Organic Electronics: Foundations to Applications

This course is divided into two semesters with the following objectives:

- **Semester 1-Foundations topics:** Crystal structure and binding, Optical and electronic properties of organics, and materials growth and patterning. This semester covers material in Chapters 1-5.
- **Semester 2-Applications topics:** Light emitters, light detectors, transistors (including phototransistors), and selected other topics. This semester covers material in Chapters 1-9.

Week 2-1

Review of Semester 1: Foundations

Light Emitters 1

OLED Basics

Displays

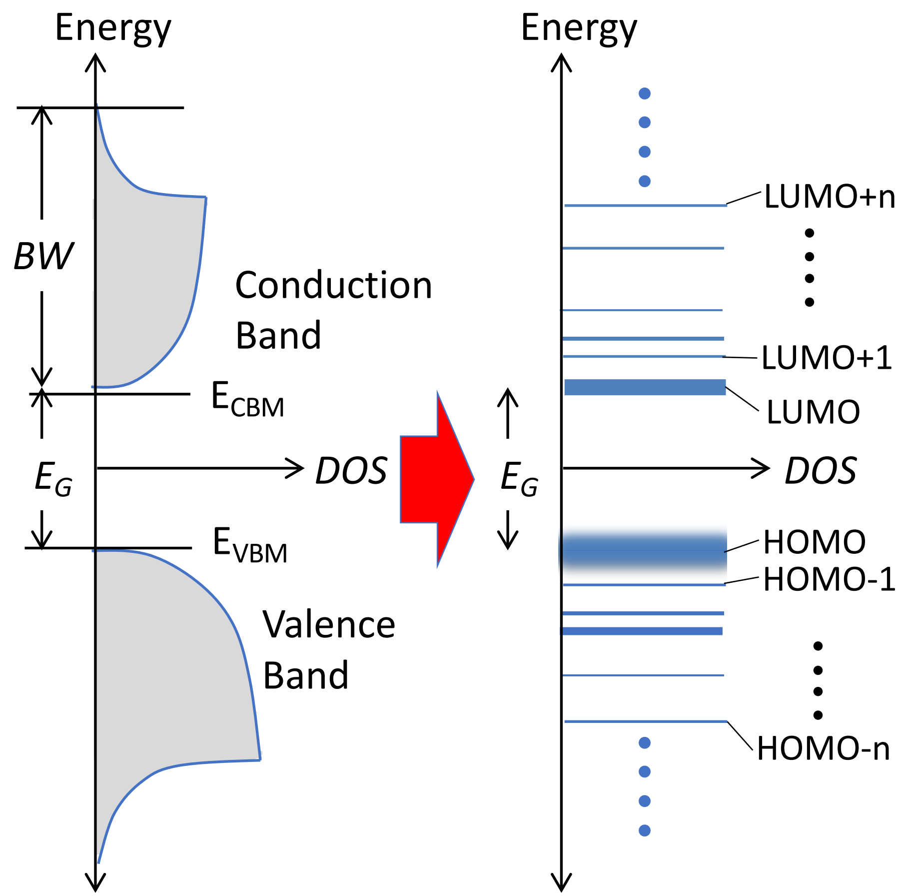
Ch. 6.1, 6.4

Organic Electronics
Stephen R. Forrest

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

Band Structure is Replaced by Energy Levels



Conventional Semiconductor

Organic Semiconductor

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.

This Chart Explains Why Organic Semiconductors are Unique

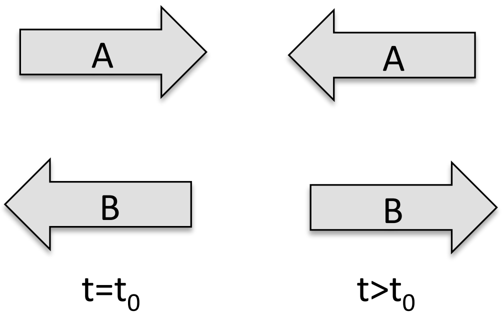
Property	Organics	Inorganics
Bonding	van der Waals	Covalent/Ionic
Charge Transport	Polaron Hopping	Band Transport
Mobility	~1 $cm^2/V\cdot s$	~1000 $cm^2/V\cdot s$
Absorption	10^5-10^6 cm^{-1}	10^4-10^5 cm^{-1}
Excitons	Frenkel	Wannier-Mott
Binding Energy	~500-800 meV	~10-100 meV
Exciton Radius	~10 Å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

Review of optical and electronic properties

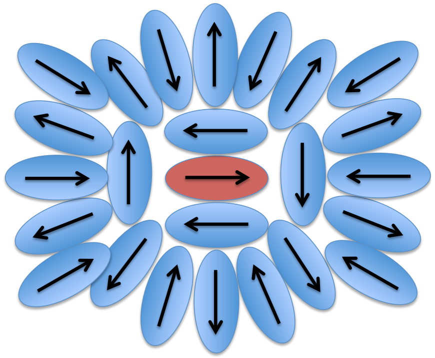
- What makes organics interesting and unique and adapted to device applications?

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

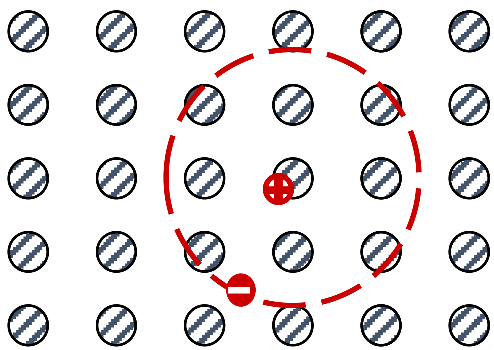
$$U(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$: Lennard-Jones 6-12 potential (includes core repulsion)

Organic Semiconductors are Excitonic Materials

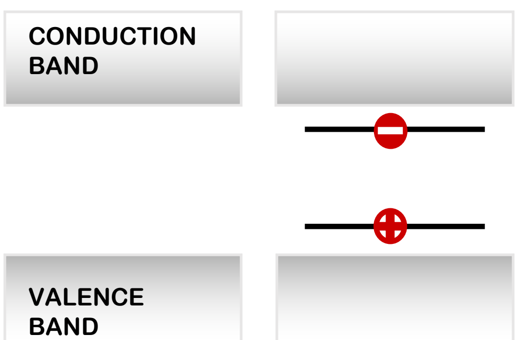
Inorganics | **Organics**

Wannier exciton

Inorganic semiconductors



SEMICONDUCTOR PICTURE

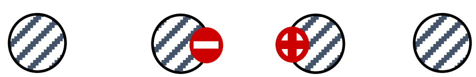


GROUND STATE WANNIER EXCITON

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

Charge Transfer (CT) Exciton

(bridge between W and F)

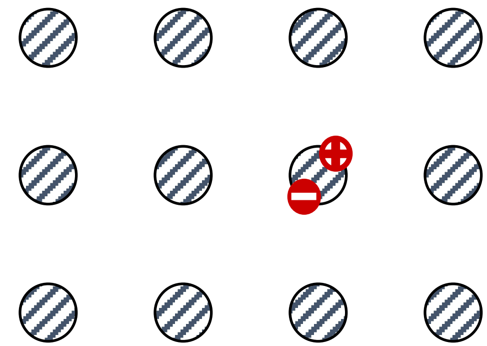


treat excitons as chargeless particles capable of diffusion.

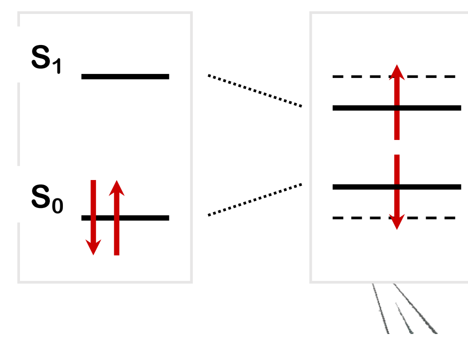
Transport of energy (not charge)

