Week 2-2

Light Emitters 2

OLED Basics, cont’d

OLED Design

Color & Efficiency

Emission Processes

Materials

Ch. 6.1 – 6.3.3

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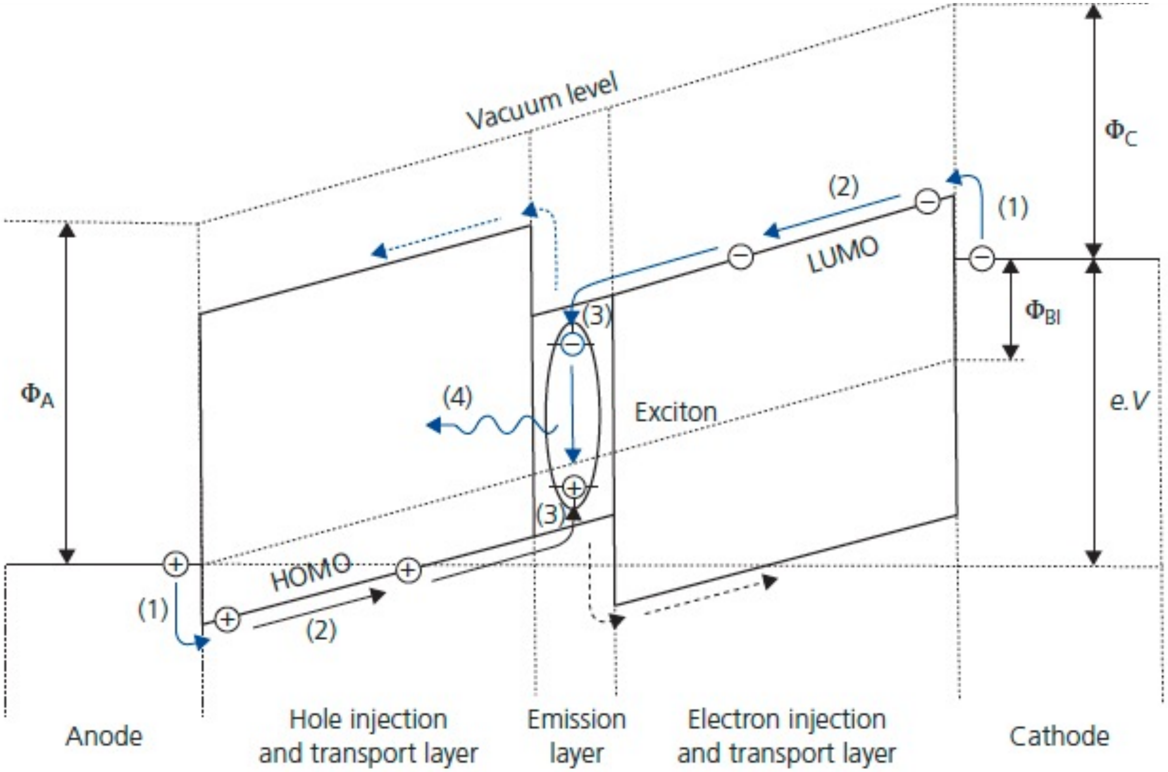
Electroluminescence Process in an OLED



1. Charge injection
2. Charge transport
3. Exciton formation
4. Exciton radiative recombination

OLED efficiency

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

γ: charge carrier balance factor
ratio of e/h

χ_r: luminescent exciton production

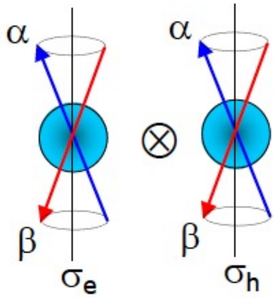
ϕ_p: quantum efficiency of fluorescence

η_{out}: light out-coupling efficiency

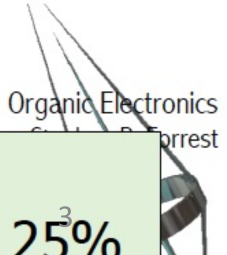
1. Fluorescence is restricted to singlet excitons $\chi_r \sim 25\%$

