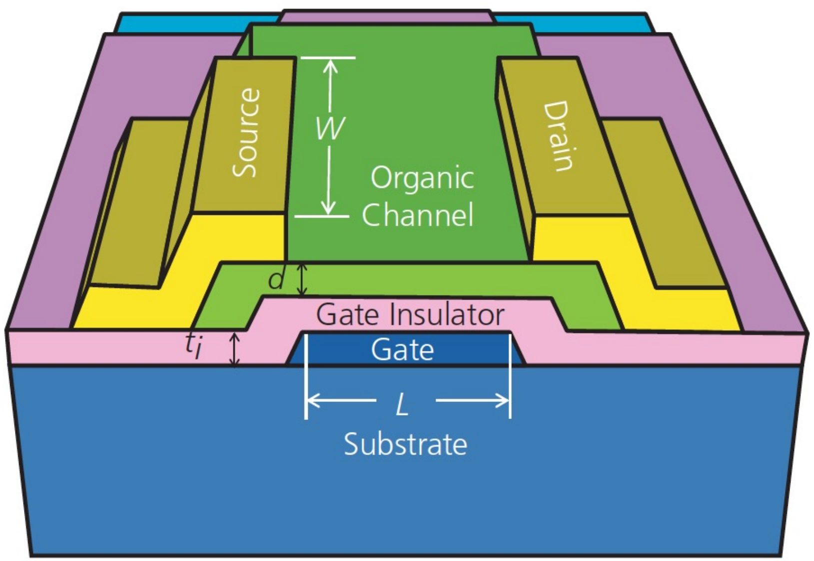
Quantifying OPV Lifetimes



What an OTFT looks like

- Several different configurations
  - Bottom gate, top gate, bottom SD contact, top SD contact
- Properties strongly influenced by dielectric/organic interface
- Configuration similar to inorganic TFTs
  - Metal oxide
  - a-Si
  - Etc.





Definitions of Contacts and Dimensions

OTFT applications must exploit advantages, and cannot be vulnerable to disadvantages

- PROs
  - Flexible, conformable, ultralight
  - Can be made over very large areas
  - Suitable for large scale R2R manufacture
- CONs
  - Cannot source large currents
  - Characteristics drift over long periods in operation
  - Limited bandwidth ($\leq$ 1 MHz in many cases)

Organic Materials are Interesting for Electronics Because…

- They are *potentially* inexpensive
- Their properties can be ”easily” modified through chemical synthesis
- They can be deposited on large area, flexible and/or conformable substrates
- They can be very lightweight
- They have excellent optical properties
- They can be manufactured “by the kilometer”

But remember…..

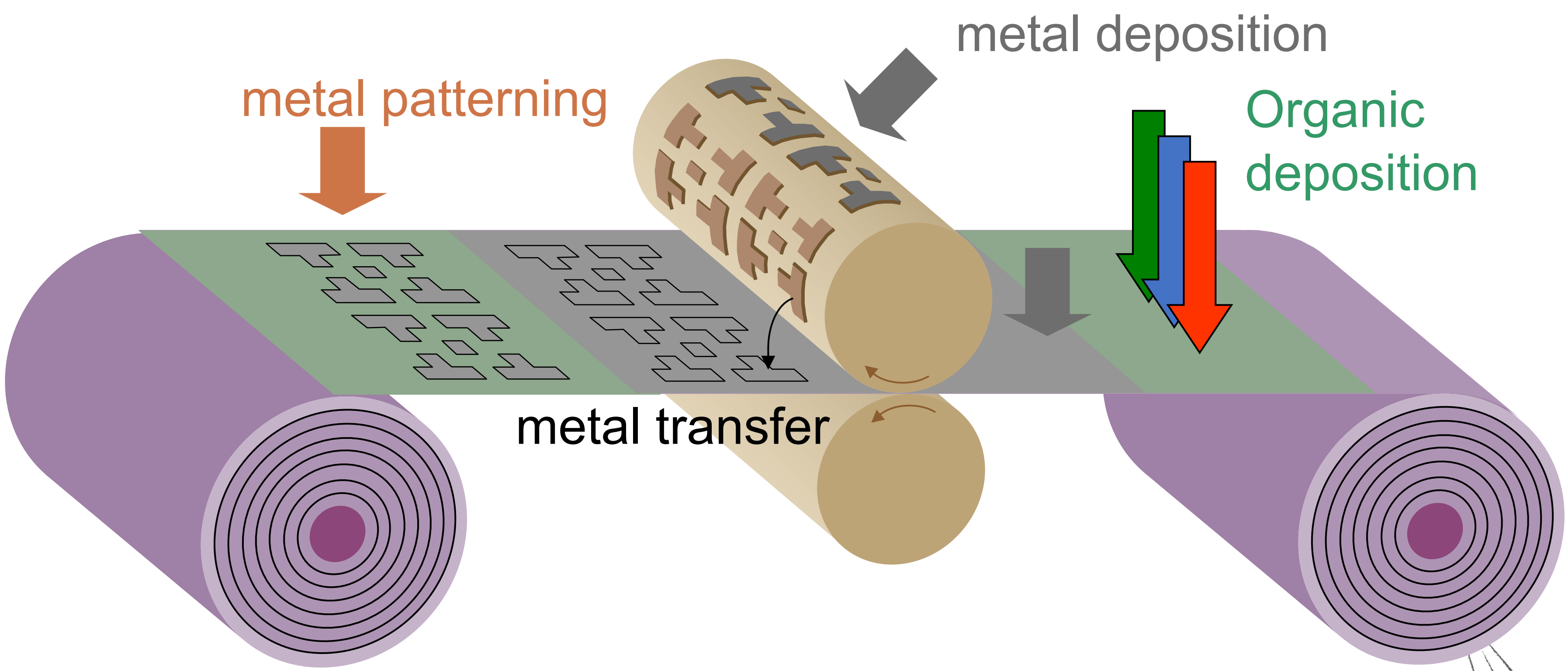
If you are competing with silicon, go home. You’ve already lost!

What organic electronics are good for

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

The Promise of Organics

Making Large Area Electronics "By the Mile"



R2R-processing of organic devices