Frenkel exciton

Organic materials



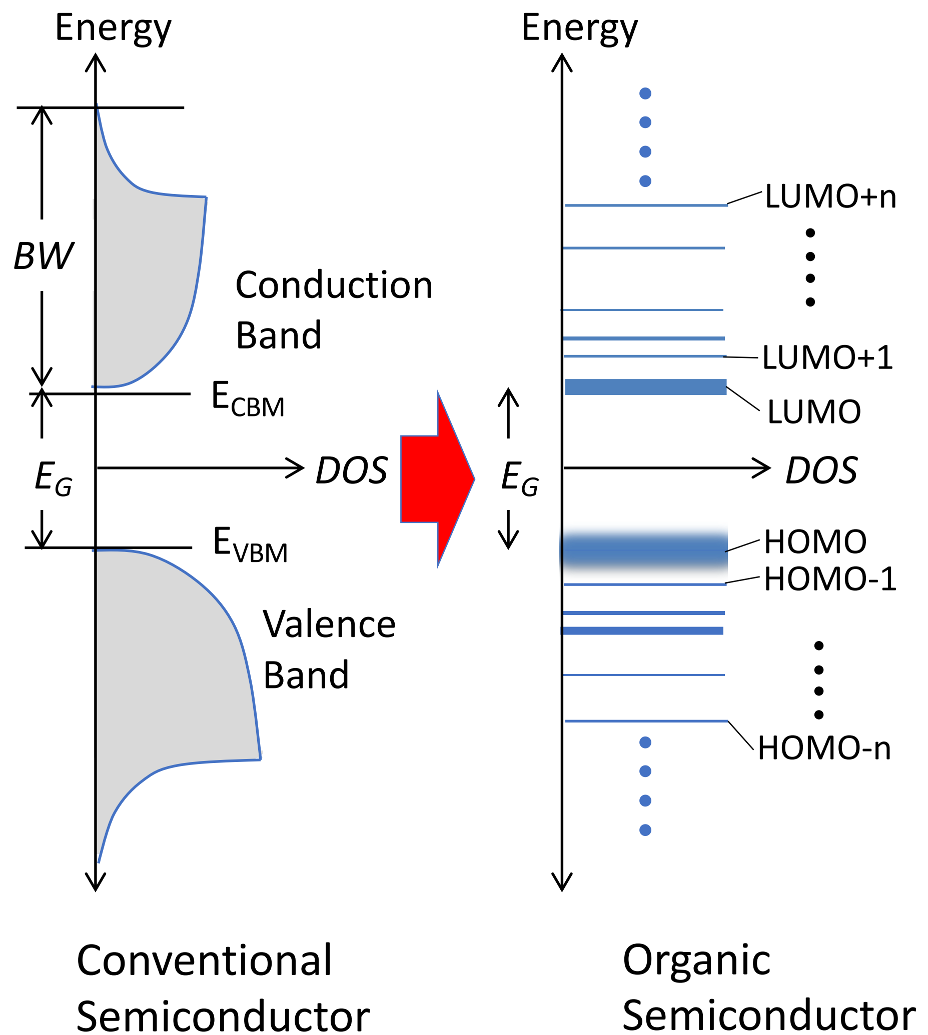
MOLECULAR PICTURE



GROUND STATE FRENKEL EXCITON

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

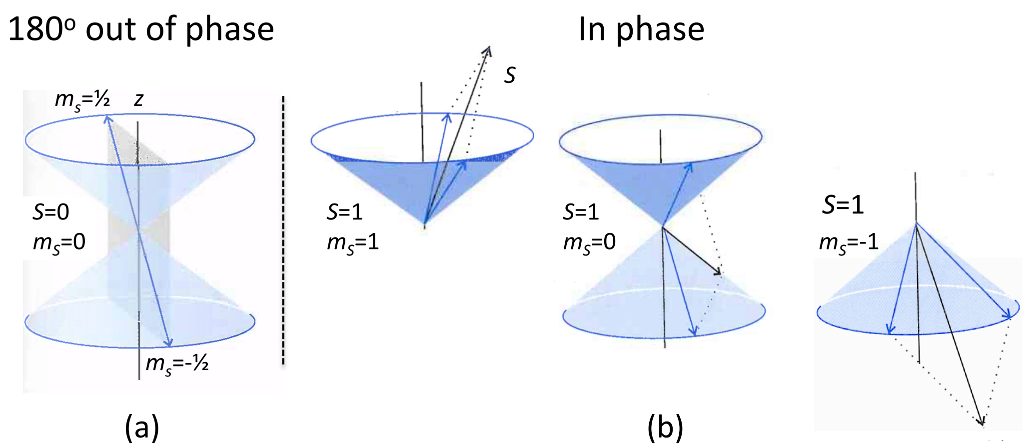
$$\psi(\mathbf{r}_1,\mathbf{r}_2;1,1)=\frac{1}{\sqrt{2}}\left(\phi_a(\mathbf{r}_1)\phi_b(\mathbf{r}_2)-\phi_a(\mathbf{r}_2)\phi_b(\mathbf{r}_1)\right)\alpha_1\alpha_2$$

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

and

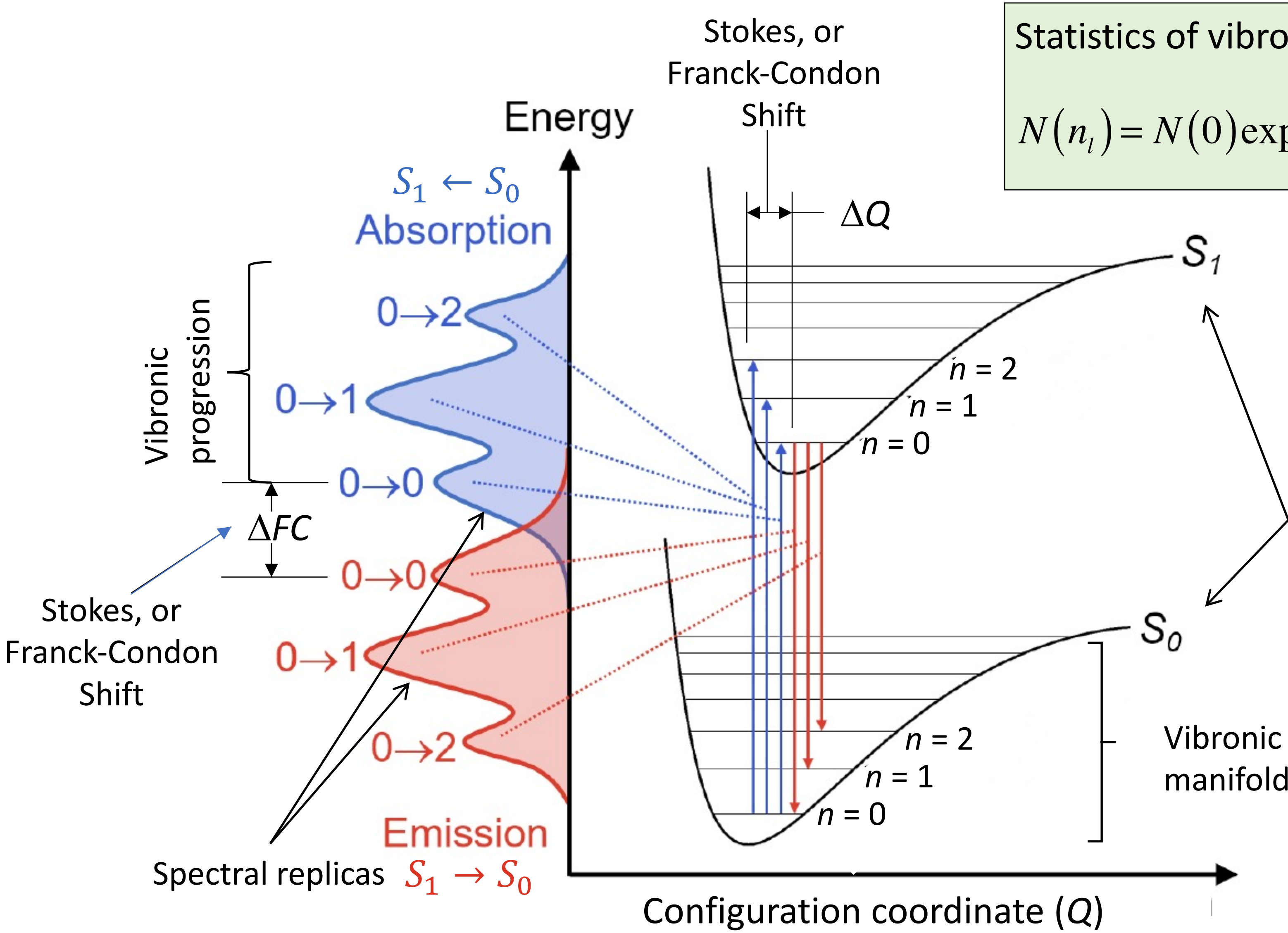
$$\psi(\mathbf{r}_1,\mathbf{r}_2;1,-1)=\frac{1}{\sqrt{2}}\left(\phi_a(\mathbf{r}_1)\phi_b(\mathbf{r}_2)-\phi_a(\mathbf{r}_2)\phi_b(\mathbf{r}_1)\right)\beta_1\beta_2$$