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

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

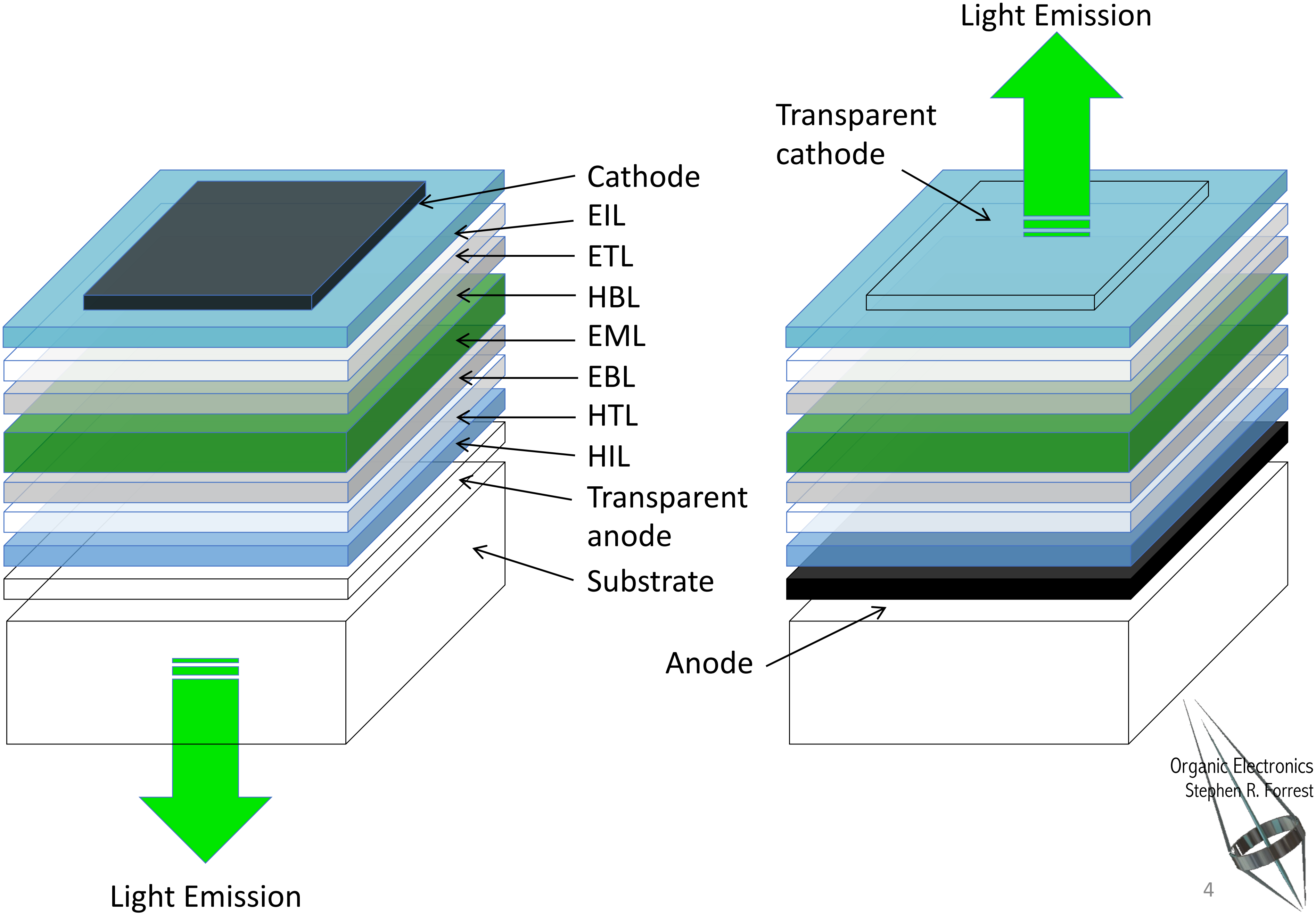


2. Only ~ 20% of photons are coupled out of OLED devices due to TIR



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

