Week 8

Light Emitters 1

OLED Basics

Quantifying Efficiency for Displays and Lighting

Fluorescence and Phosphorescence

Thermally Activated Delayed Fluorescence

Chapter 6.1 – 6.3.4, 6.4

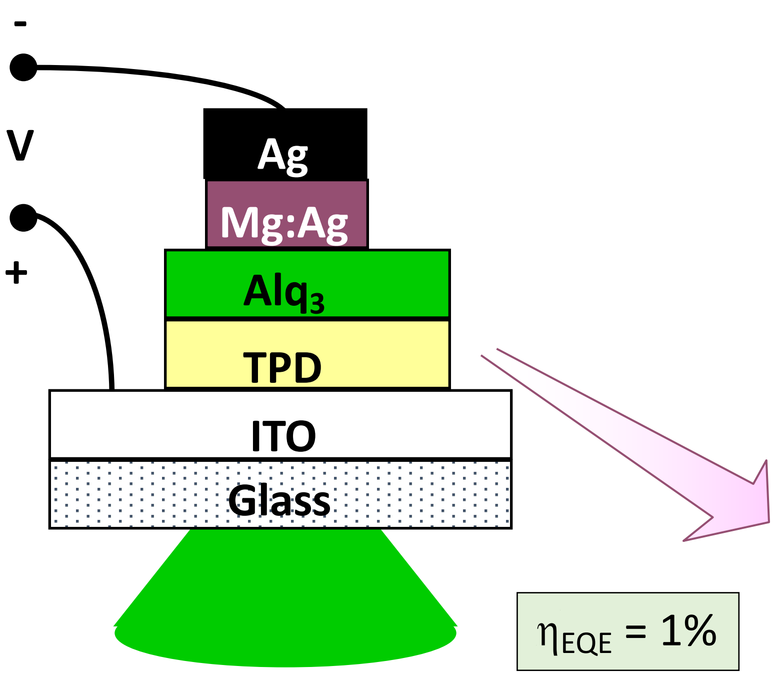
Objectives

- Learn about vision: what makes a good display or lighting fixture?
- Gain a knowledge of how fundamental properties of organics leads to arguably the most important organic electronic device: OLEDs
- Learn about challenges yet to be met before OLEDs completely dominate the display market
- Learn about the challenges for lighting

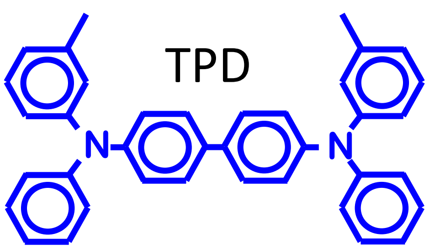
OLEDs

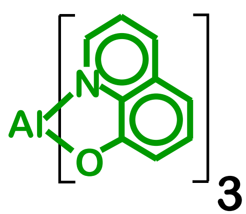
- Basic concepts
- Displays and Lighting
  - R-G-B pixellation
  - WOLEDs
  - TOLEDs
- Getting light out
- Intensity roll-off and annihilation
- Device reliability
- Lasing

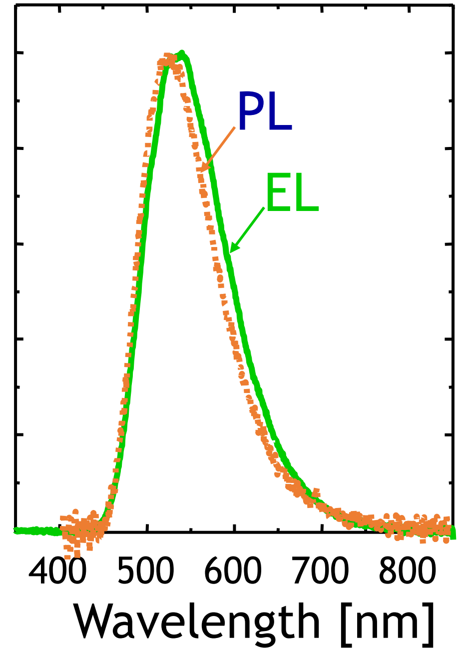
Organic Light Emitting Diode (OLED)



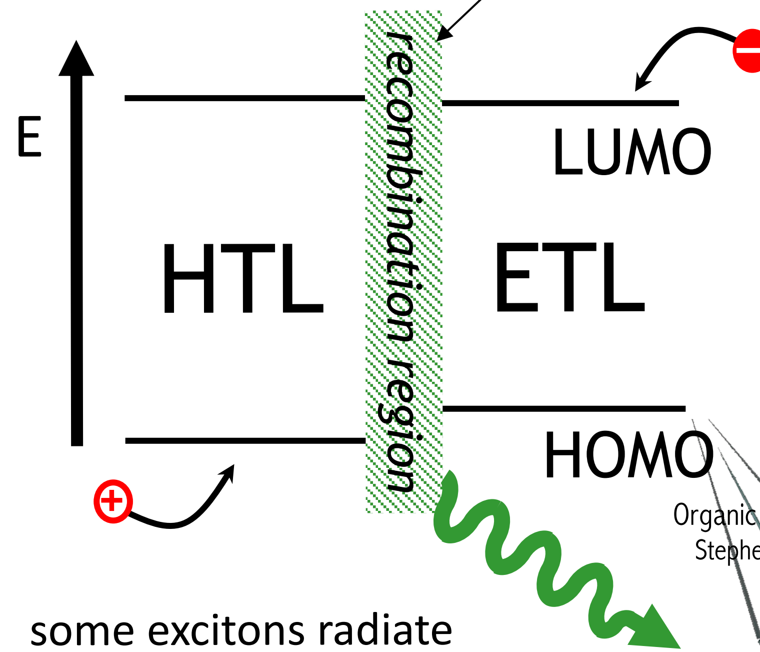
η_{EQE} = 1%







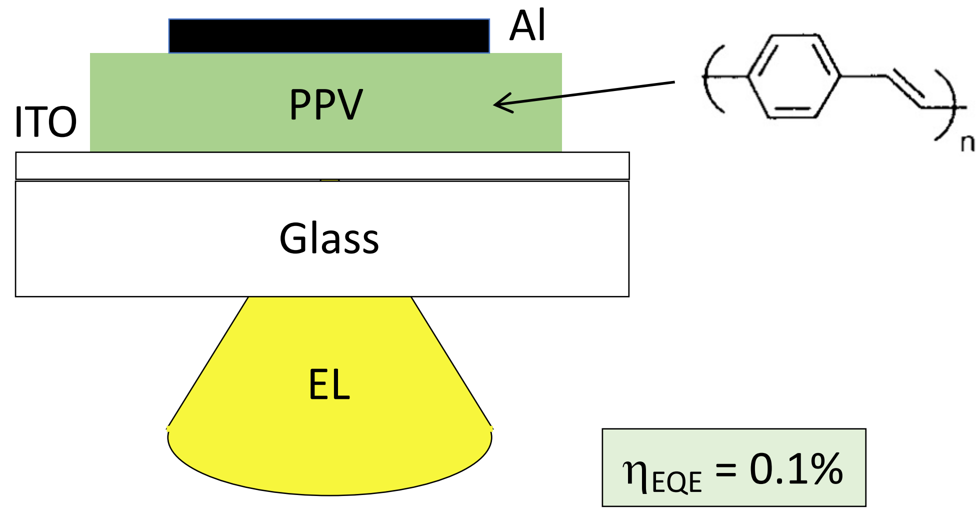
electrons and holes form excitons (bound e--h+ pairs)



some excitons radiate

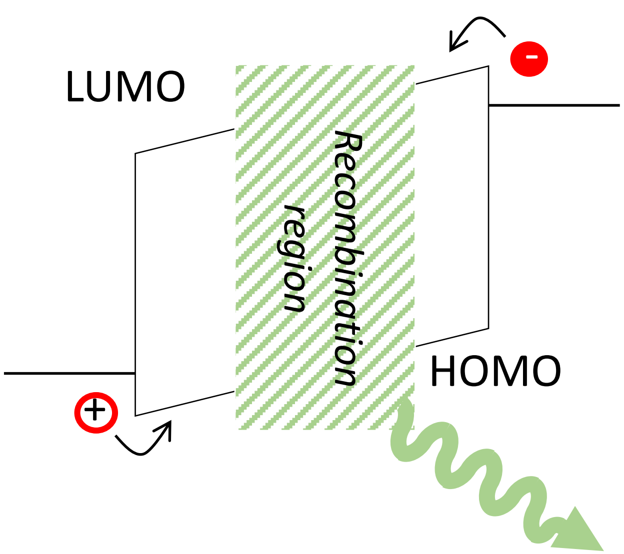
Tang & van Slyke, Appl. Phys. Lett., **51**, 913 (1987)

First Polymer OLED

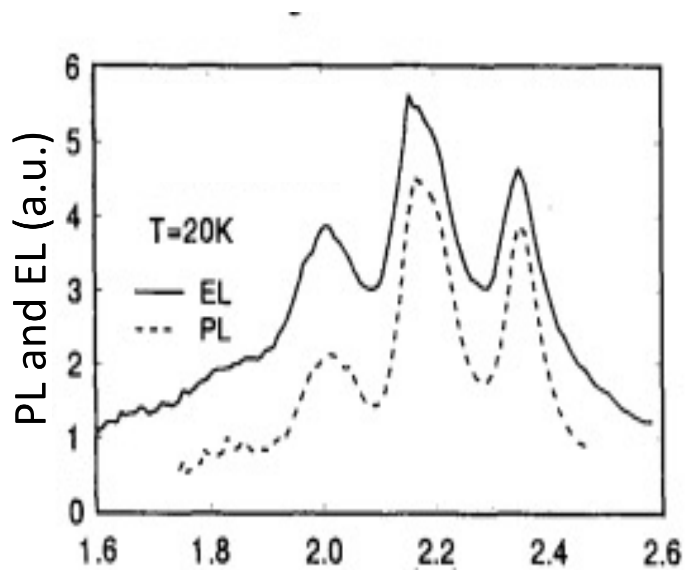


$\eta_{EQE} = 0.1\%$

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

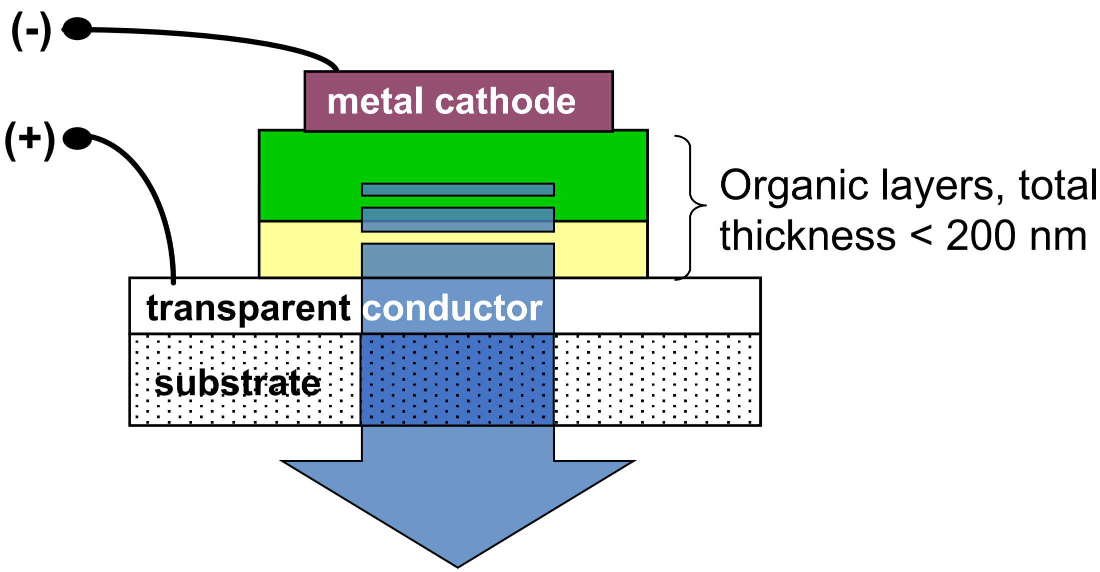


Recombination zone not well-defined



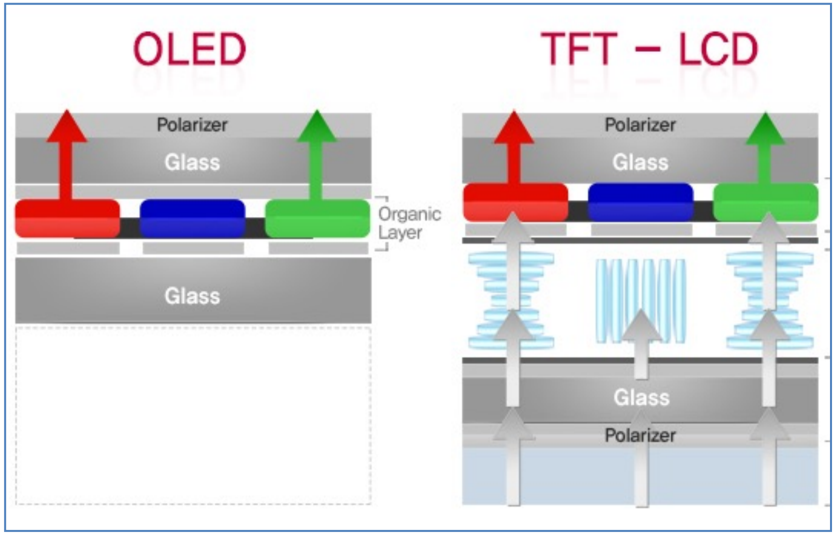
Organic Electronics
Stephen R. Forrest

Benefits of OLEDs



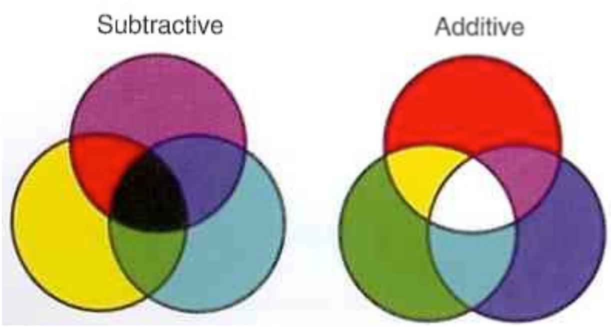
- Can be prepared on any substrate - active materials are amorphous
- Low cost materials and fabrication methods, scalable to large area
- Readily tuned color and electronic properties *via* chemistry
- Can be transparent when off
- Device characteristics
  - Efficiency ~ 100% demonstrated, white > 120 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