Triplet
S=1
m_s=±1, 0



Pauli Exclusion Principle: Total wavefunctions must be antisymmetric

Understanding molecular spectra

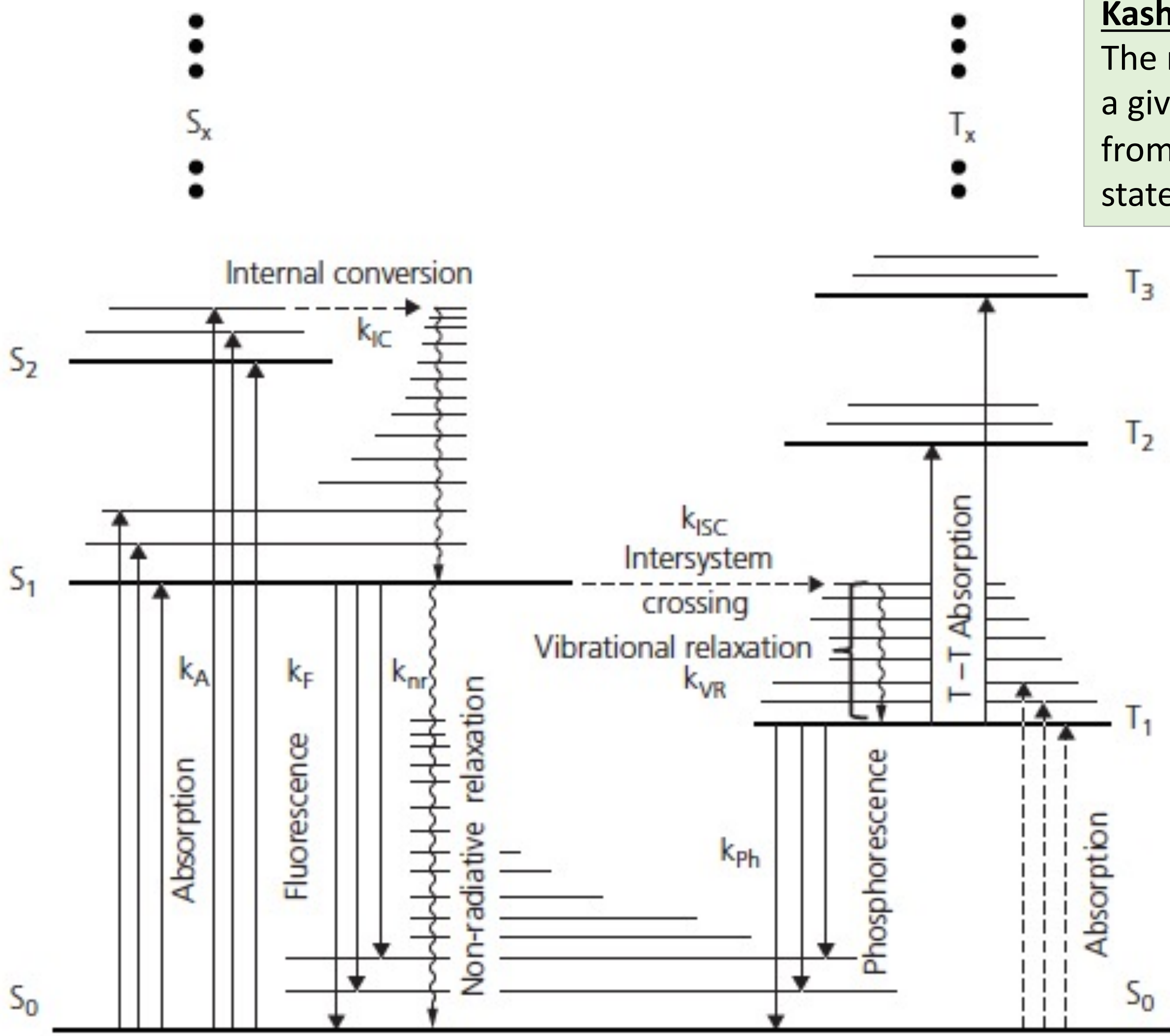


Statistics of vibronic state filling:

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

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

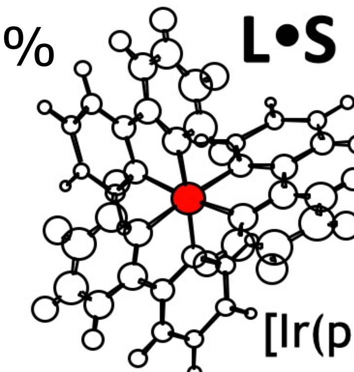
Baldo, et al., Nature **395**, 151 (1998)

MOLECULAR EXCITED STATES
AFTER ELECTRICAL EXCITATION

Singlet 25%
spin anti-symmetric

75% **Triplet**
spin symmetric

100%



$[Ir(ppy)_3]$

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

Relaxation disallowed
slow, inefficient
'Phosphorescence'

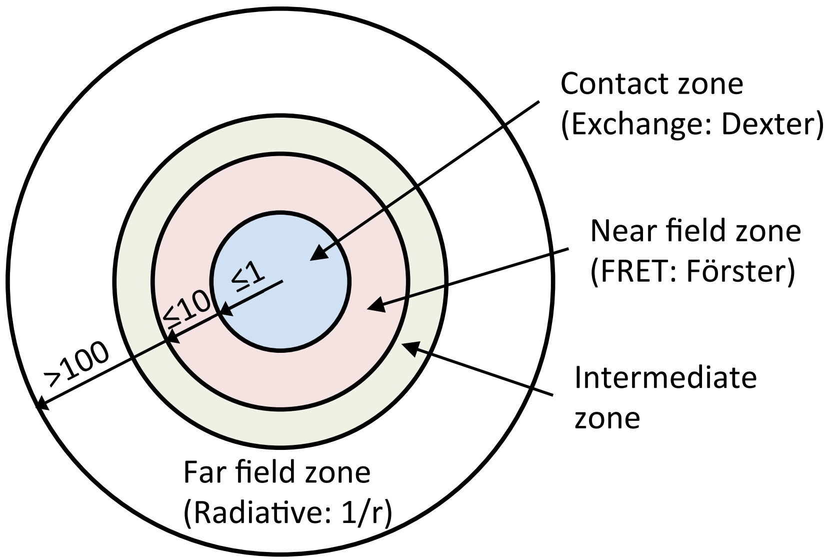
Phosphorescence enhanced by mixing S+T eg: spin-orbit coupling via heavy metal atom

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

GROUND STATE
spin anti-symmetric

Energy Transfer

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

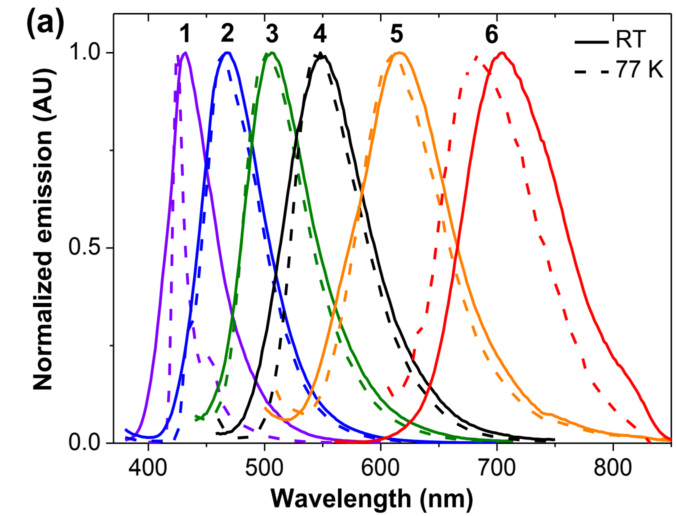


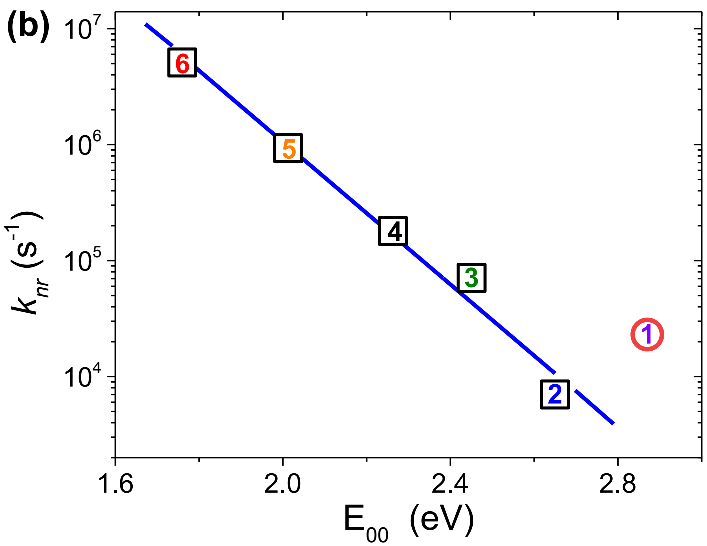
Different transfer ranges accessed by different processes