Today's OLEDs Are Not So Simple



Light Emission

Transparent cathode

Cathode

EIL

ETL

HBL

EML

EBL

HTL

HIL

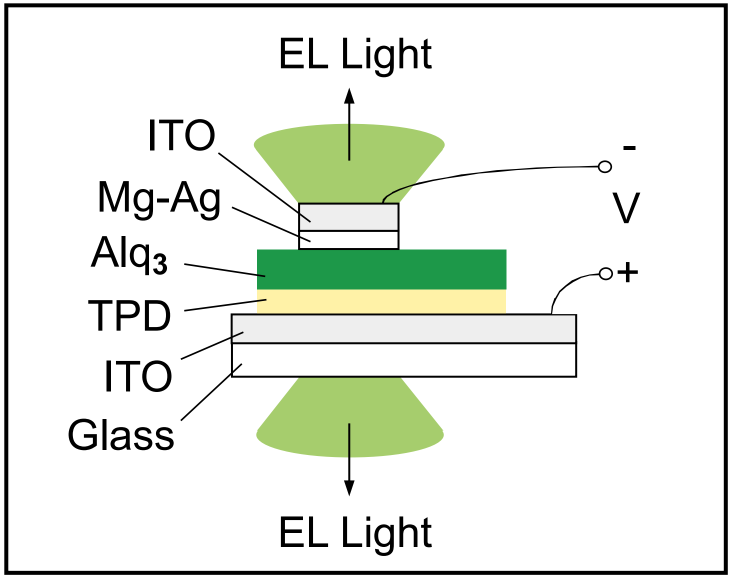
Transparent anode

Substrate

Anode

Light Emission

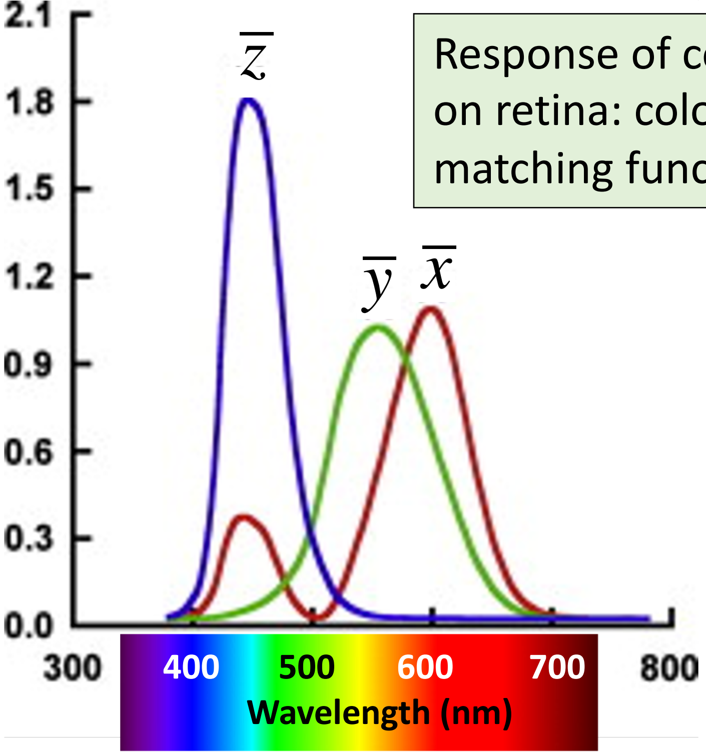
Transparent OLED (TOLED)