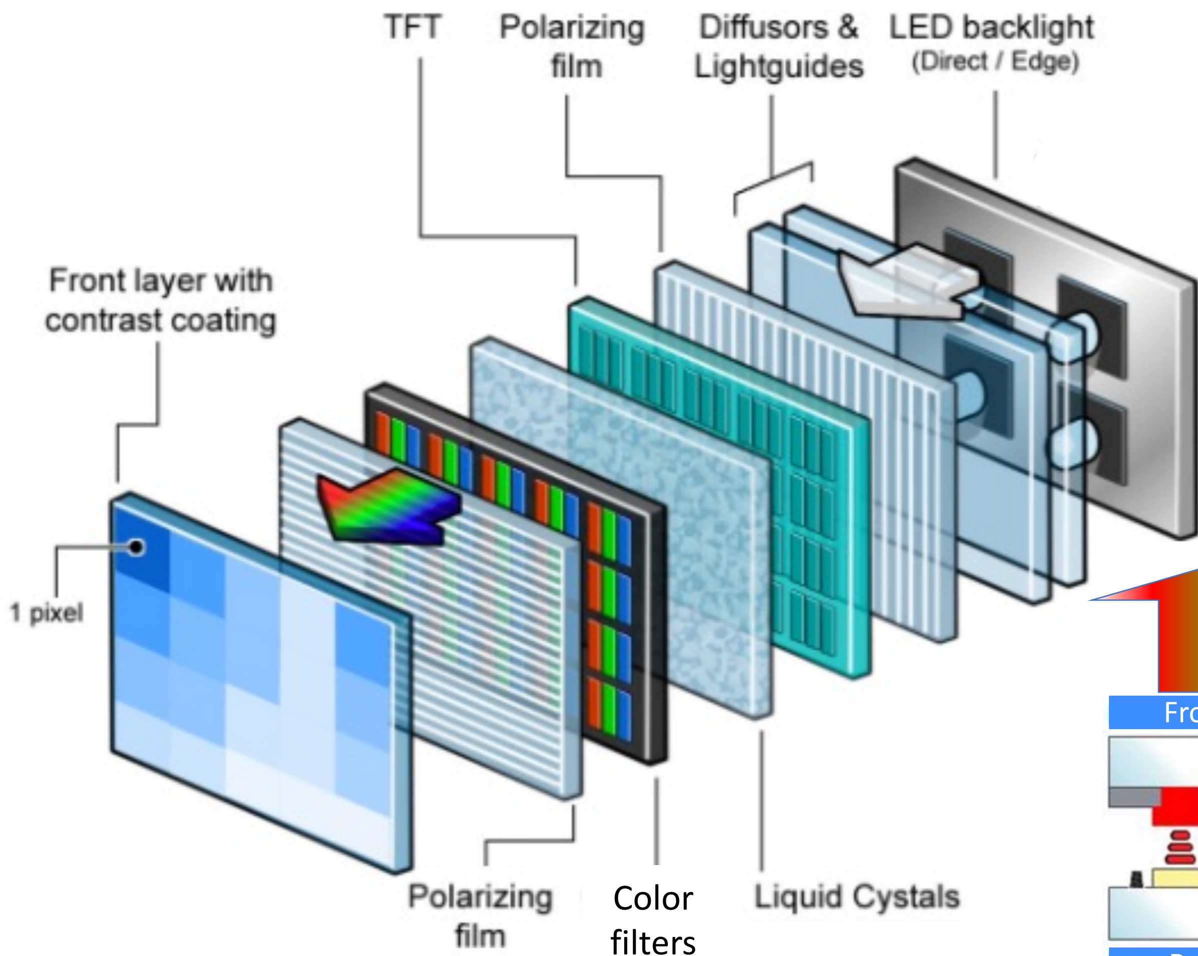
Color Mixing

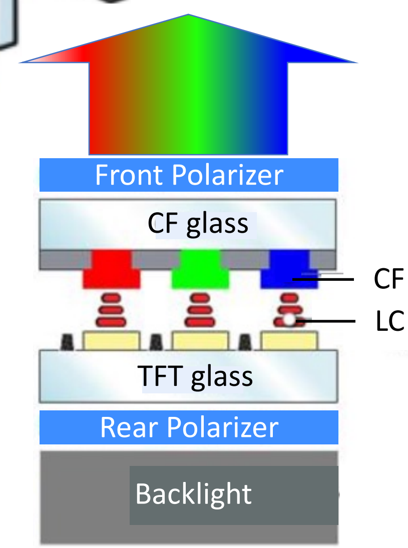


LCD

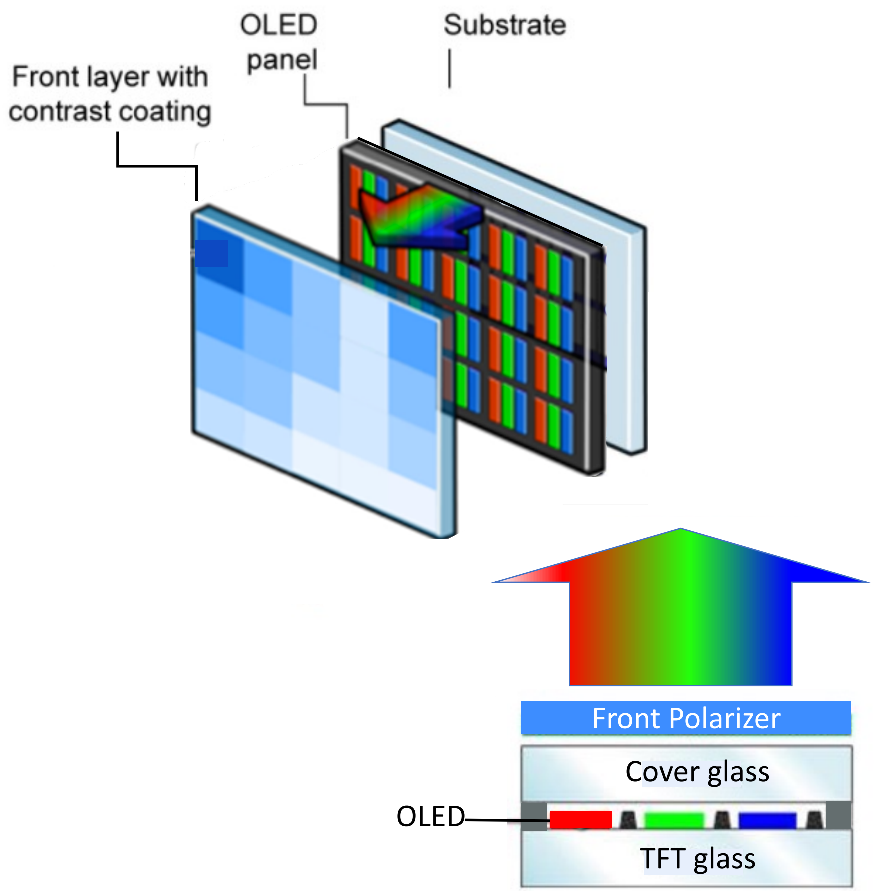
OLED
Plasma
CRT

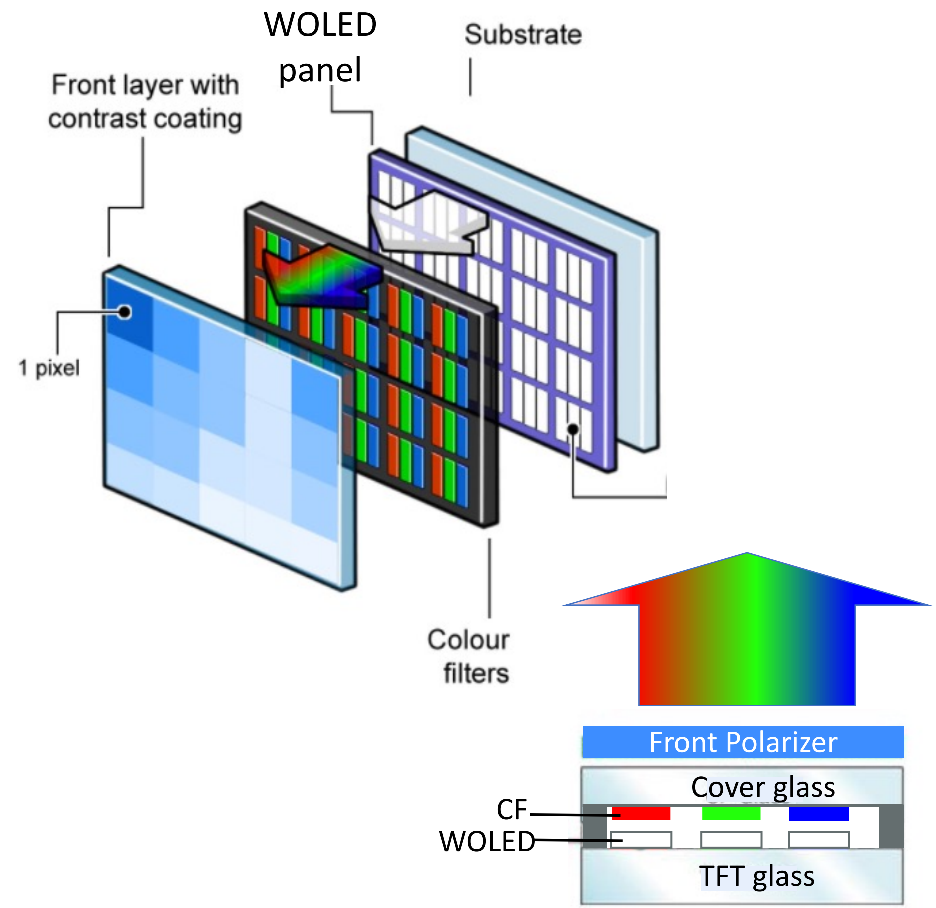
LCD/LED Displays





Two Types of OLED Displays





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

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

OLED efficiency

$$\eta_{ext} = \eta_{\mathrm{int}}\eta_{out} = \underbrace{\gamma}_{\sim 100\%}\underbrace{\chi_r}_{?}\underbrace{\phi_p}_{\sim 100\%}\underbrace{\eta_{out}}_{\sim 20\%}$$

γ: charge carrier balance factor
ratio of e/h

χ_r: luminescent exciton production

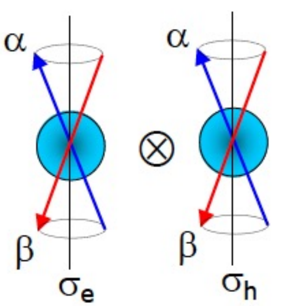
ϕ_p: quantum efficiency of fluorescence

η_{out}: light out-coupling efficiency

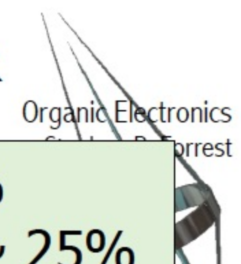
1. Fluorescence is restricted to singlet excitons χ_r ~ 25%

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

Triplet
$$\left\{\begin{array}{l} \alpha(\sigma_e)\otimes\alpha(\sigma_h) \\ \beta(\sigma_e)\otimes\beta(\sigma_h) \\ \frac{1}{\sqrt{2}}\left(\alpha(\sigma_e)\otimes\beta(\sigma_h)+\alpha(\sigma_h)\otimes\beta(\sigma_e)\right) \end{array}\right.$$

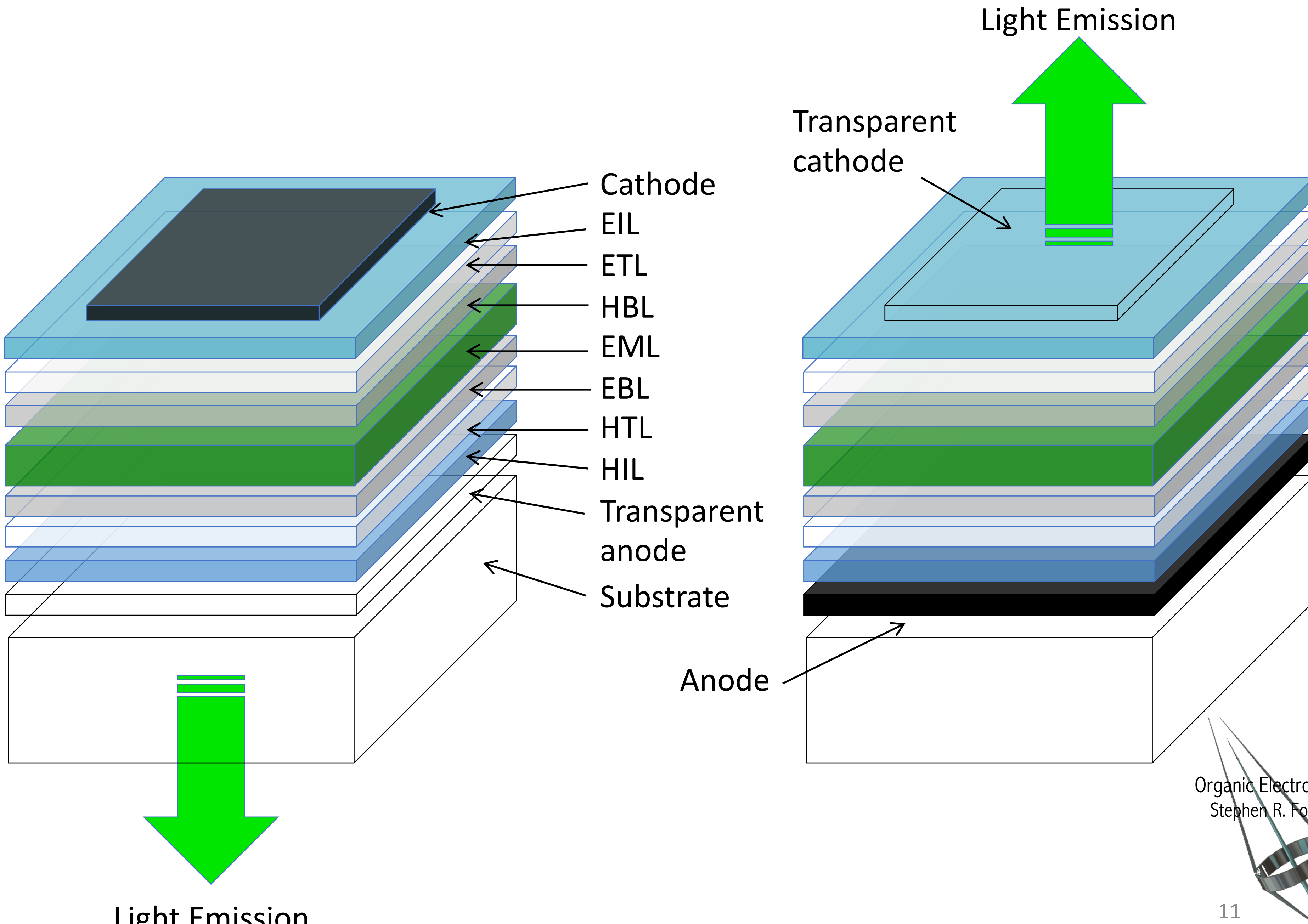


2. Only ~ 20% of photons are coupled out of OLED devices due to TIR

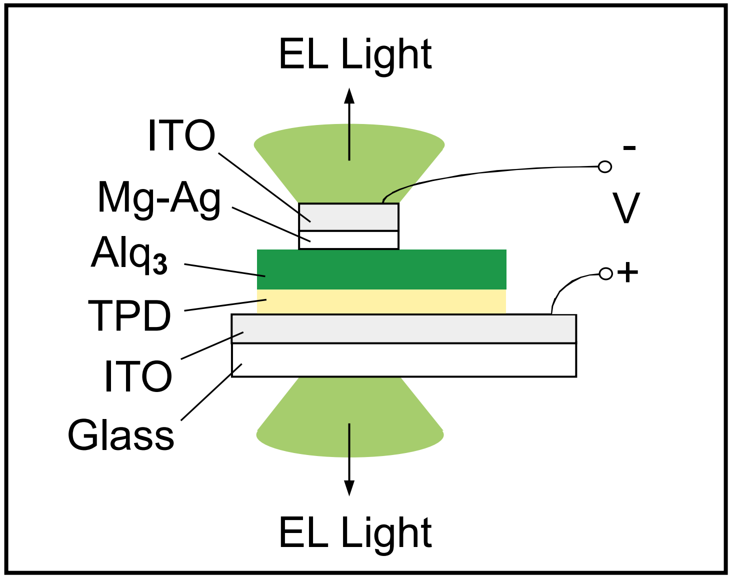


Maximum Fluorescence External Quantum Efficiency on Glass ~ 5%
Maximum Phosphorescence External Quantum Efficiency on Glass ~ 25%

Today's OLEDs Are Not So Simple



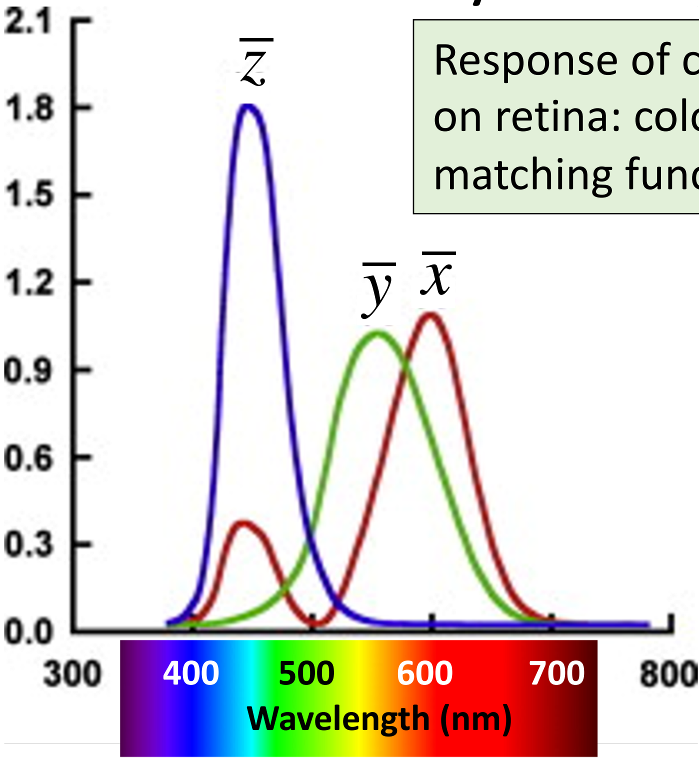
Transparent OLED (TOLED)



- Devices can be > 90% transparent
- Thin metal or electron injection layer is capped with ITO
- Transparent cathode can also be used to prepare top emitting structures
  - OLEDs on metal sheets
  - OLEDs on Si backplanes in AMOLED displays

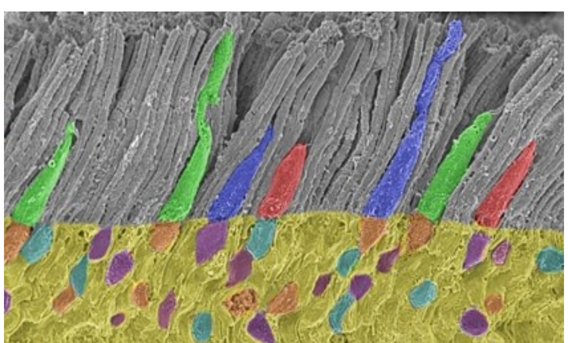
Bulovic, V., et al. 1996, Nature, 380, 29.