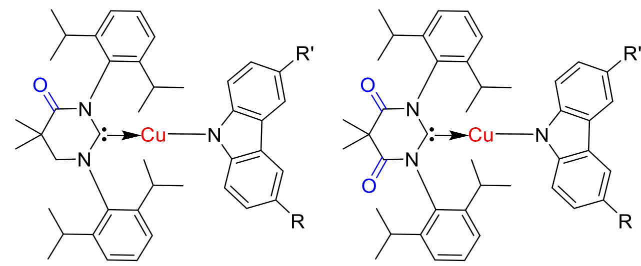
Energy Gap Law

- 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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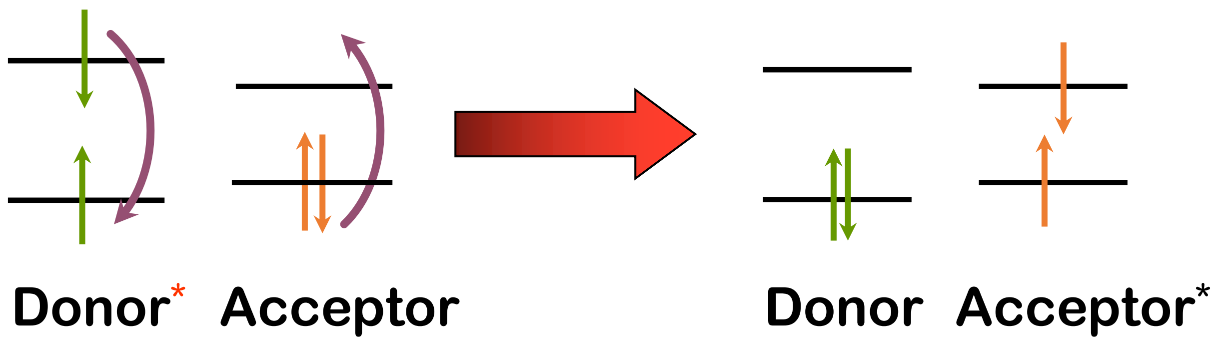
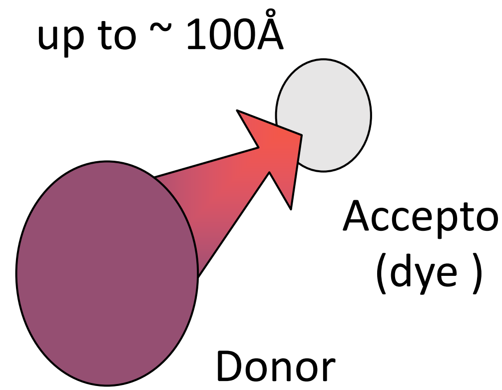
Stephen R. Forrest

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

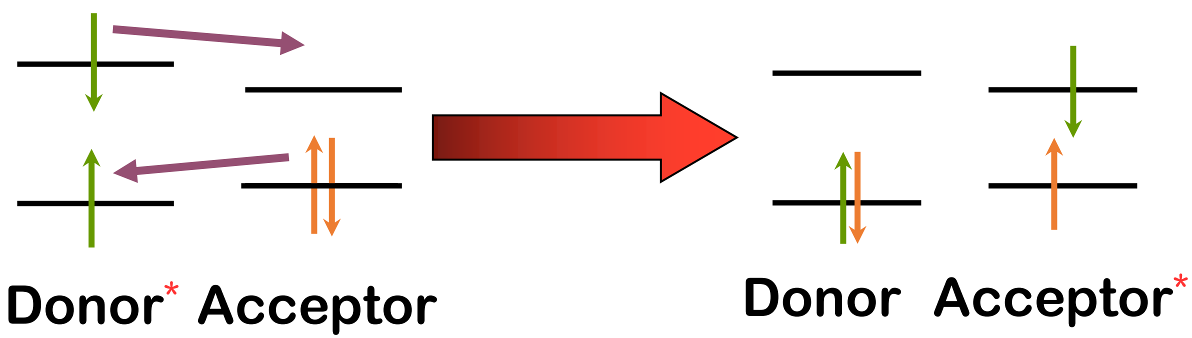
Energy Transfer from Host to Dopant: A Review

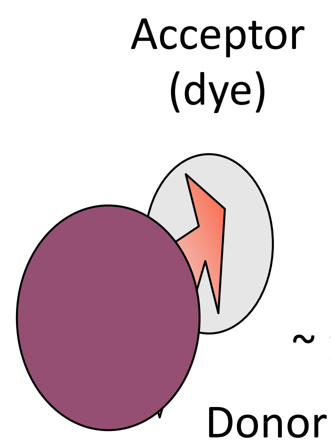
<u>Förster</u>:
- resonant dipole-dipole coupling
- donor and acceptor transitions must be allowed





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

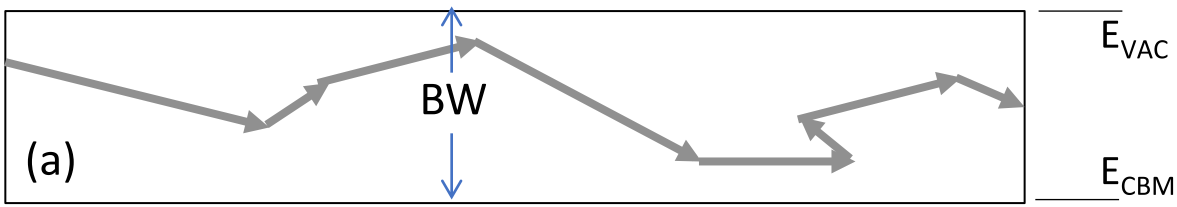




spin is conserved: e.g. singlet-singlet or triplet-triplet

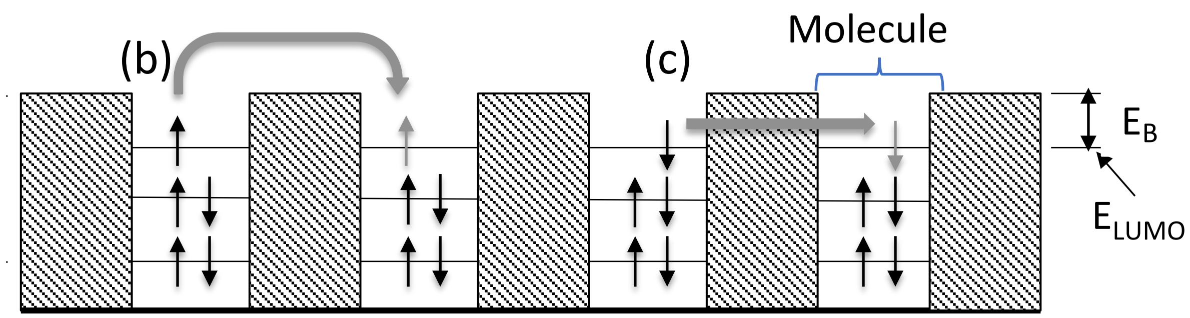
Modes of Conduction

Band transport



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

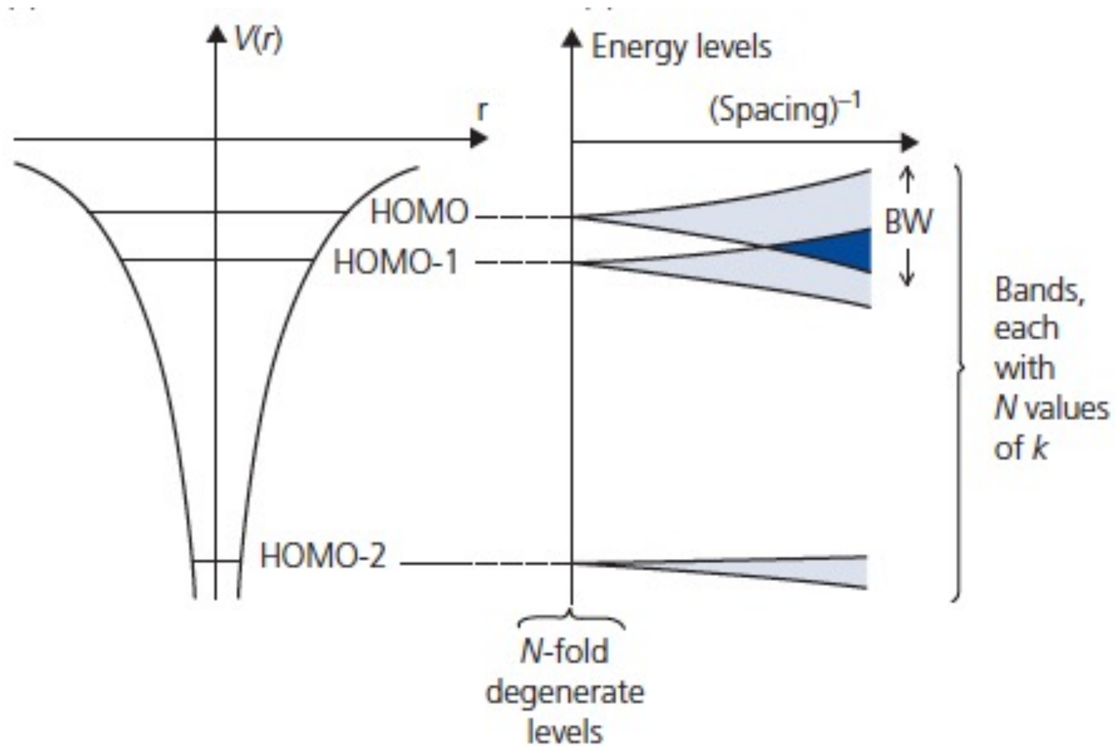
Hopping and tunneling transport



- Incoherent (each step independent of previous)
- Charge mean free path $\lambda \sim a$
- Tunneling between states of equal energy <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