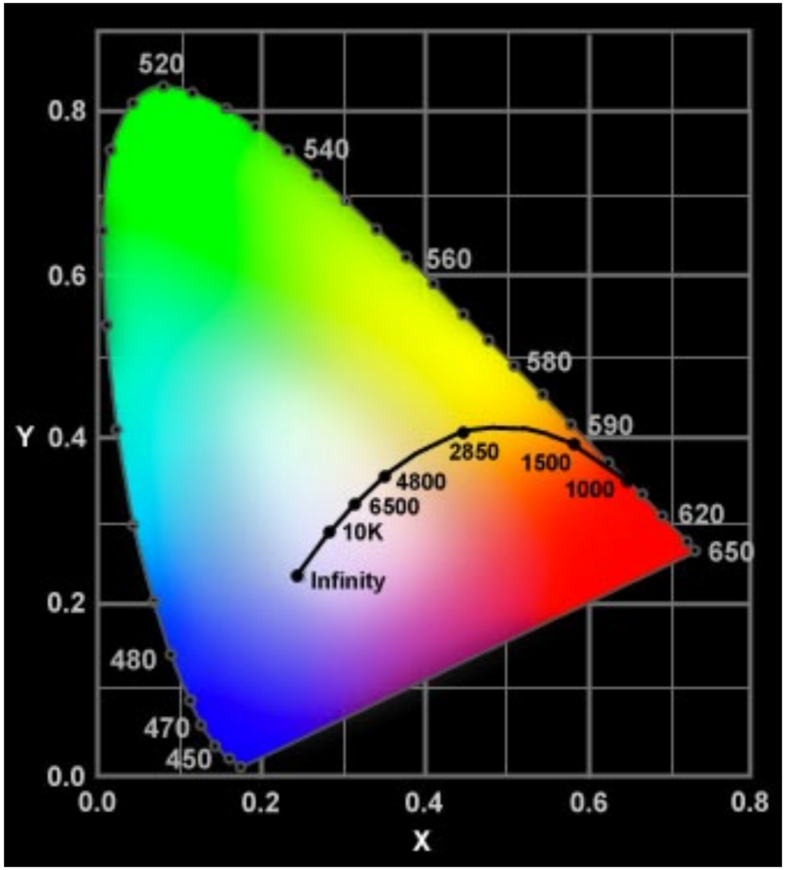
- Devices can be > 90% transparent
- Thin metal or electron injection layer is capped with ITO
- Transparent cathode can also be used to prepare top emitting structures
  - OLEDs on metal sheets
  - OLEDs on Si backplanes in AMOLED displays

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

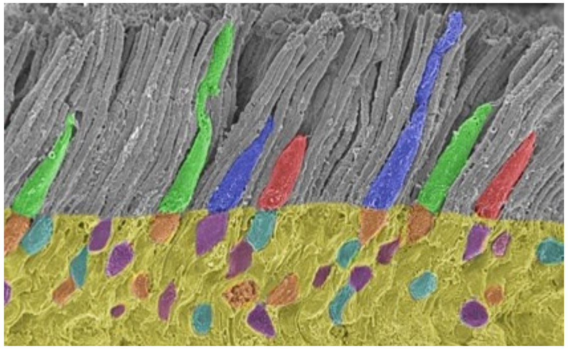
How We See Color: Tri-Stimulus Curves and Chromaticity



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

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

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

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Scotopic vs. Photopic Vision Response

How things appear at night

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

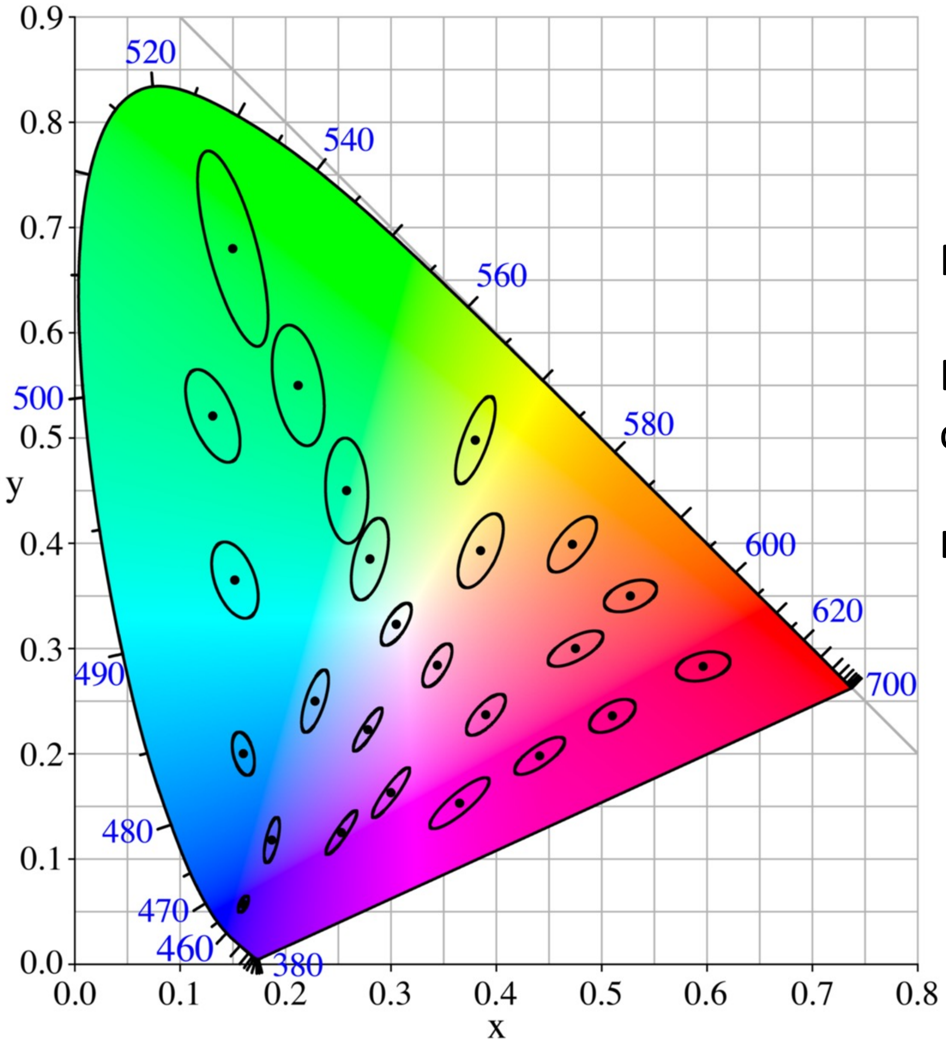
(simulation)