How We See Color: Tri-Stimulus Curves and Chromaticity



Response of cones on retina: color matching functions

Rod & cone cells in retina



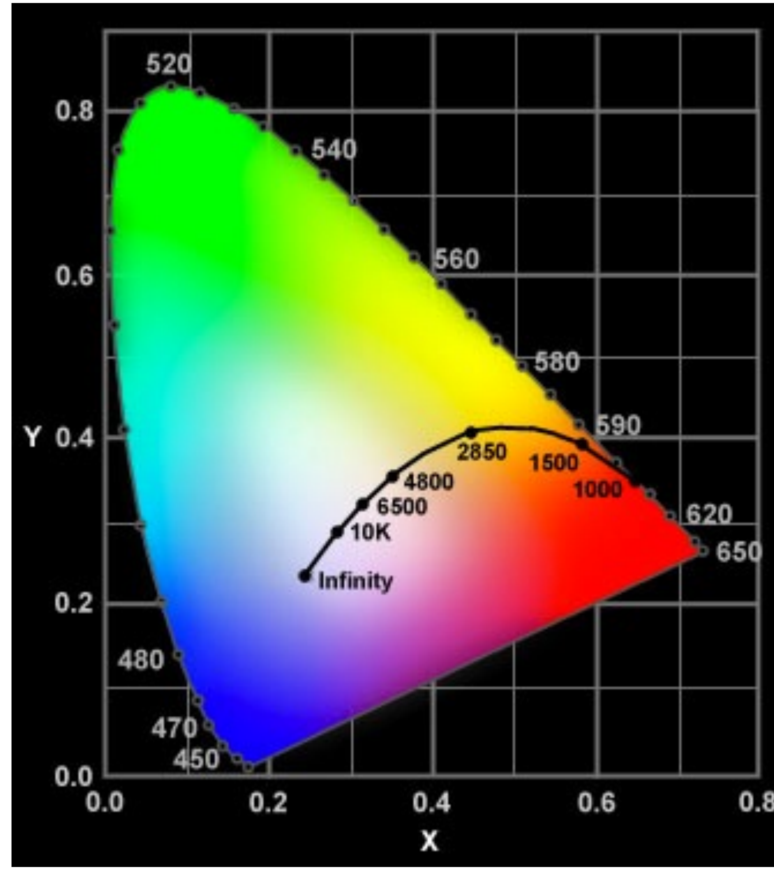
Tri-stimulus values

$$X = \int I(\lambda)\bar{x}(\lambda)\,d\lambda$$

$$Y = \int I(\lambda)\bar{y}(\lambda)\,d\lambda$$

$$Z = \int I(\lambda)\bar{z}(\lambda)\,d\lambda$$

$I(\lambda)$=un-normalized spectral intensity



CIE Coordinates

$$x = \frac{X}{X+Y+Z};\quad y = \frac{Y}{X+Y+Z};\quad z = \frac{Z}{X+Y+Z}$$

$$x + y + z = 1 \quad \Rightarrow \quad z = 1 - x - y$$

Scotopic vs. Photopic Vision Response

How things appear at night

Scotopic vision due to the rod cells
– only sense luminosity (brightness) but not color

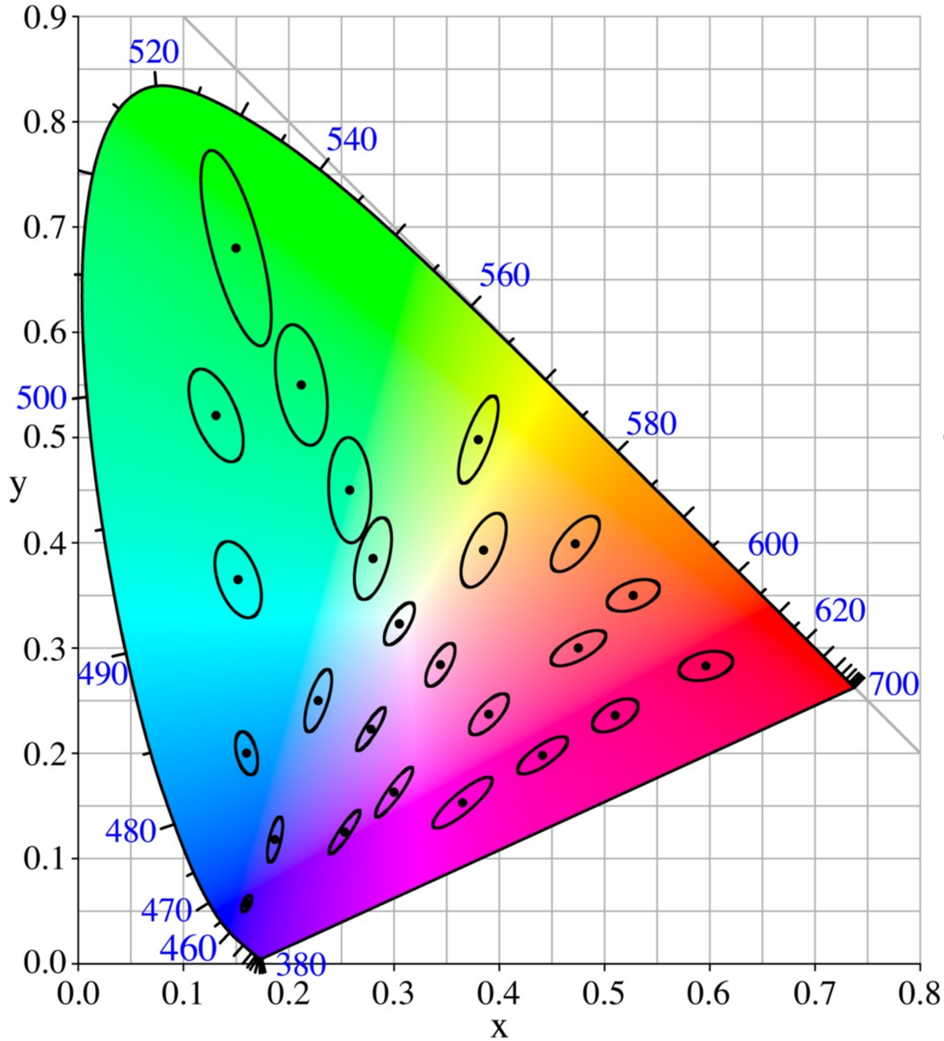
(simulation)

How things actually are at night

Photopic, or daytime vision senses color from cone cells – but not capable at sensing low light levels

North wall, Yosemite Valley, CA in March

Limits to color perception

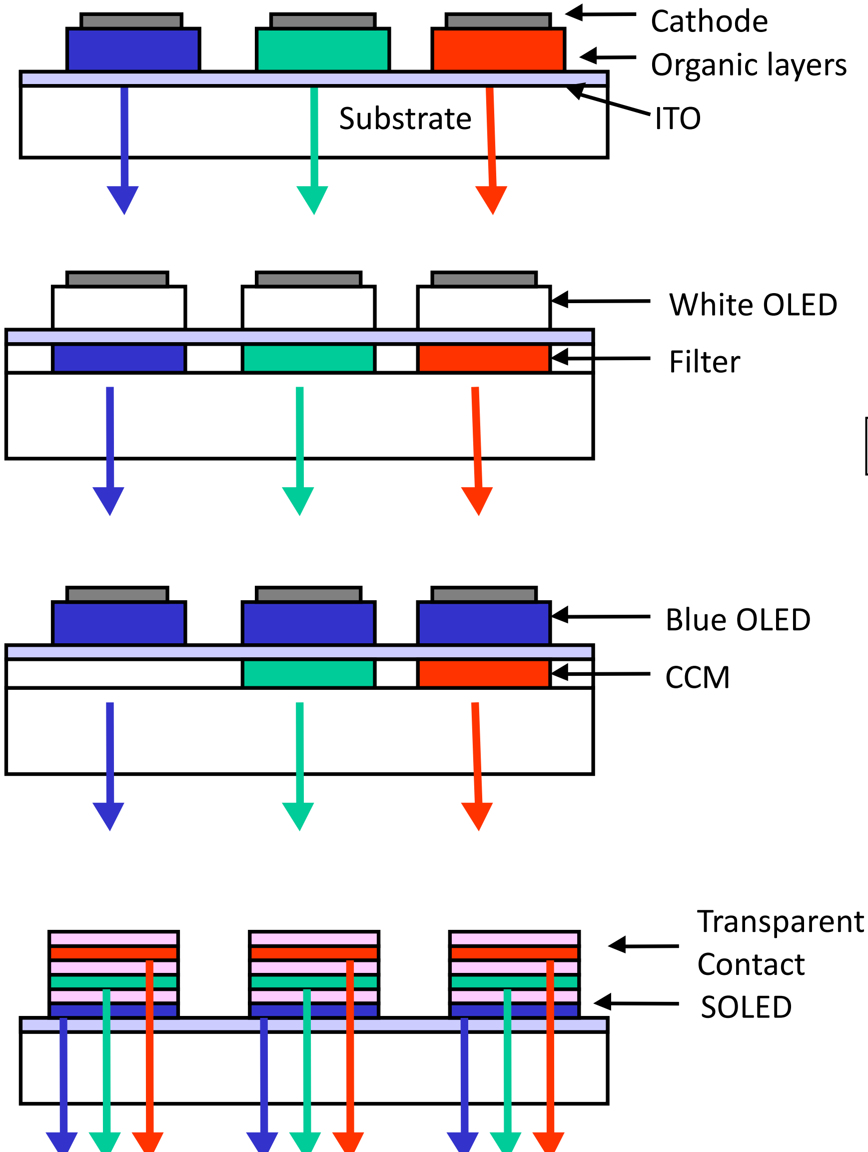


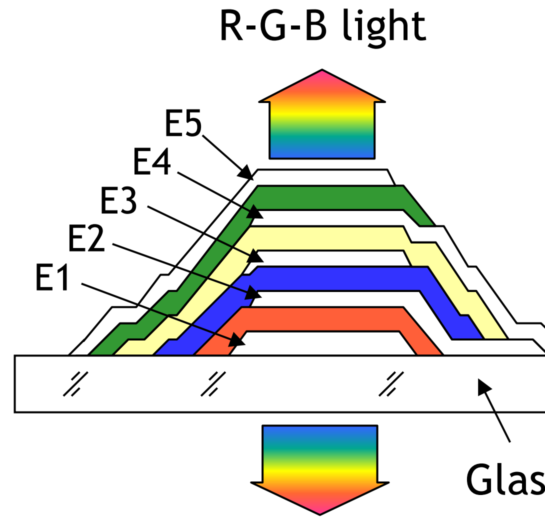
MacAdams Ellipses:

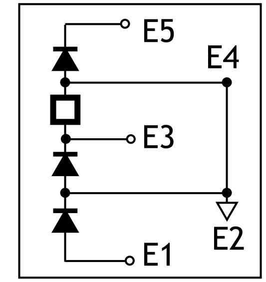
Define the amount of change in color that can be perceived