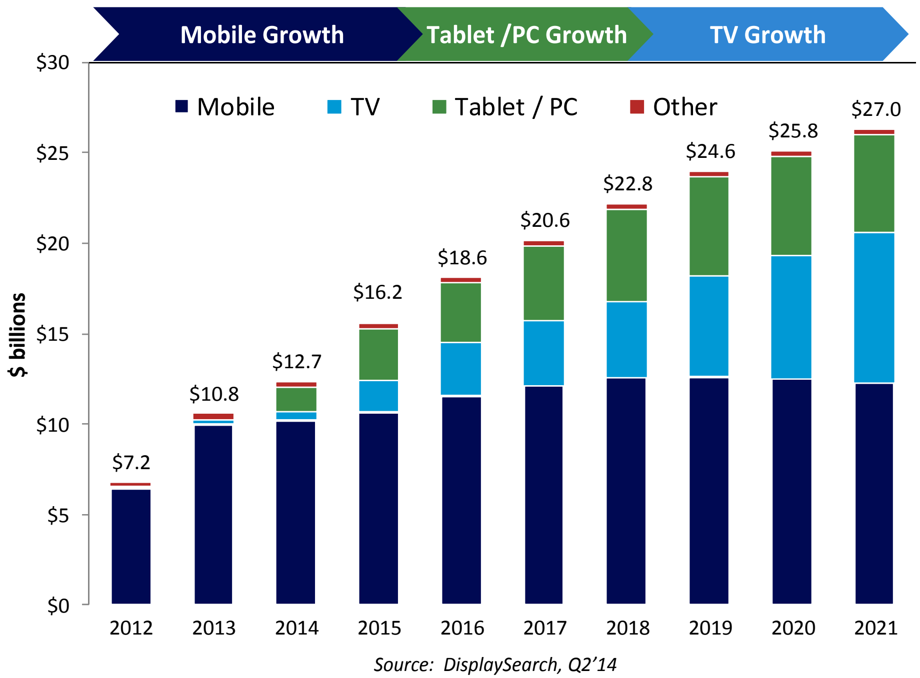
Light Emitters: Objectives

- Learn about vision: what makes a good display or lighting fixture?
- Gain a knowledge of how fundamental properties of organics leads to two important light emitting device types
  - OLEDs
  - Organic lasers
- Learn about challenges yet to be met before OLEDs completely dominate the display market
- Learn about the challenges for lighting and lasing

OLEDs

- Basic concepts
- Displays and Lighting
  - R-G-B pixellation
  - WOLEDs
  - TOLEDs
- Getting light out
- Intensity roll-off and annihilation
- Device reliability
- Lasing

AMOLED Displays: Driving the Technology



2010: Galaxy Phones
Phosphorescent R,G
>2 Billion sold ?!

2012: LG 55” & Samsung
Phosphorescent TV, $1500
2017: iPhone X

2014-15: 65” and 77” OLED TVs
2016: 4K OLED TV

Panasonic, Sony, Toshiba….(2017)

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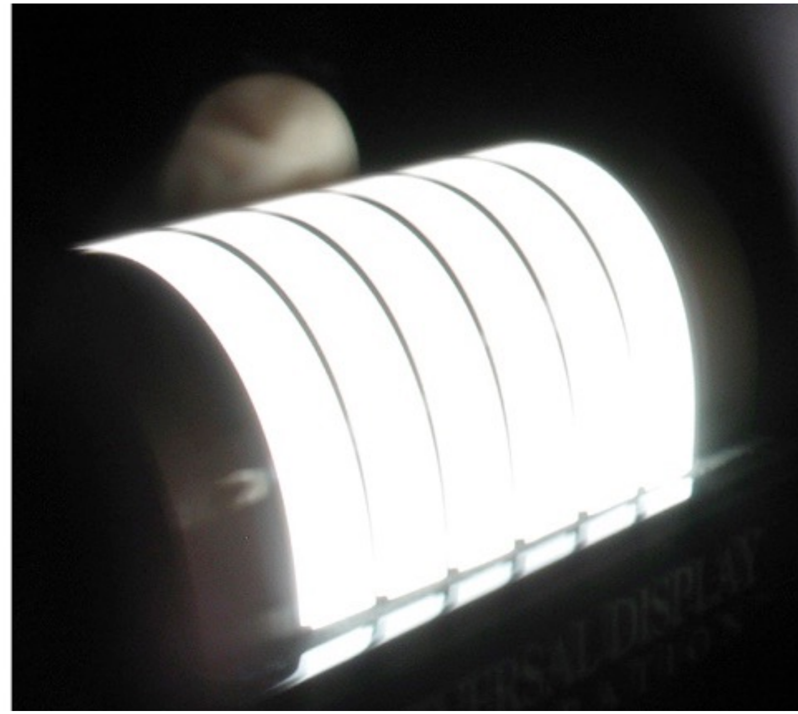
R. Forrest

The Future is Flexible



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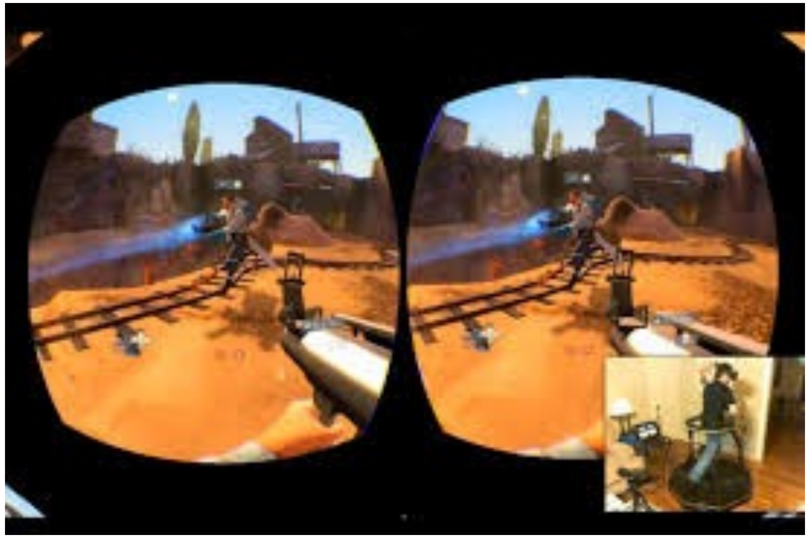
Virtual and Augmented Reality Enabled by OLEDs

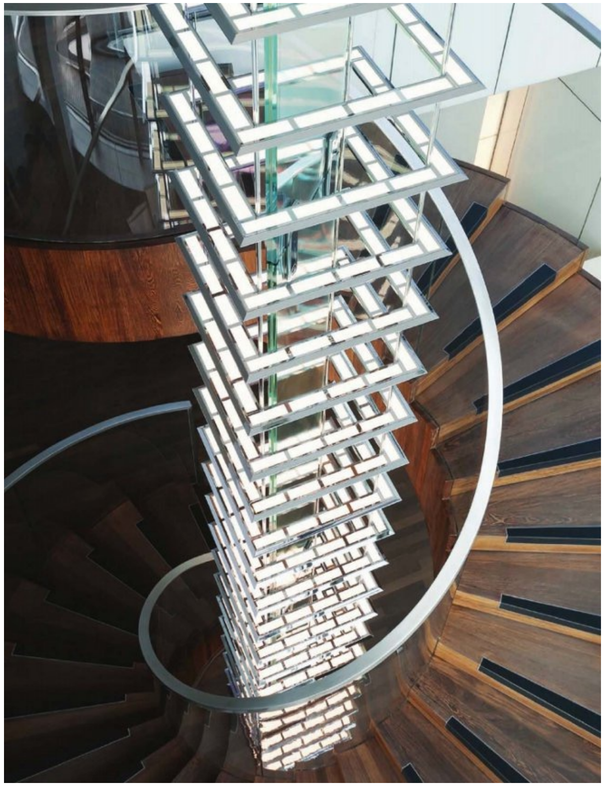


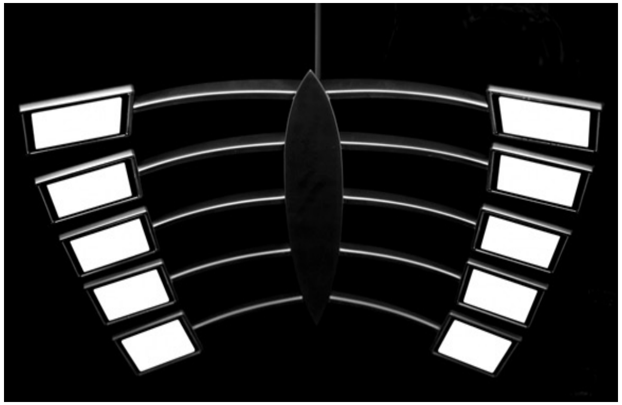
Requirements

Fast
Bright
Ultrahigh resolution

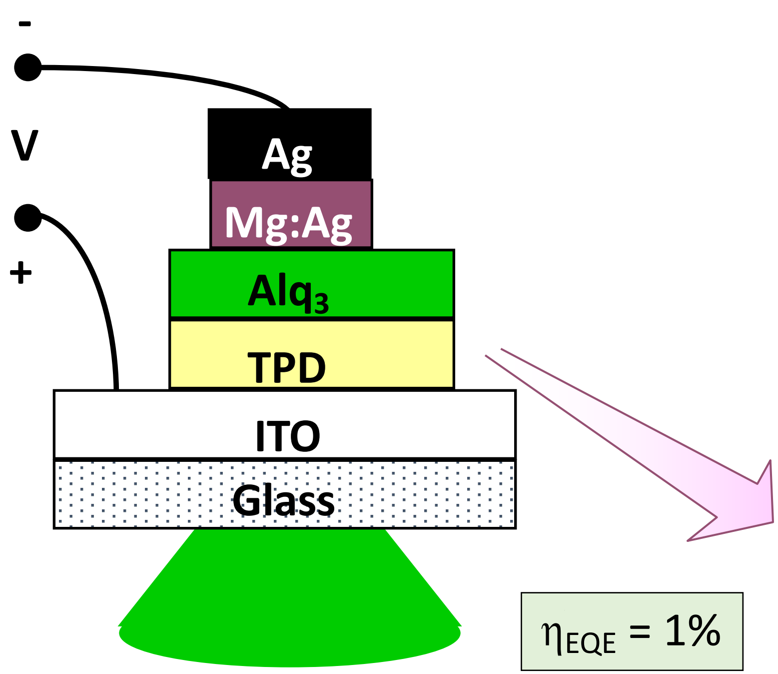
Electronics
en R. Forrest

White Lighting is Rapidly Becoming a Reality

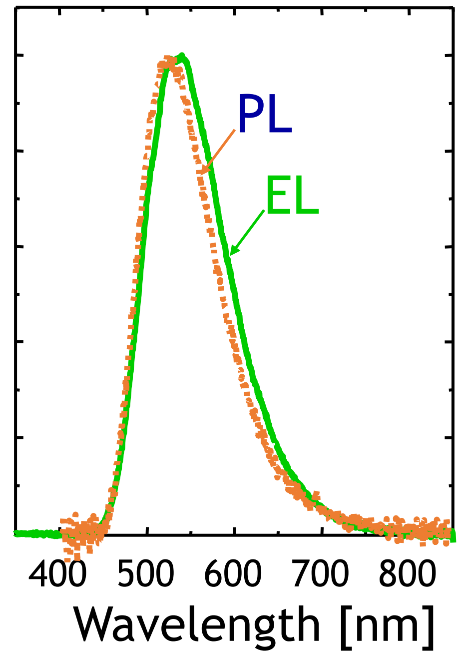


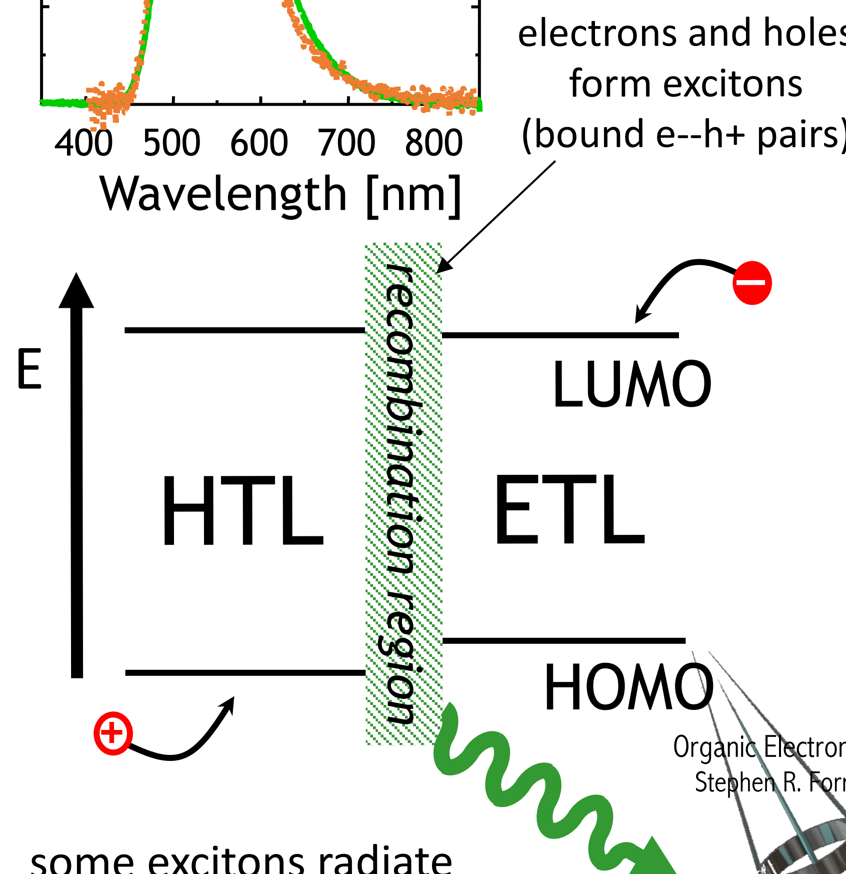


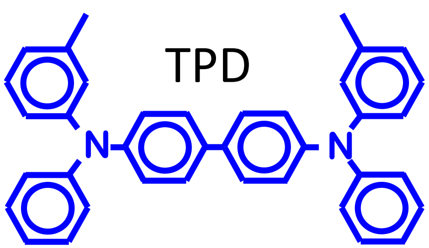
Organic Light Emitting Diode (OLED)

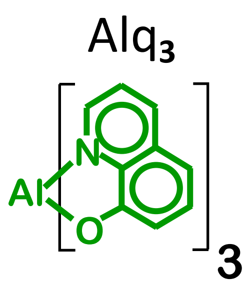


η_{EQE} = 1%



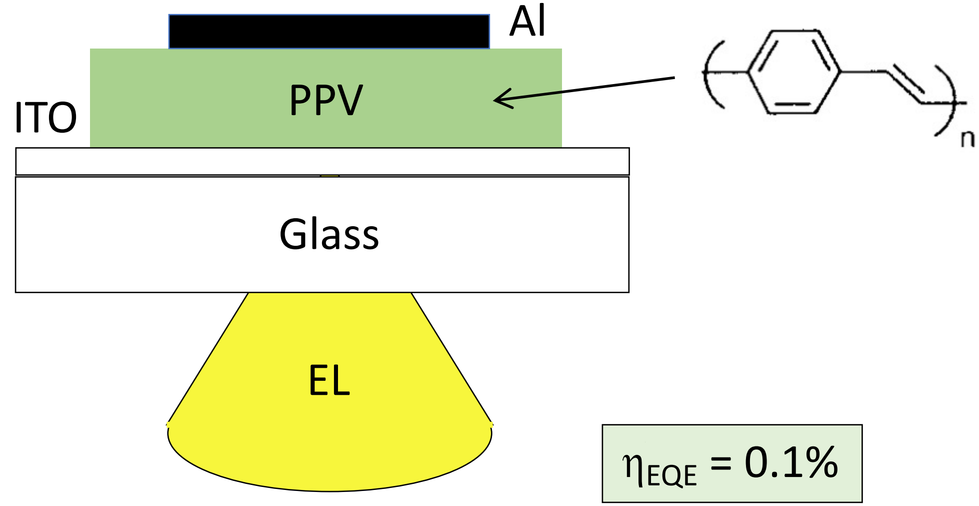






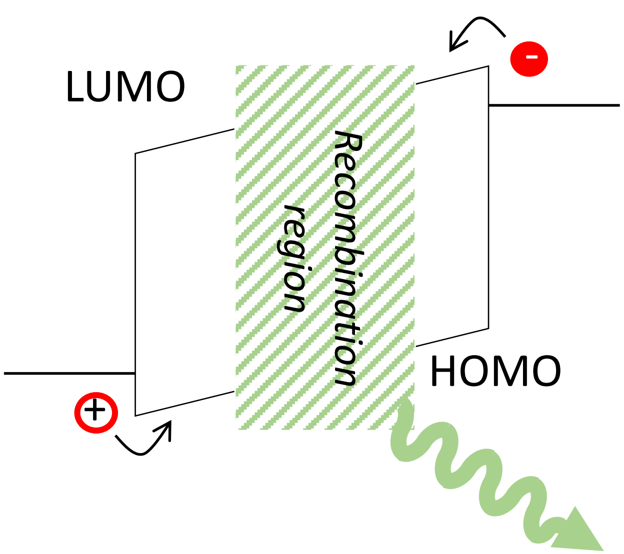
Tang & van Slyke, Appl. Phys. Lett., **51**, 913 (1987)