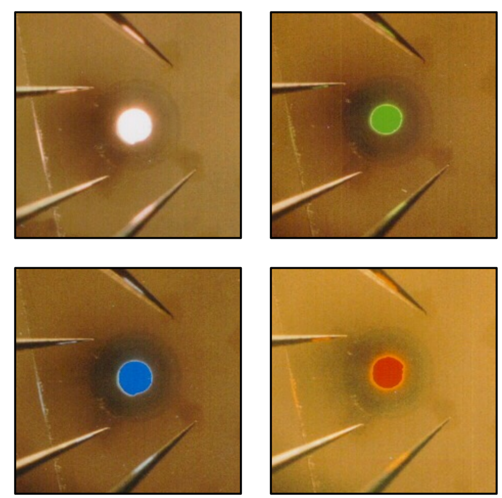
Each ellipse magnified 10X

Pixel Arrangements for OLED Displays



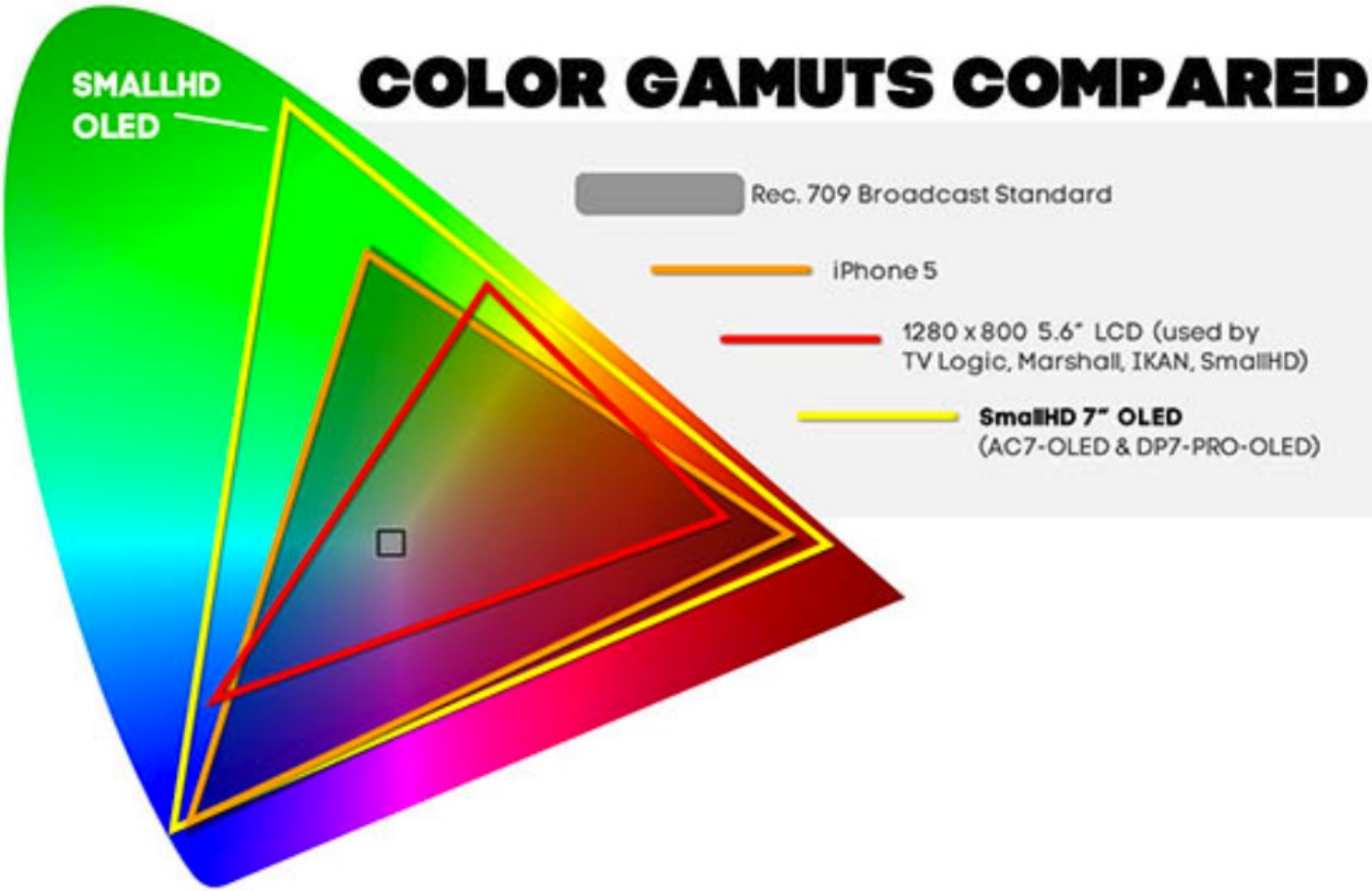






G. Parthasarathy, et al., *Adv. Mater.*, **11**, 907 (1999).

Various Display Color Gamuts



Radiometric and Photometric Quantities

Radiometric Units				Photometric Units			
Quantity	Symbol	Expression	Unit	Quantity	Symbol	Expression	Unit
Radiant flux	Φ_e		W	Luminace flux	Φ		lm
External quantum efficiency	η_{ext}	$\eta_{int}\eta_{out}$	%	Luminous efficiency	η_L	$\frac{L}{j}$	cd/A
Power efficiency	η_P	$\frac{1}{jV}\frac{d\Phi_e}{dS}=\frac{E_e}{jV}$	%, or W/W	Luminous power efficiency	η_{LP}	$\frac{1}{jV}\frac{d\Phi}{dS}=\frac{E}{jV}$	lm/W
Radiant intensity	I_e	$\frac{d\Phi_e}{d\Omega}$	W/sr	Luminace intensity	L_Ω	$\frac{d\Phi}{d\Omega}$	lm/sr
Radiance	L_e	$\frac{d\Phi_e}{dS\,d\Omega\cos\theta}$	W/sr-m^2	Luminance	L	$\frac{d\Phi}{dS\,d\Omega\cos\theta}$	cd/m^2 =lm/sr-m^2
Irradiance	E_e	$\frac{d\Phi_e}{dS}$	W/m^2	Illuminance	E	$\frac{d\Phi}{dS}$	lm/m^2
Radiant exitance	M_e	$\frac{d\Phi_e}{dS}$	W/m^2	Luminous exitance	M	$\frac{d\Phi}{dS}$	lm/m^2

Radiometric: Light source properties quantified using standard scientific units
Photometric: Light source properties quantified by visual *perceptive* units

Light source definitions

$$\text{External quantum efficiency} = \frac{\text{No. photons viewed}}{\text{No. of electrons injected}} = \frac{q\lambda P_{meas}}{(hc)\, I_{OLED}}$$

$$\text{Internal quantum efficiency} = \frac{\text{No. photons emitted}}{\text{No. of electrons injected}} = \frac{q\lambda P_{meas}}{\eta_{out}\,(hc)\, I_{OLED}}$$

$$\text{Power efficiency} = \frac{\text{Optical power emitted}}{\text{Elect. power injected}} = \frac{P_{meas}}{I_{OLED}V_{OLED}} \quad [\text{W/W}]$$

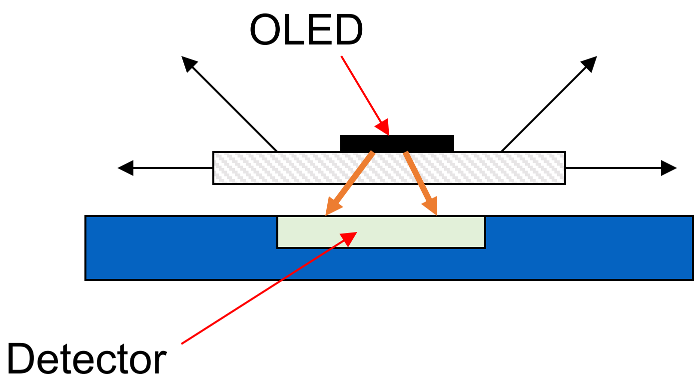
$$\text{Luminance power efficiency} = \frac{\text{Luminance}}{\text{Elect. power injected}} = \frac{L_{meas}}{I_{OLED}V_{OLED}} \quad [\text{lm/W}]$$

$$\text{Luminance efficiency} = \frac{\text{Luminance}}{\text{Current injected}} = \frac{L_{meas}}{I_{OLED}} \quad [\text{cd/A}]$$

Luminance units: cd/m^2 = nits; cd=lumens/π (for a Lambertian source)

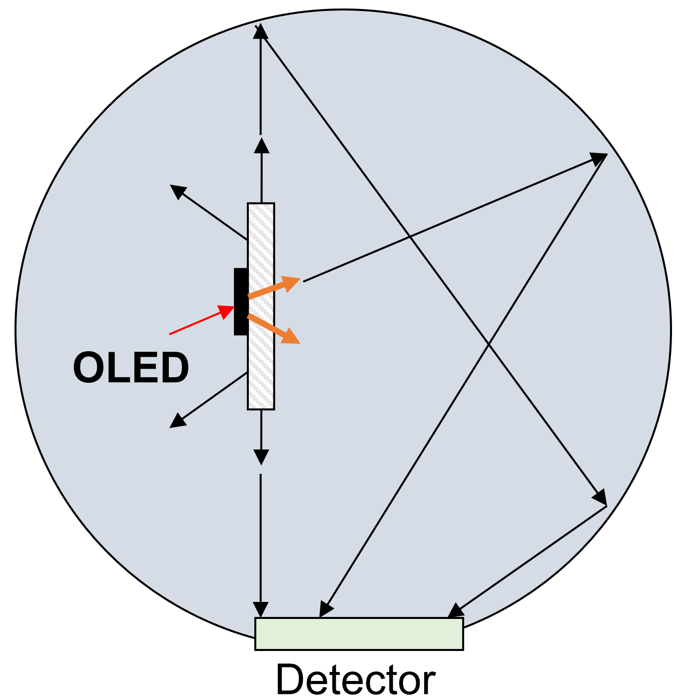
Measuring Quantum Efficiency

External QE



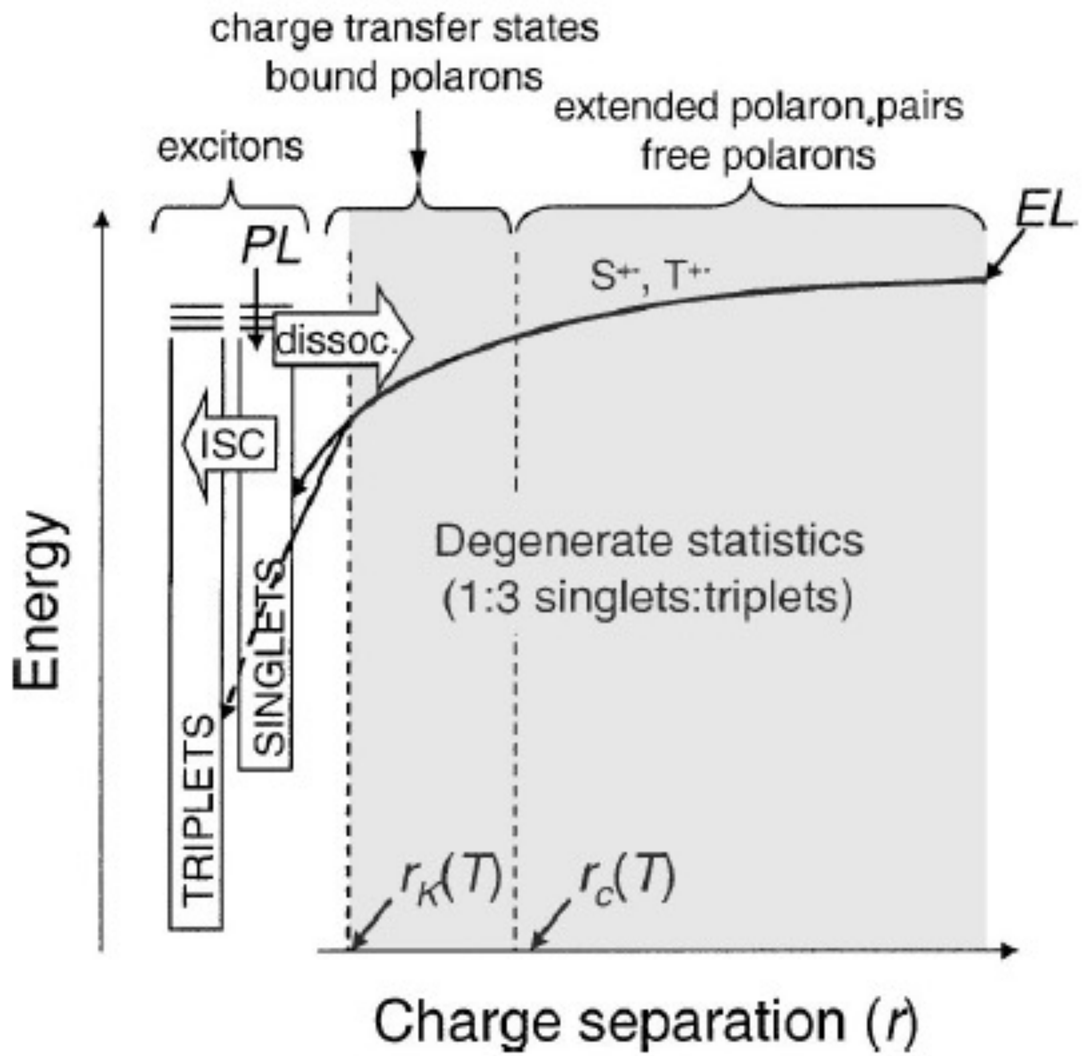
- Measure in forward (viewing) direction only
- Mask waveguided and scattered light
- Place OLED on detector for max. accuracy

Internal QE

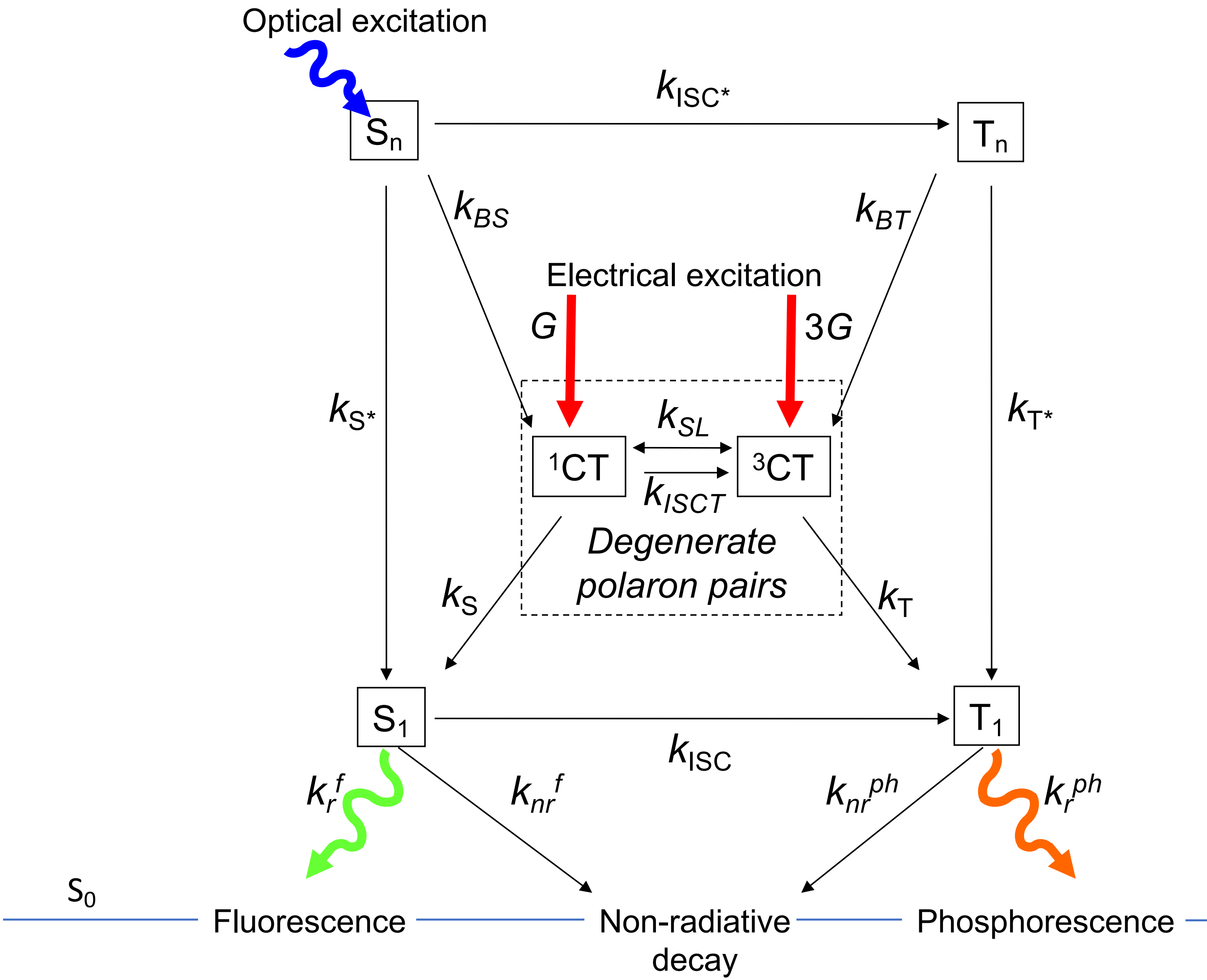


- Measure using integrating sphere
- Must correct for losses in structure

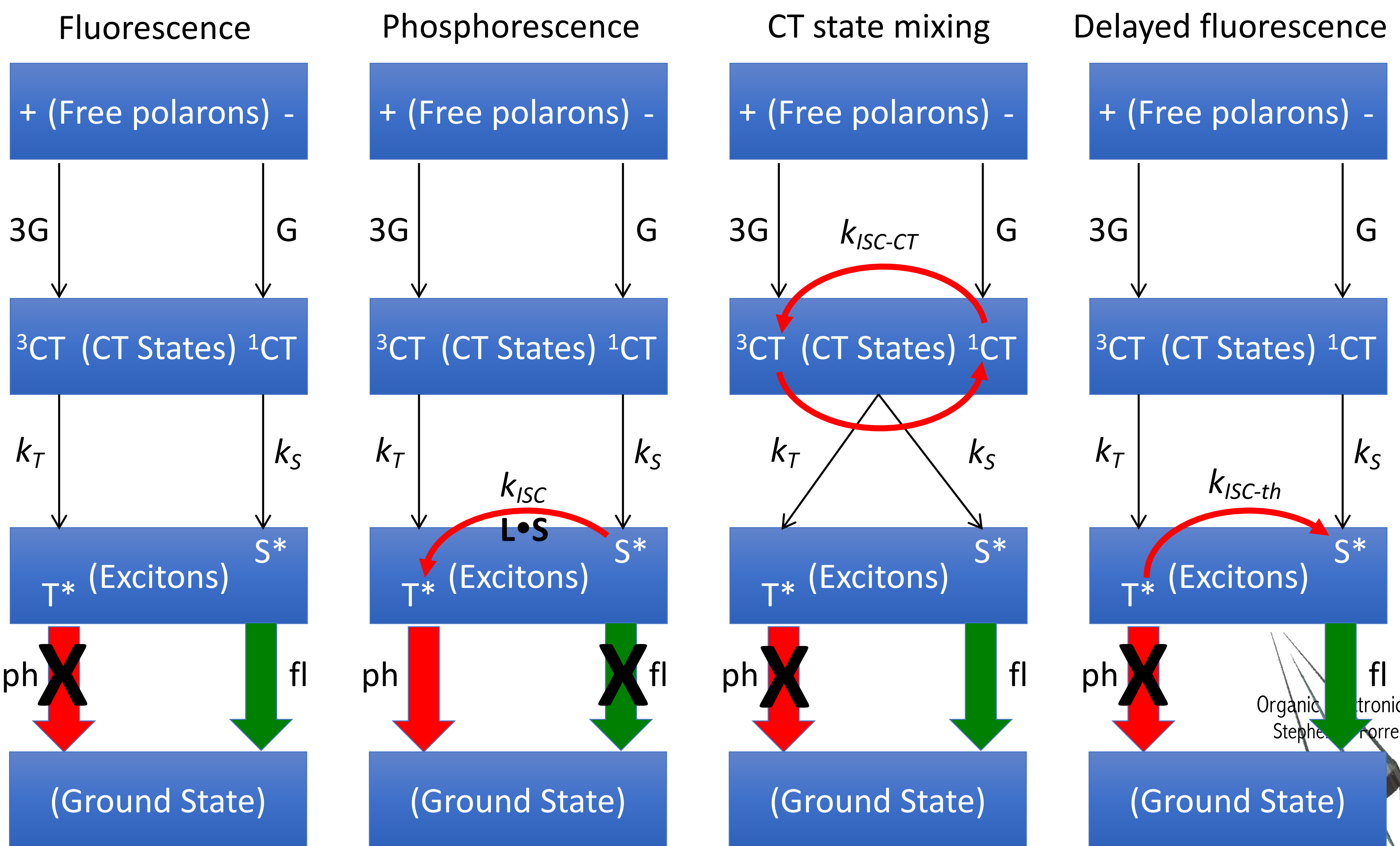
Formation dynamics of singlets and triplets



Exciting Dopant Molecules in an OLED

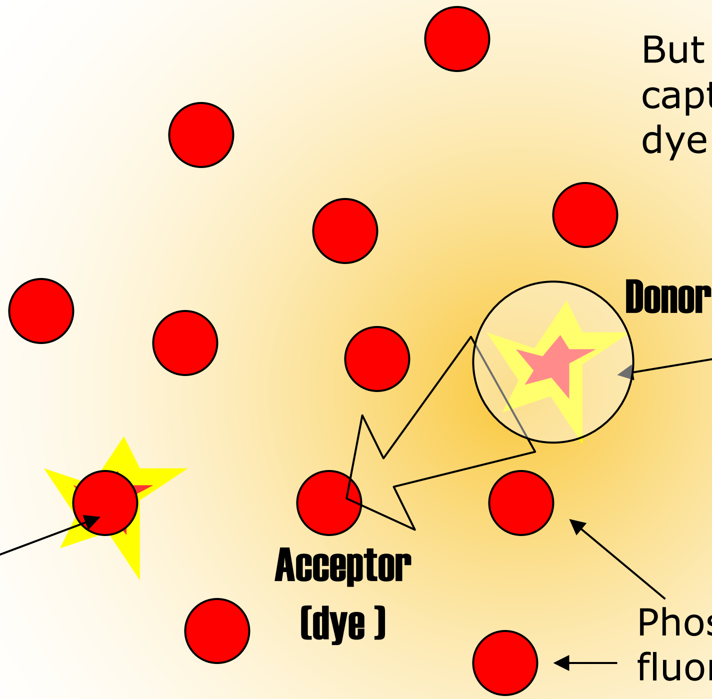


Singlet and triplet formation in OLEDs



Efficiency Improves if Dopant Dispersed in Host

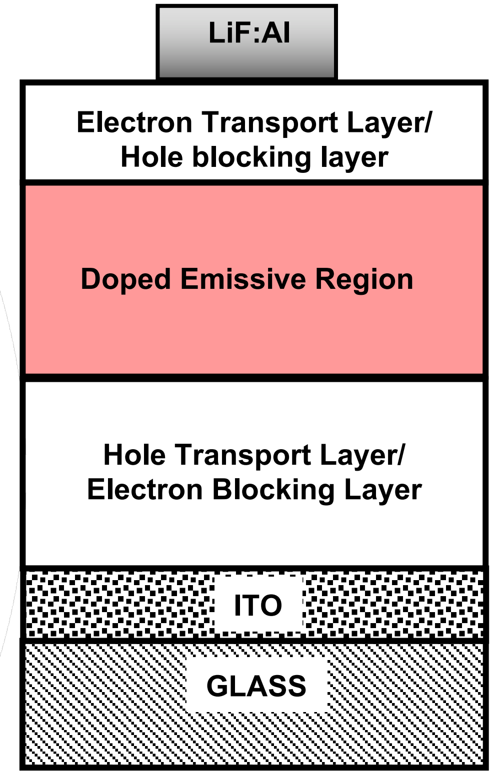
But excitons must be captured by dispersed dye



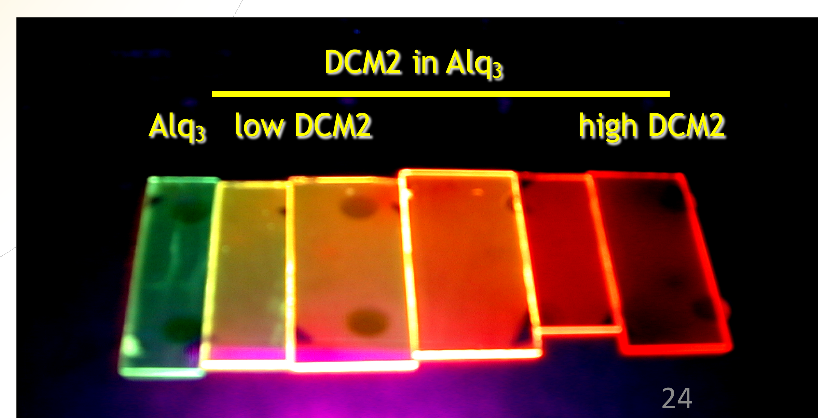
Förster or Dexter Energy transfer up to ~ 100Å

Charge trapping

Phosphorescent or fluorescent molecules



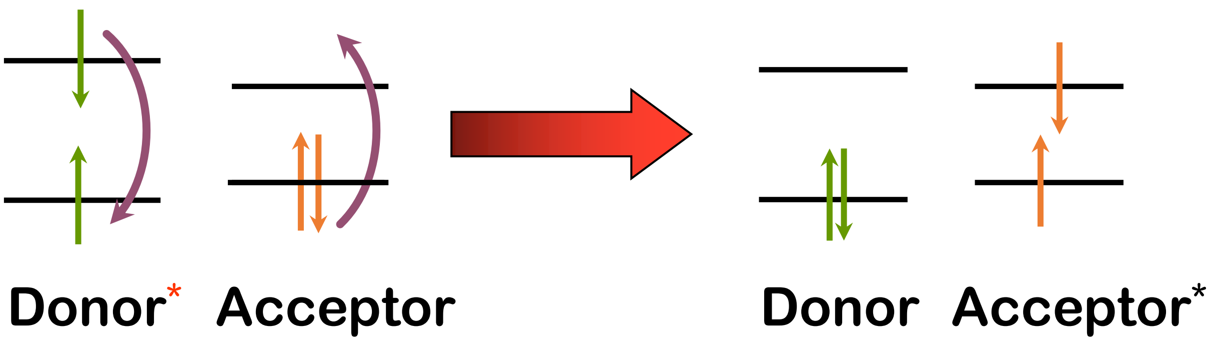
1. Charges trapped on dye molecules
2. Energy transferred from host
3. Effect used to increase color range and efficiency of OLEDs

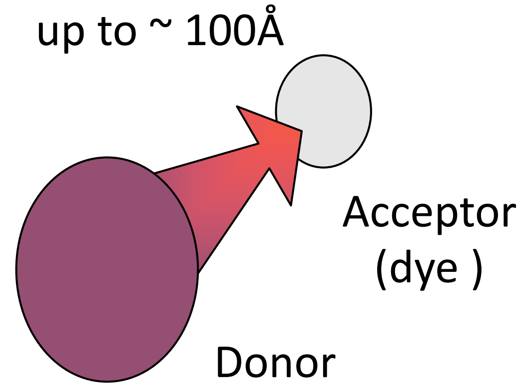


C. W. Tang, et al. 1989. *J. Appl. Phys.*, 65, 3610.

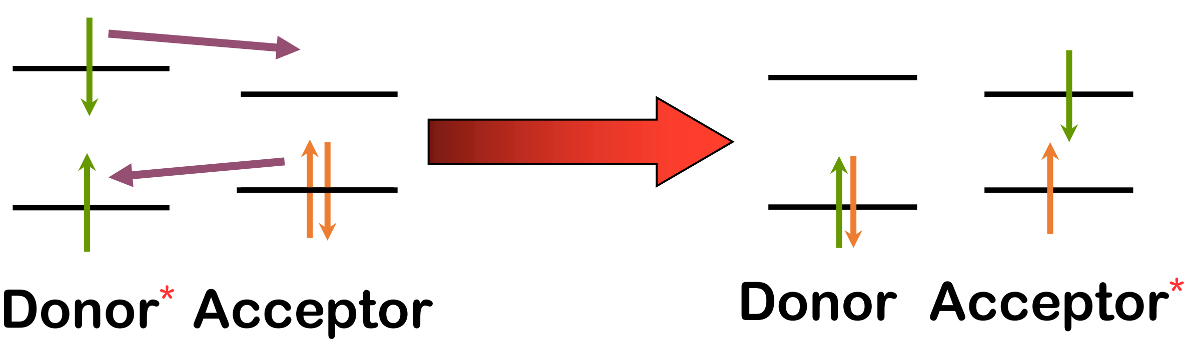
Energy Transfer from Host to Dopant: A Review

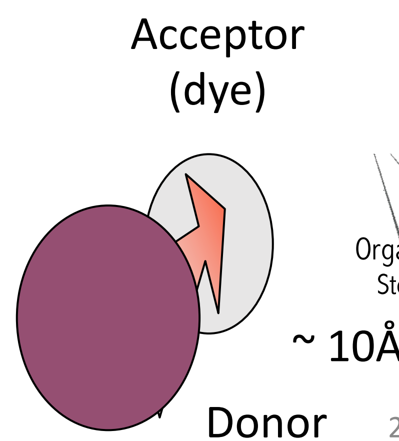
<u>Förster</u>:
- resonant dipole-dipole coupling
- donor and acceptor transitions must be allowed





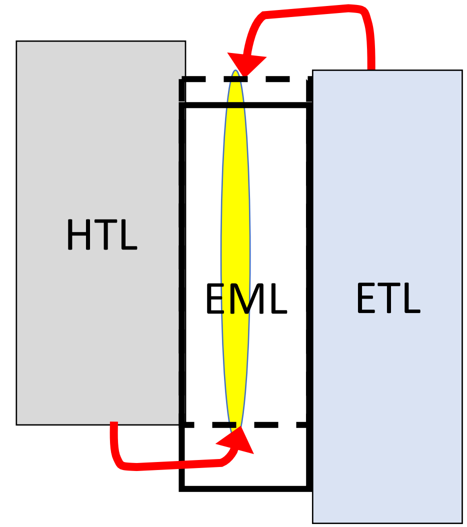
<u>Electron Exchange (Dexter)</u>:
- diffusion of excitons from donor to acceptor by simultaneous charge exchange: <u>short range</u>



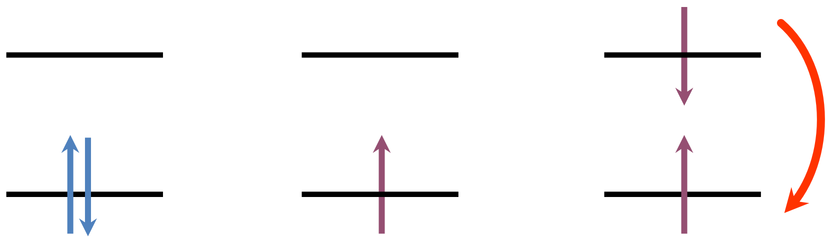


spin is conserved: e.g. singlet-singlet or triplet-triplet

Direct trapping on the lumophore

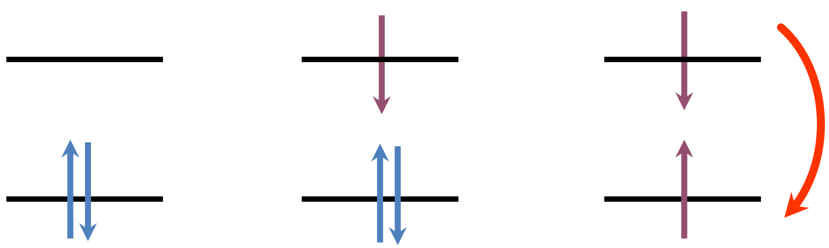


Cation formation by electrical injection

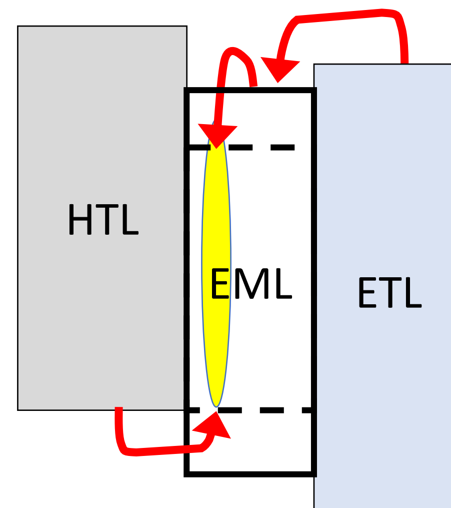


Acceptor^0 Acceptor$^+$ Acceptor* Acceptor^0

Or, anion formation



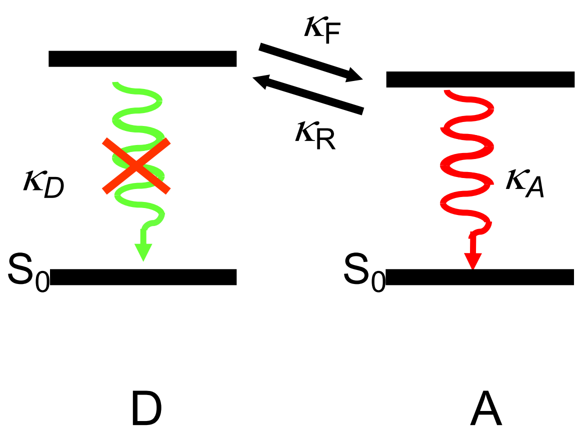
Acceptor^0 Acceptor$^-$ Acceptor* Acceptor^0



Processes can also involve trapping from the host (donor)
Prevalent mechanism for blue PHOLEDs

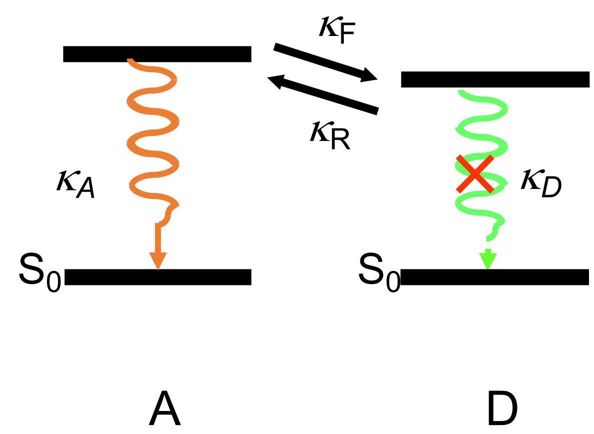
Energy transfer rates and directions

Forward (exothermic) transfer



- Donor energy > Acceptor energy
- k_F~ k_A > $k_{R,}$ k_D
- Radiative rate determined by k_A
- Route for red and green emission