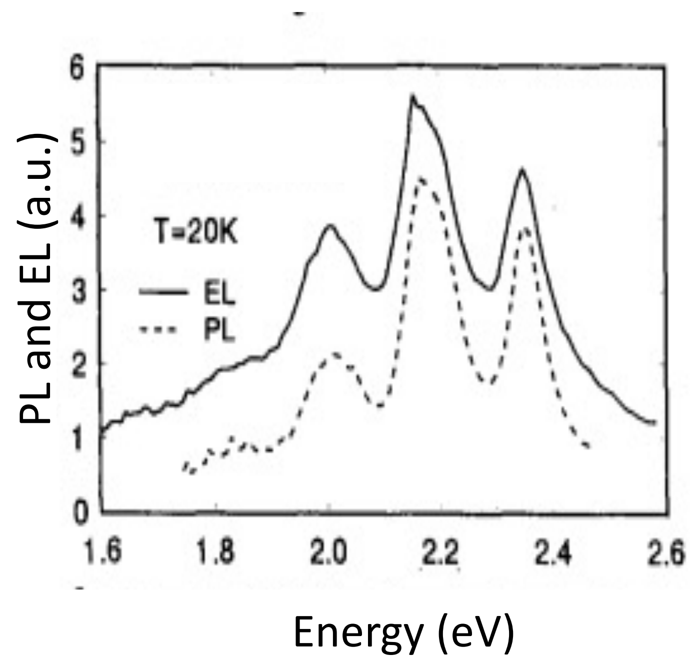
First Polymer OLED



η_{EQE} = 0.1%

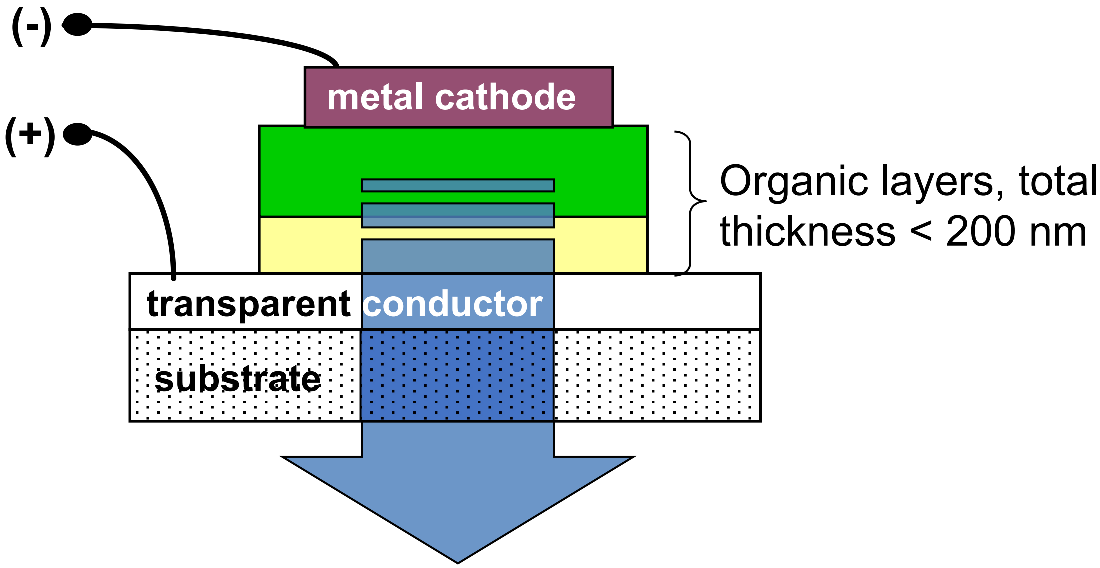
Burroughes, et al. 1990. *Nature,* 347**,** 539.





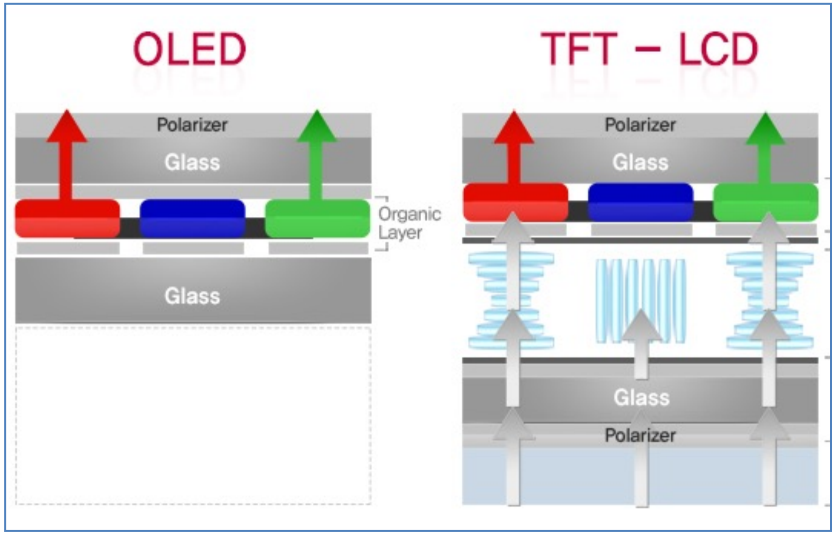
Recombination zone not well-defined

Benefits of OLEDs



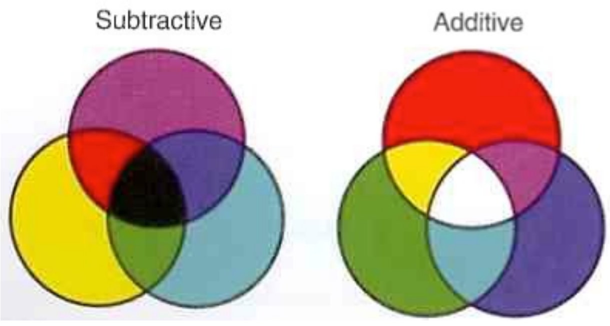
- Can be prepared on any substrate - active materials are amorphous
- Low cost materials and fabrication methods, scalable to large area
- Readily tuned color and electronic properties *via* chemistry
- Can be transparent when off
- Device characteristics
  - Efficiency ~ 100% demonstrated, white > 120 lm/W
  - > 1,000,000 hour (100 years) lifetime
  - Can be very bright: 10^6 cd/m^2, CRT = 100 cd/m^2, fluorescent panel = 800 cd/m^2
  - Turn-on voltages as low as 3 Volts

OLED vs. Liquid Crystal Displays (LCDs)