Reverse (endothermic) transfer

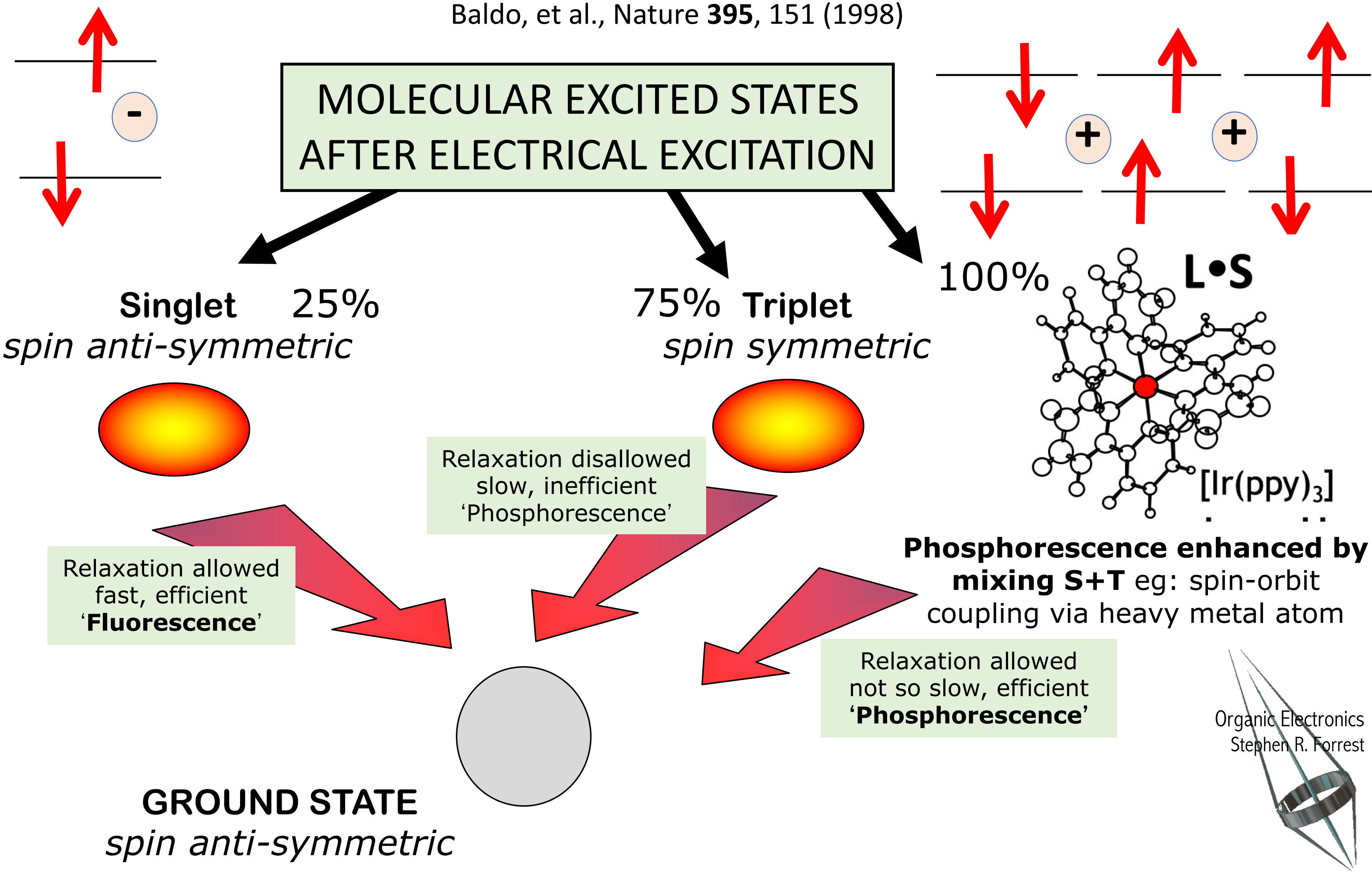


- Acceptor energy ~ Donor energy
- k_F~ k_R > k_A > k_D
- Radiative rate determined by $k_{A,}$ k_R
- Route for green and blue emission
- Similar to TADF, delayed fluorescence

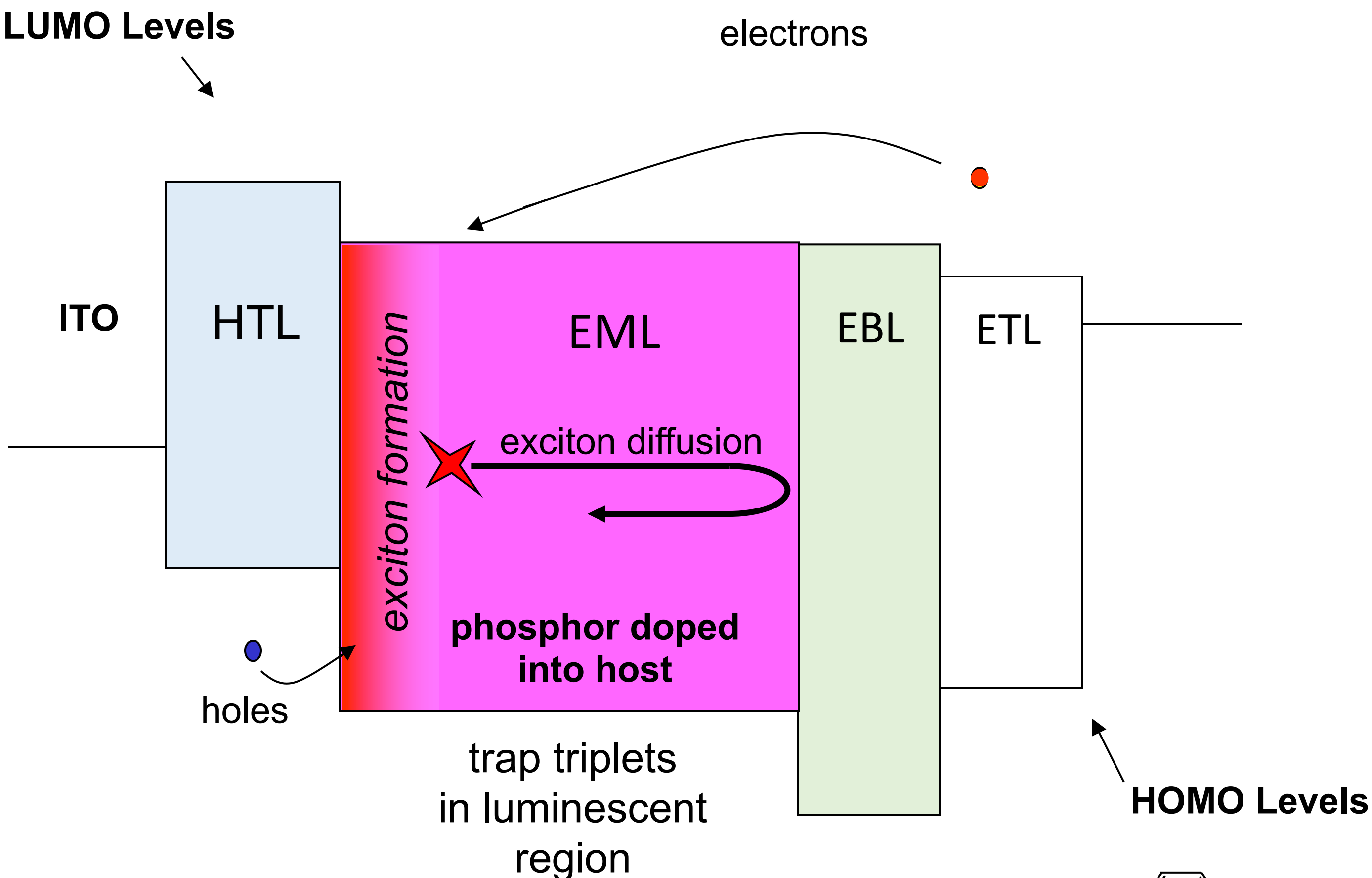
100% Internal Efficiency via Spin-Orbit Coupling

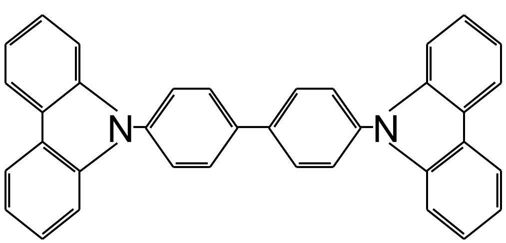
Heavy metal induced electrophosphorescence ~100% QE

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

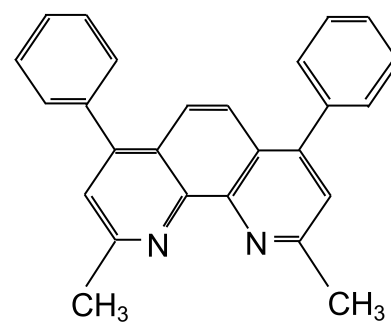


Electrophosphorescent (PHOLED) Device Structure





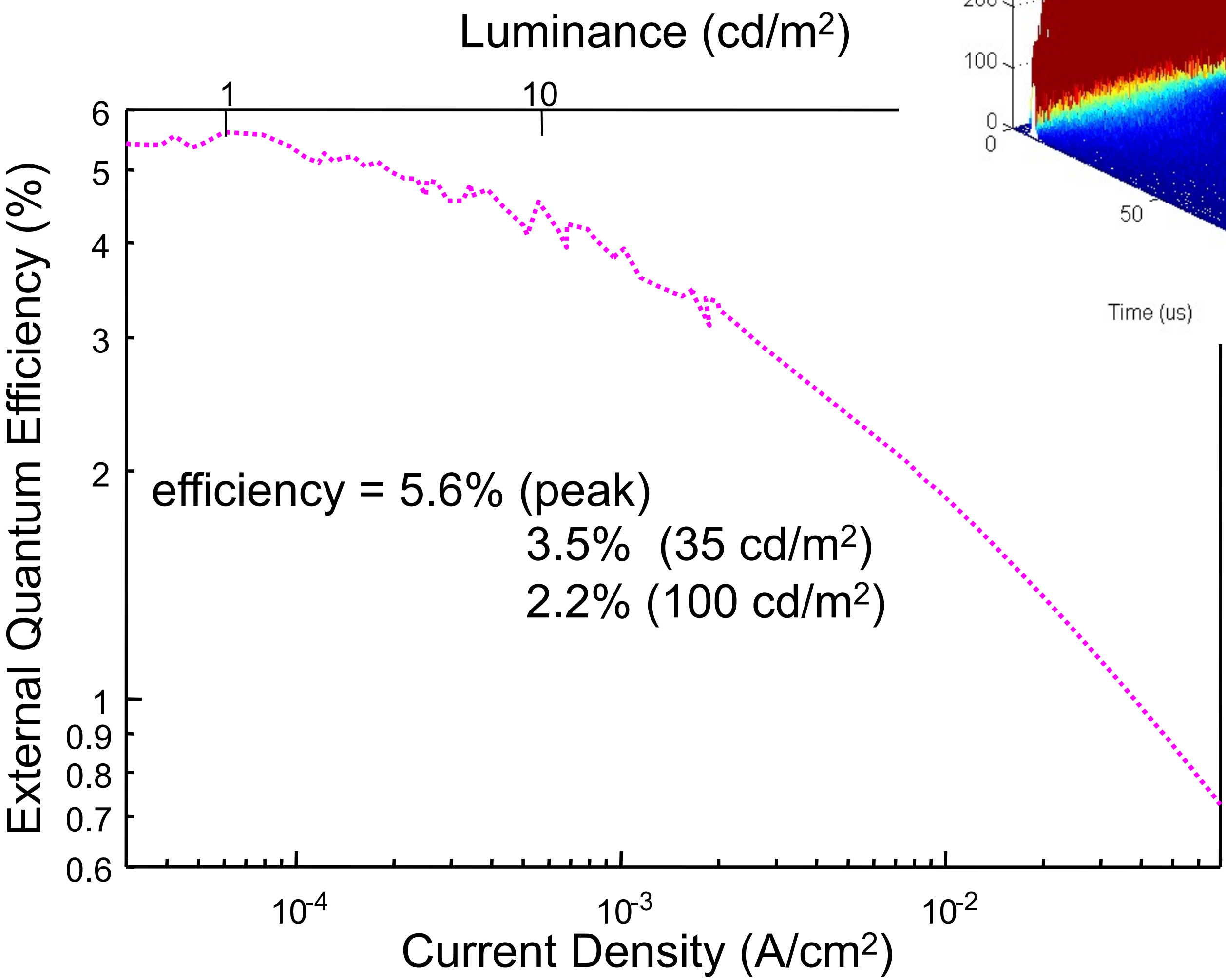
CBP
(common G,B host)

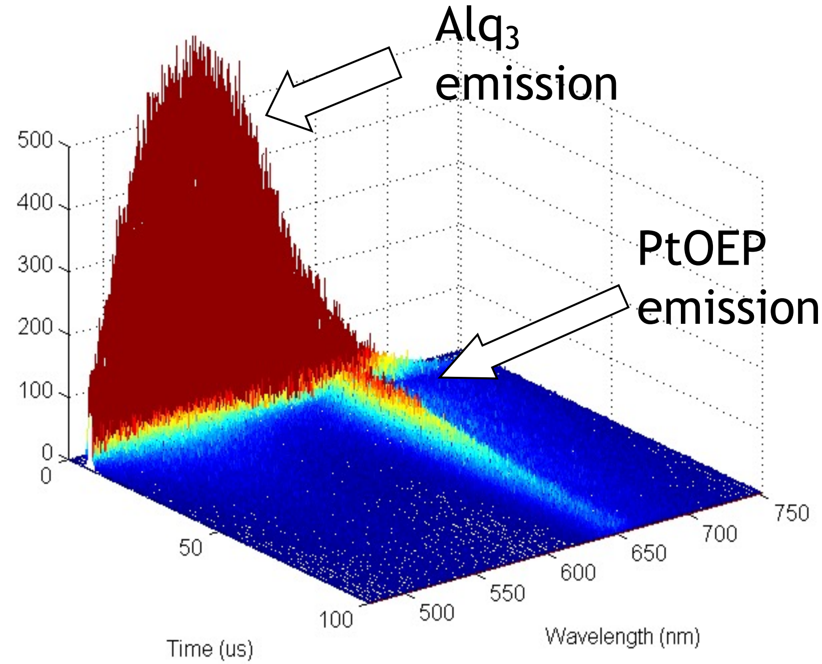


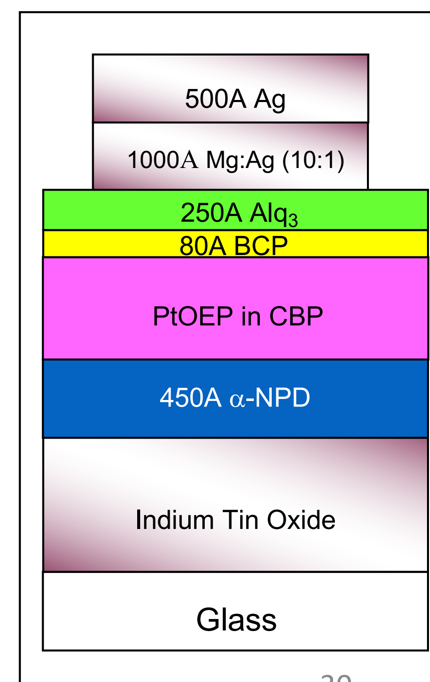
BCP
(common EBL)

6% PtOEP in CBP

- Exciton blocker increases eff. by 50%
- Roll off at modest luminance levels
- Transfer by trapping



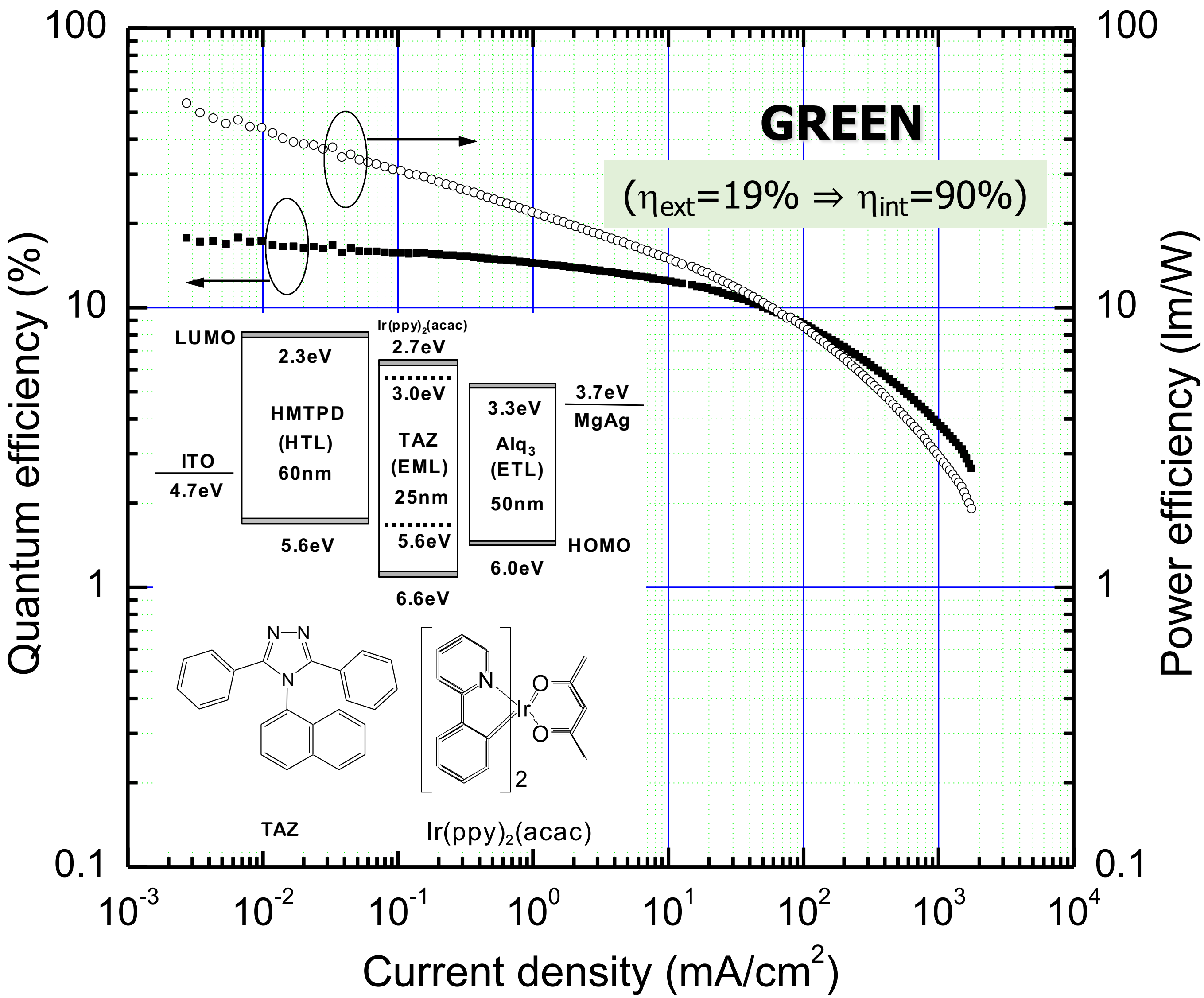




Baldo, et al., Nature **395**, 151 (1998)

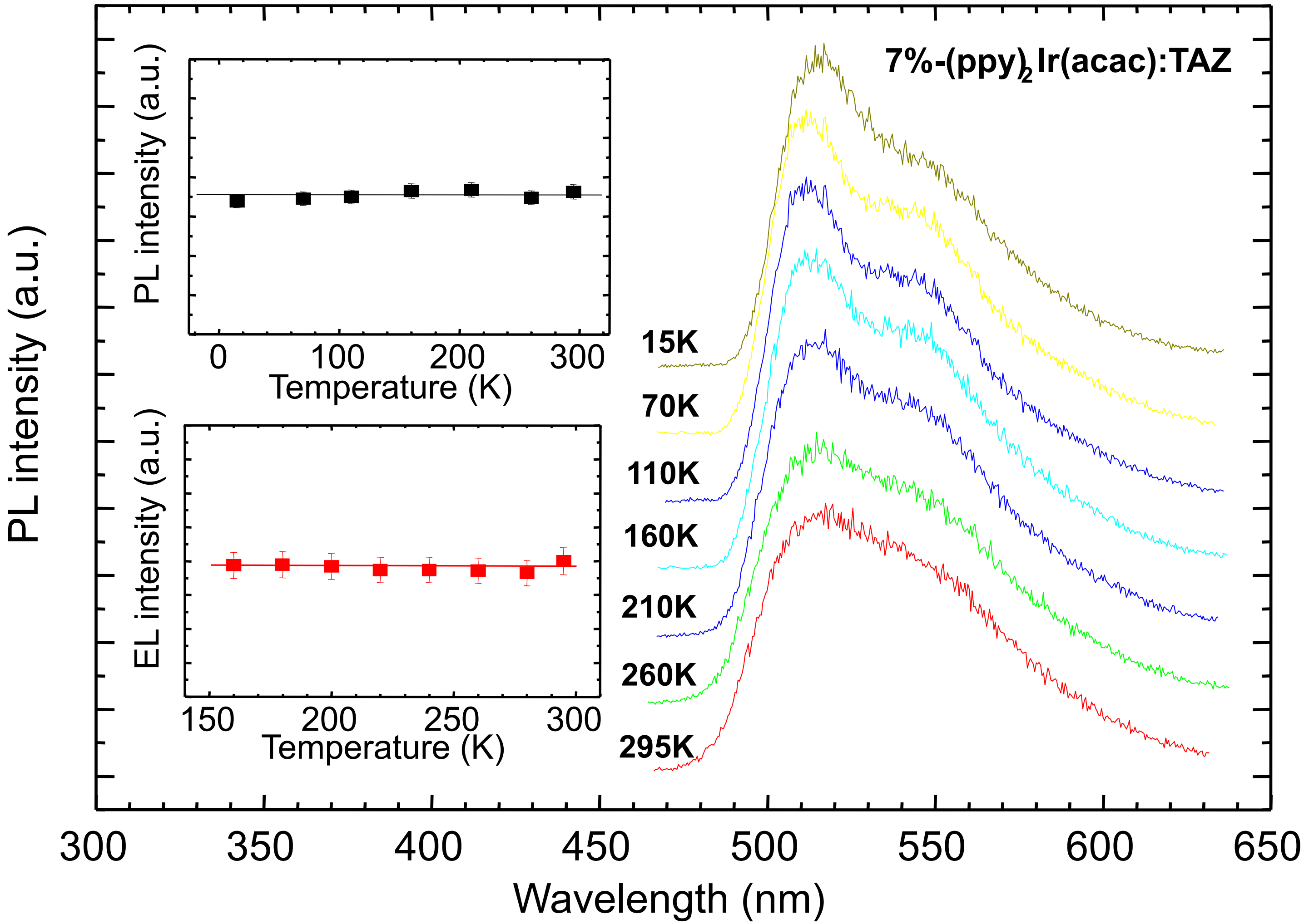
100% Efficient PHOLEDs

$Ir(ppy)_2(acac)$ doped ETL (Triazole)



Adachi, C., et al. 2001. *J. Appl. Phys.*, 90, 5048.

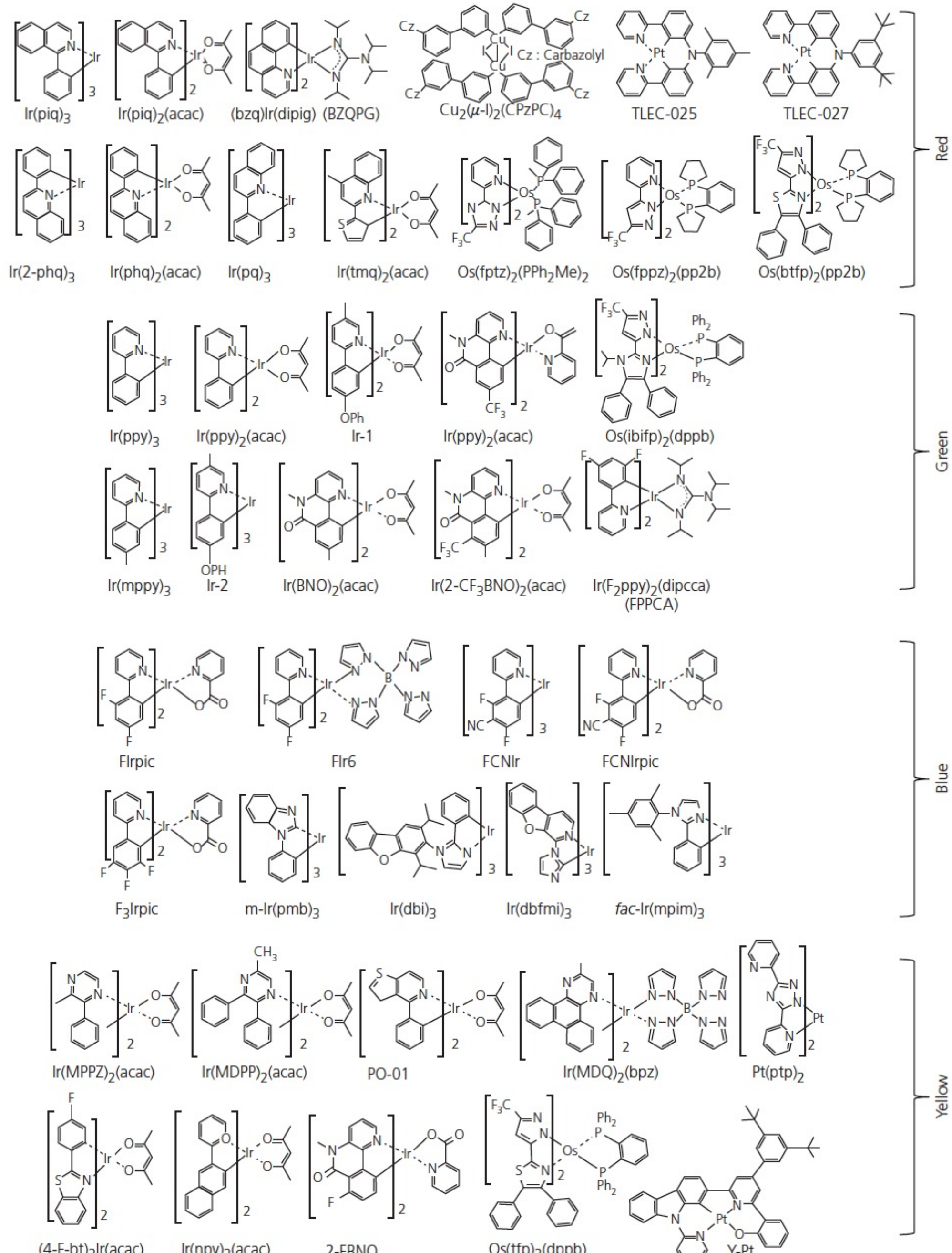
Temperature Independent PL and EL



Lack of dependence on T ⇒ No non-radiative recombination & η_{ext} ~ 20% ⇒ η_{int} ~ 100%

Adachi, C., et al. 2001. *J. Appl. Phys.,* 90**,** 5048.

Got Color? A few metalorganic complexes emitting in the visible



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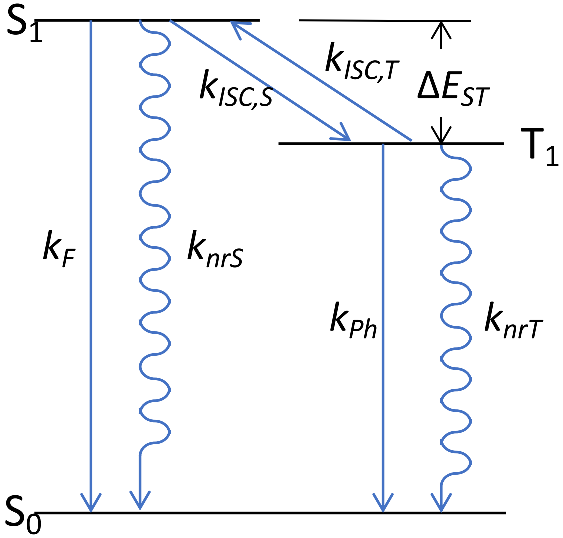
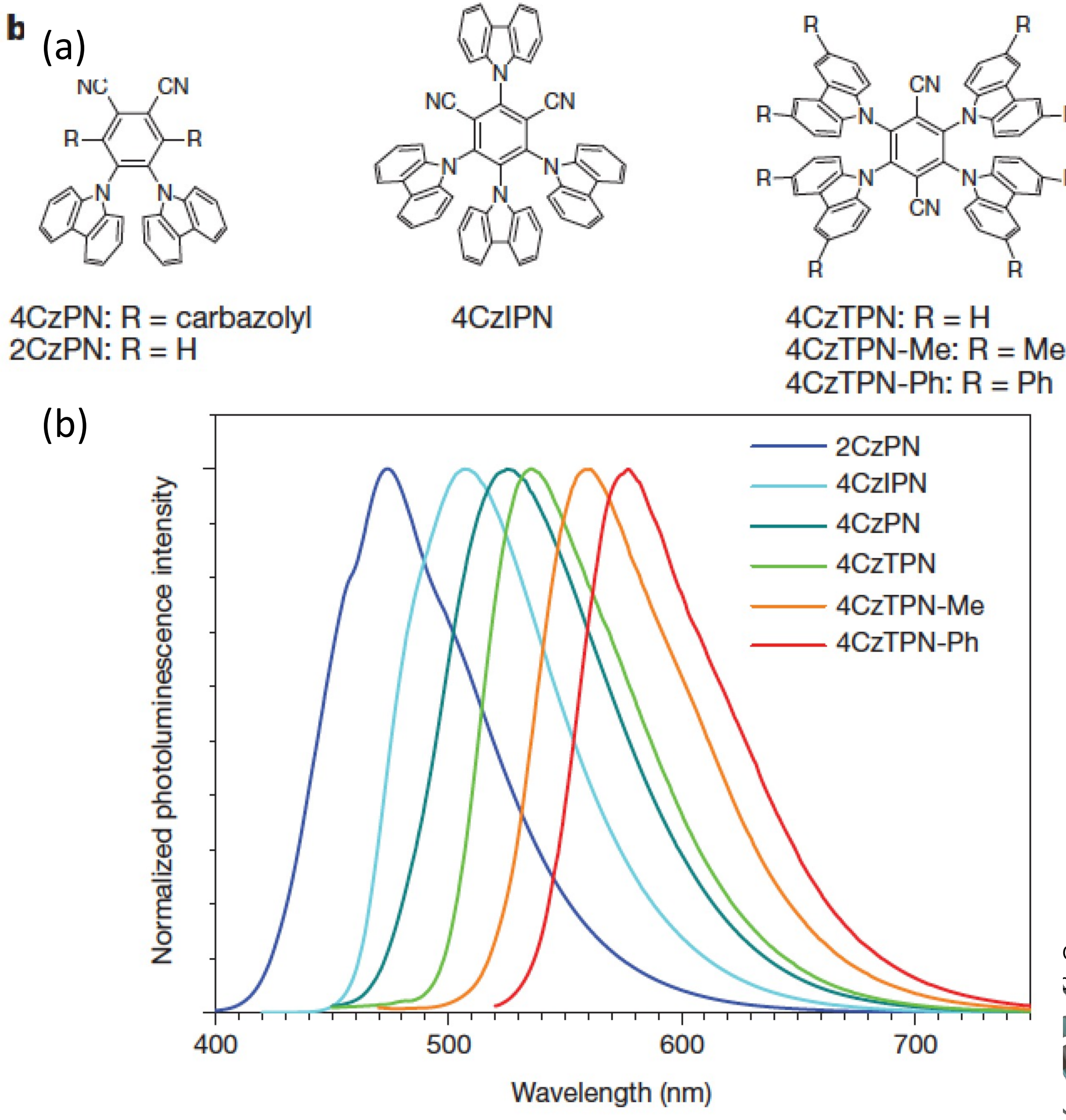
TADF: Another approach to high efficiency