Display Technologies

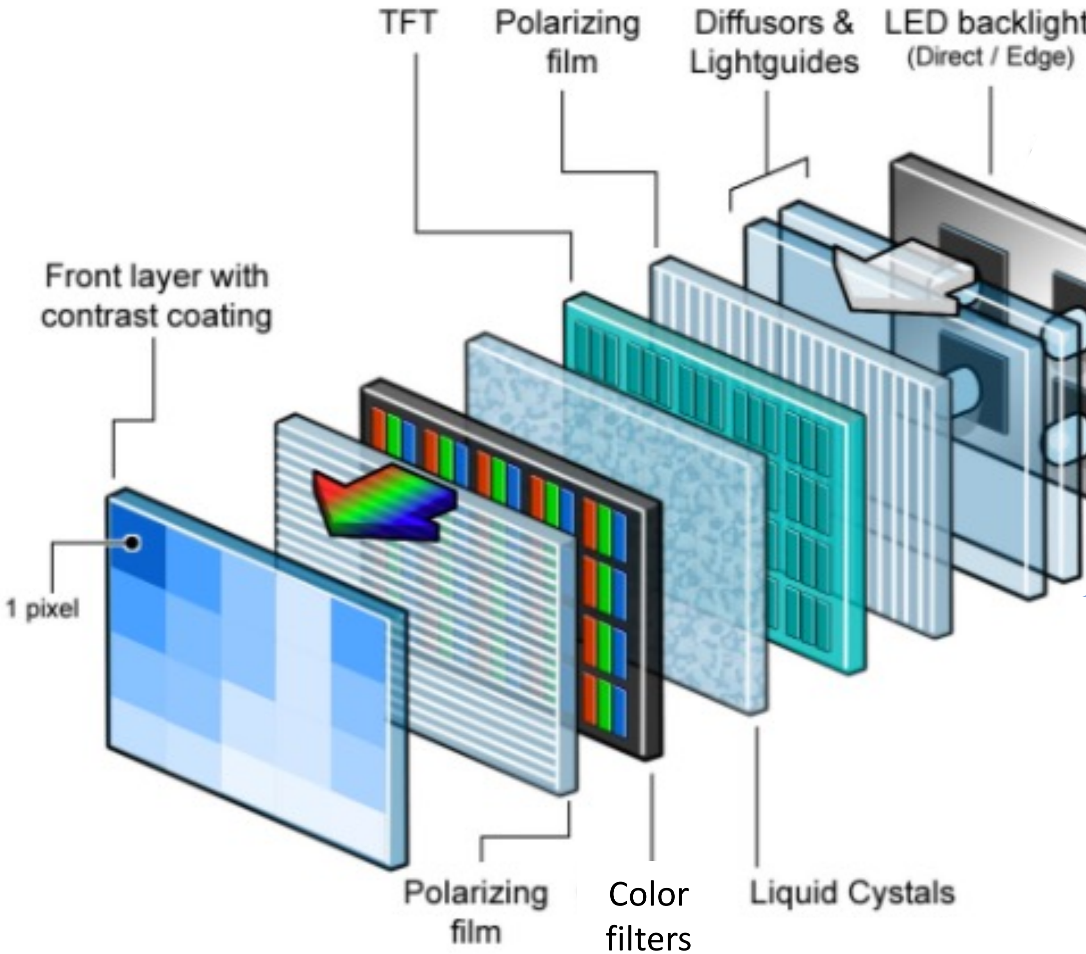
Color Mixing

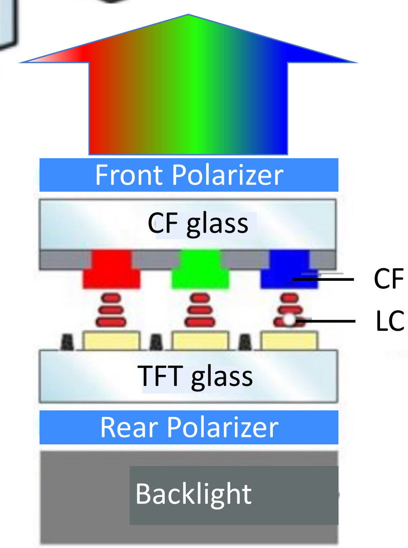


LCD

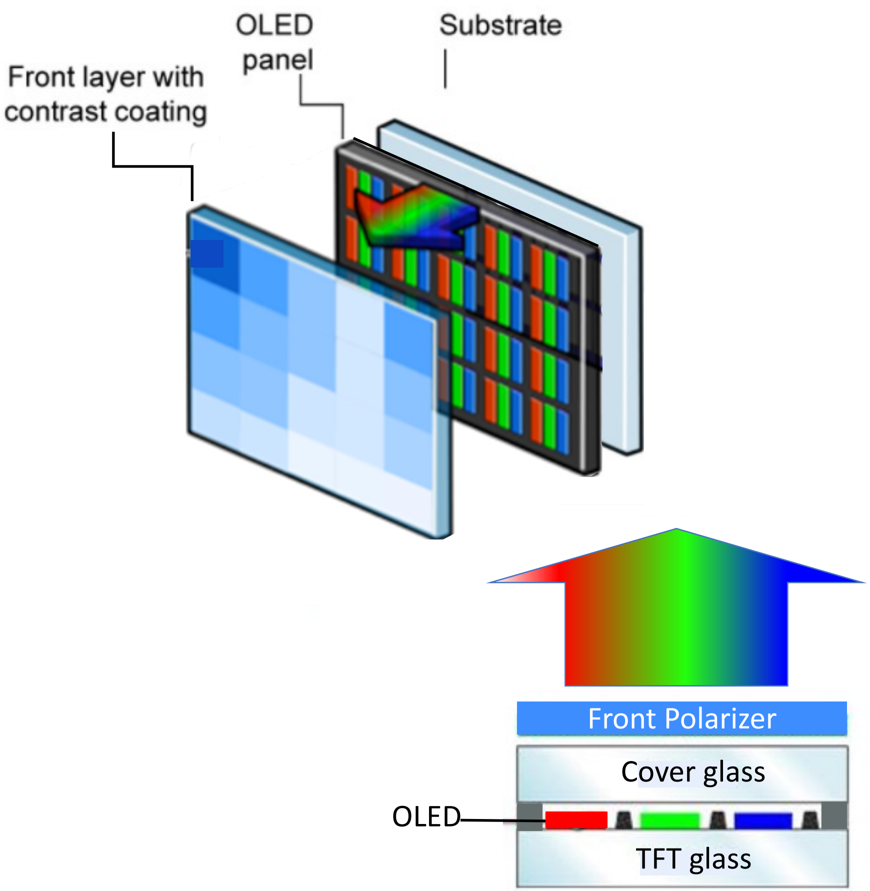
OLED
Plasma
CRT

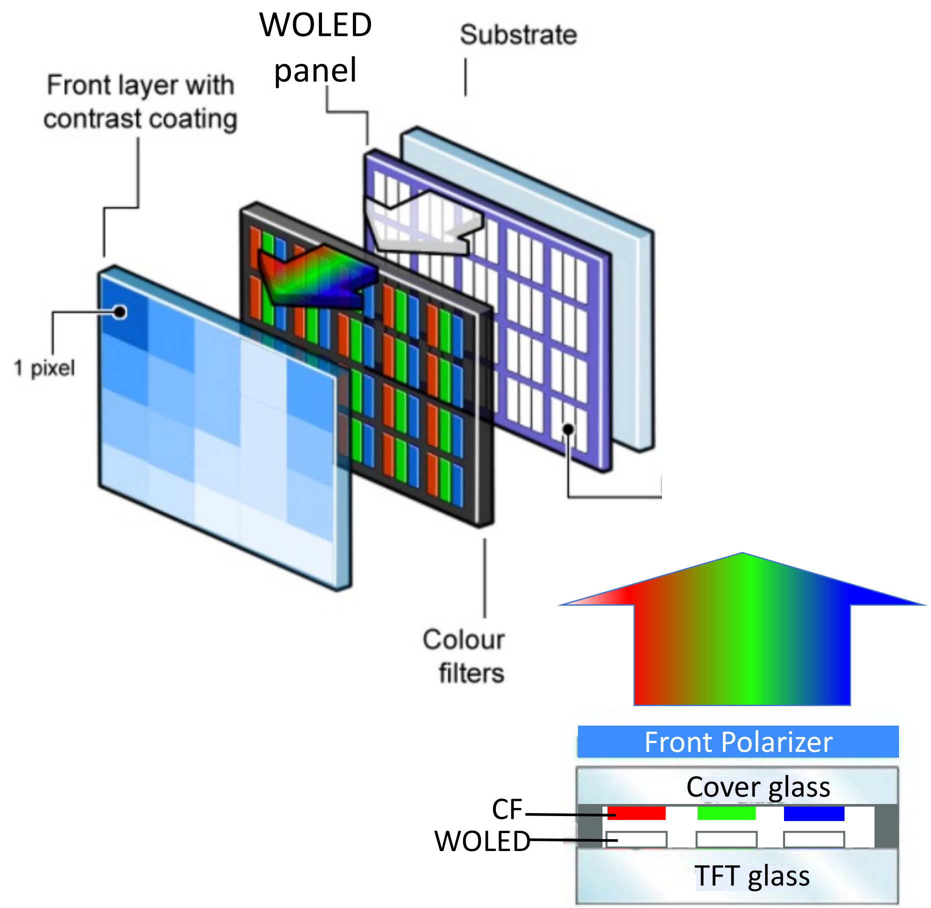
LCD/LED Displays





Two Types of OLED Displays





- RGB pixels
- Top emitting
- Dominates mobile (Samsung)

- WOLED pixels + Color filters
- Top emitting
- Dominates TVs (LG)