$\eta_{int} \sim 100\%$



$k_F \sim k_{ISC,T} >> k_{Ph}$



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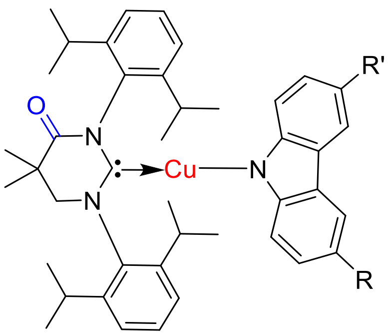
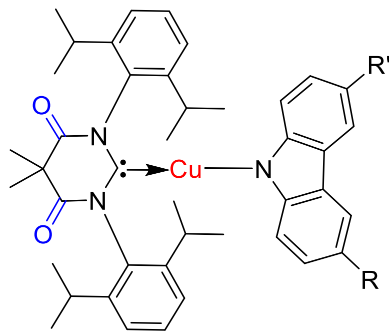
TADF Cu-complexes and the Energy Gap Law

(see Ch. 3)



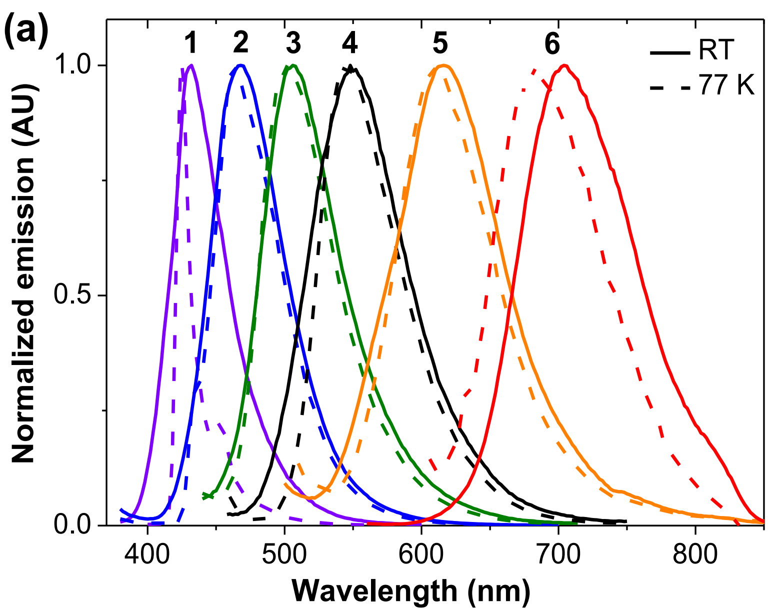
Carbene = MAC*

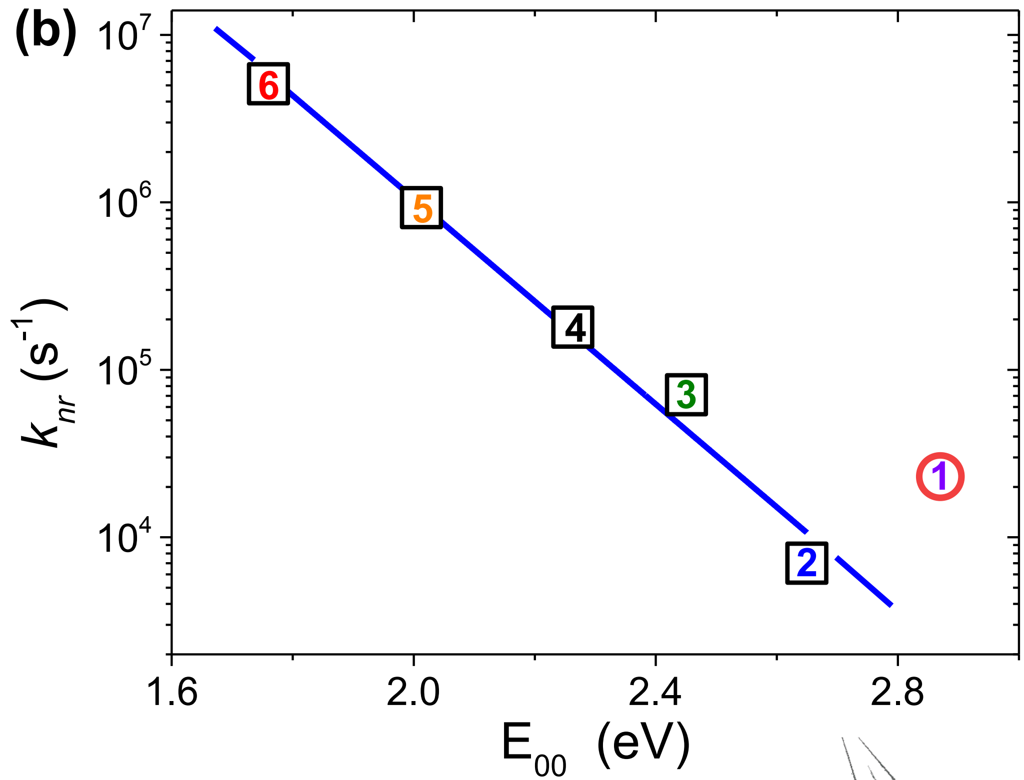
R, R' = CN (**1**)
R = CN, R' = H (**2**)
R, R' = H (**3**)



Carbene = DAC*

R, R' = CN (**4**)
R = CN, R' = H (**5**)
R, R' = H (**6**)

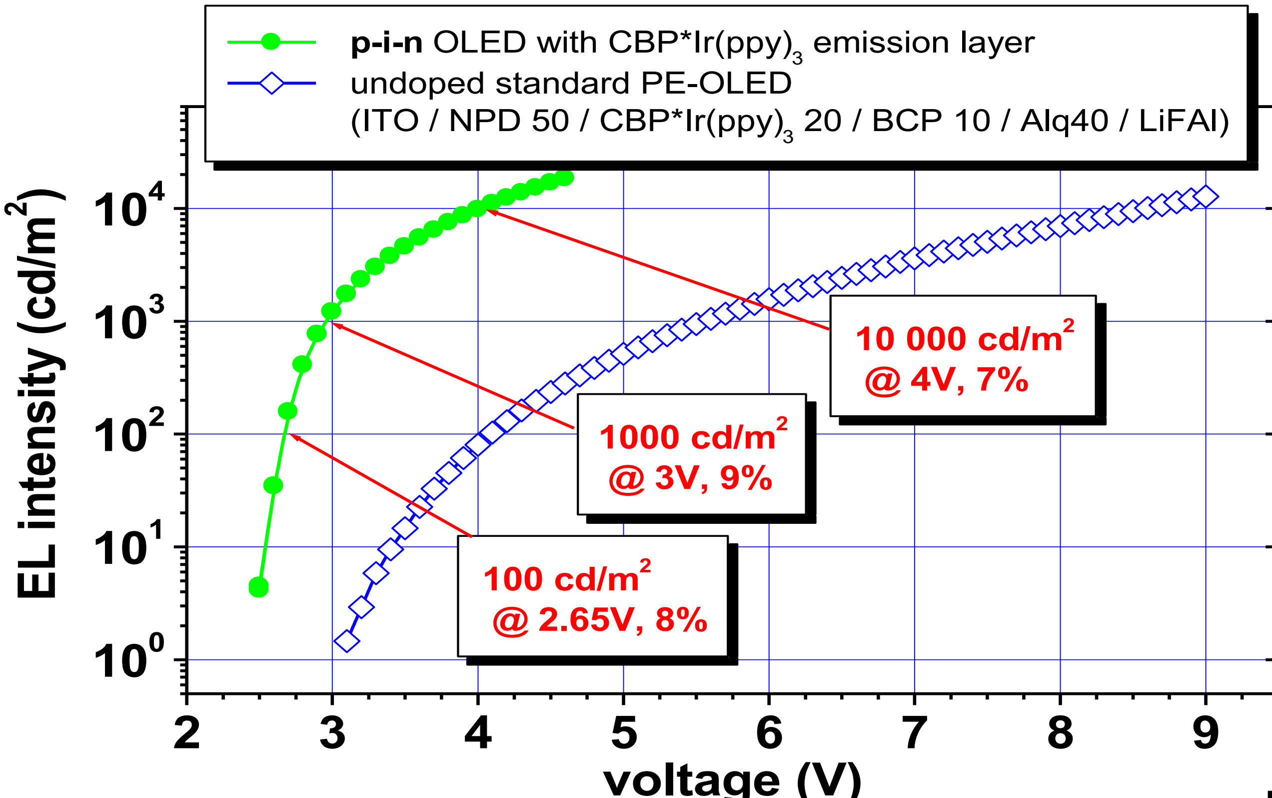


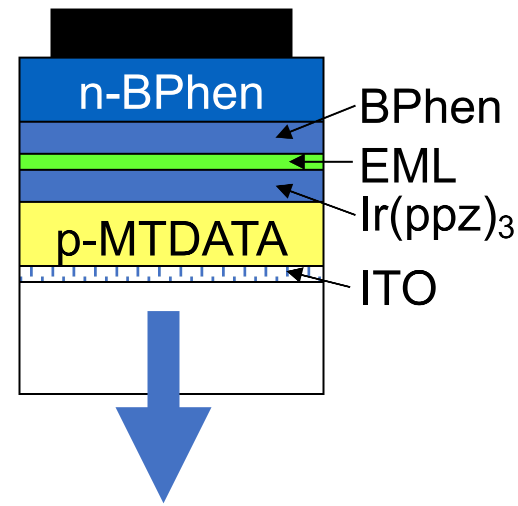


Au and Ag Complexes also show η_{int} ~ 100%

Low voltage high efficiency p-i-n PHOLEDs

Doping p and n transport regions leads to near thermodynamically limited voltage for emission



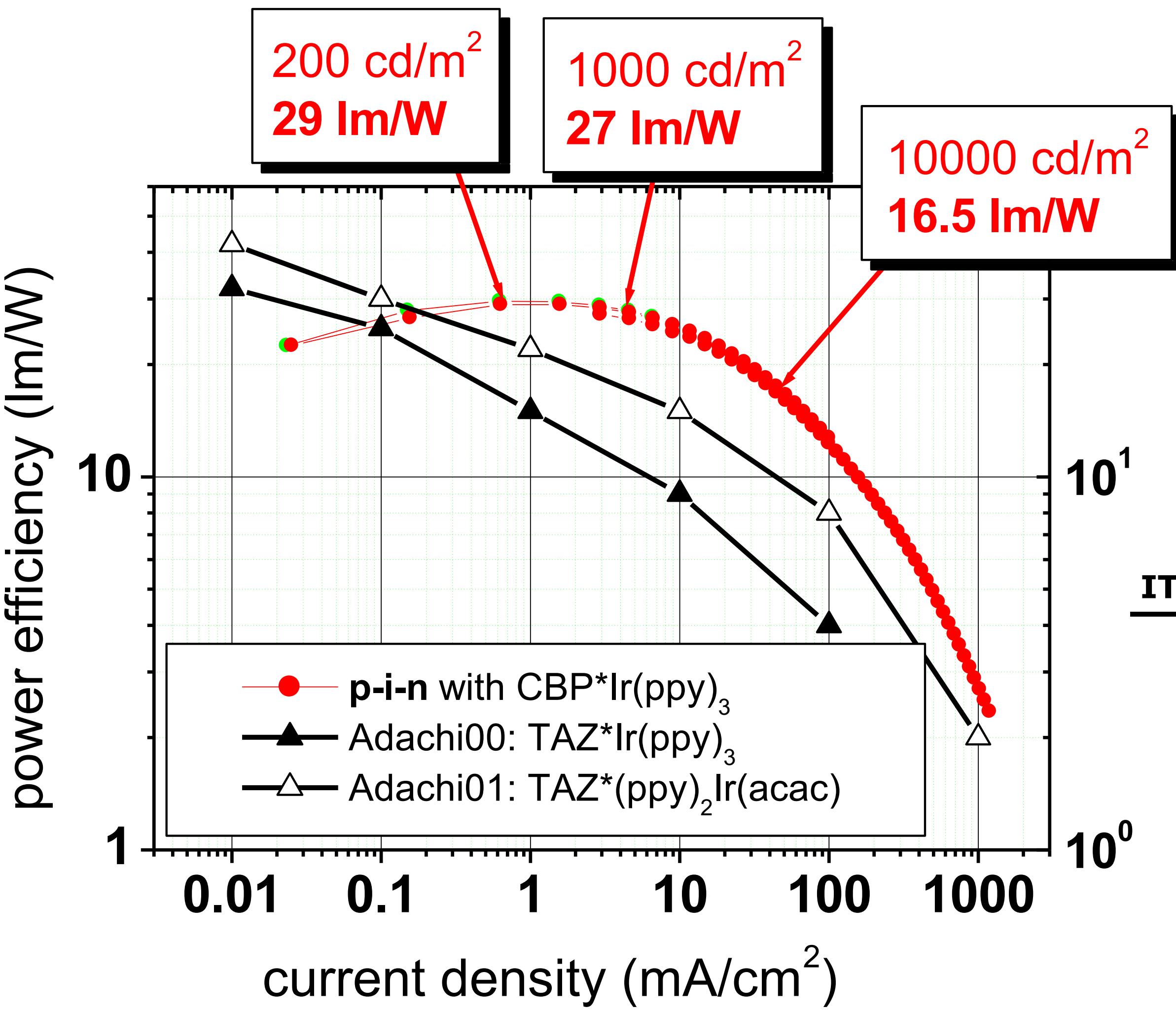


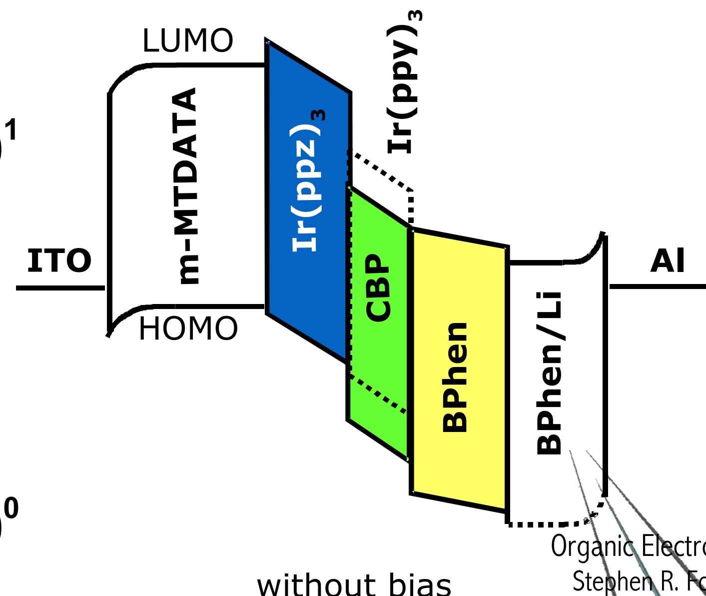
p-i-n PHOLED Structure

- p-doping by F_4-TCNQ
- n-doping by Li
- **thickness of the CBP/Ir(ppy)$_3$ emission layer: 5nm**

Pfeiffer, M., et al. 2003. *Org. Electron.,* 4**,** 89.

Low voltage high efficiency p-i-n PHOLEDs





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Pfeiffer, M., et al. 2003. *Org. Electron.*, 4, 89.