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

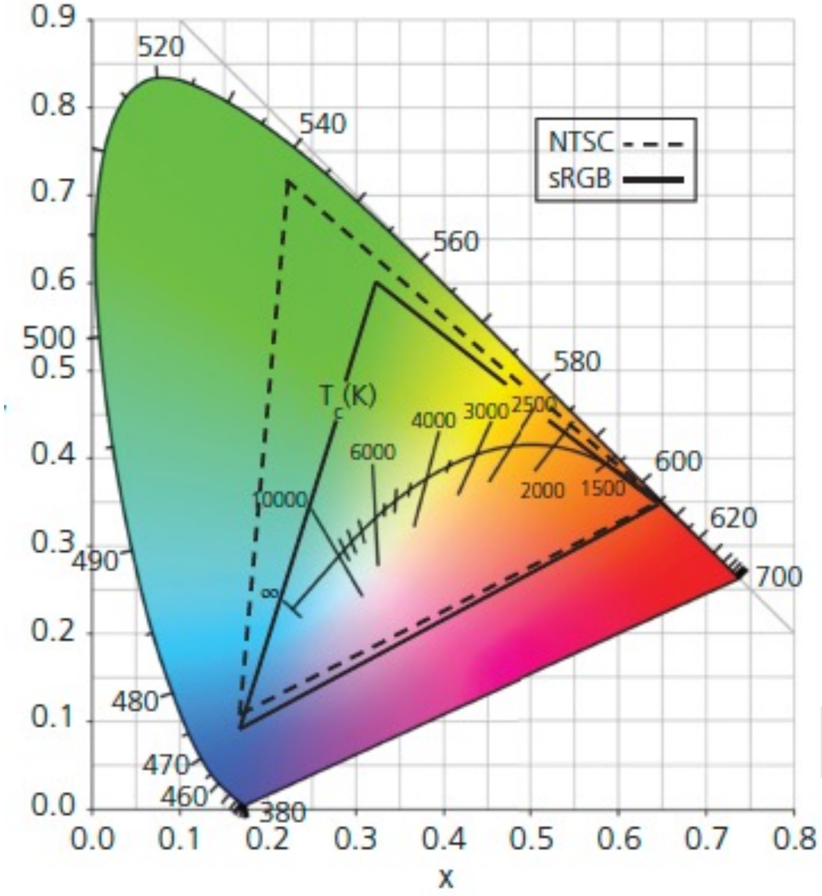


MacAdams Ellipses:

Define the amount of change in color that can be perceived

Each ellipse magnified 10X

Whites and the Color Gamut

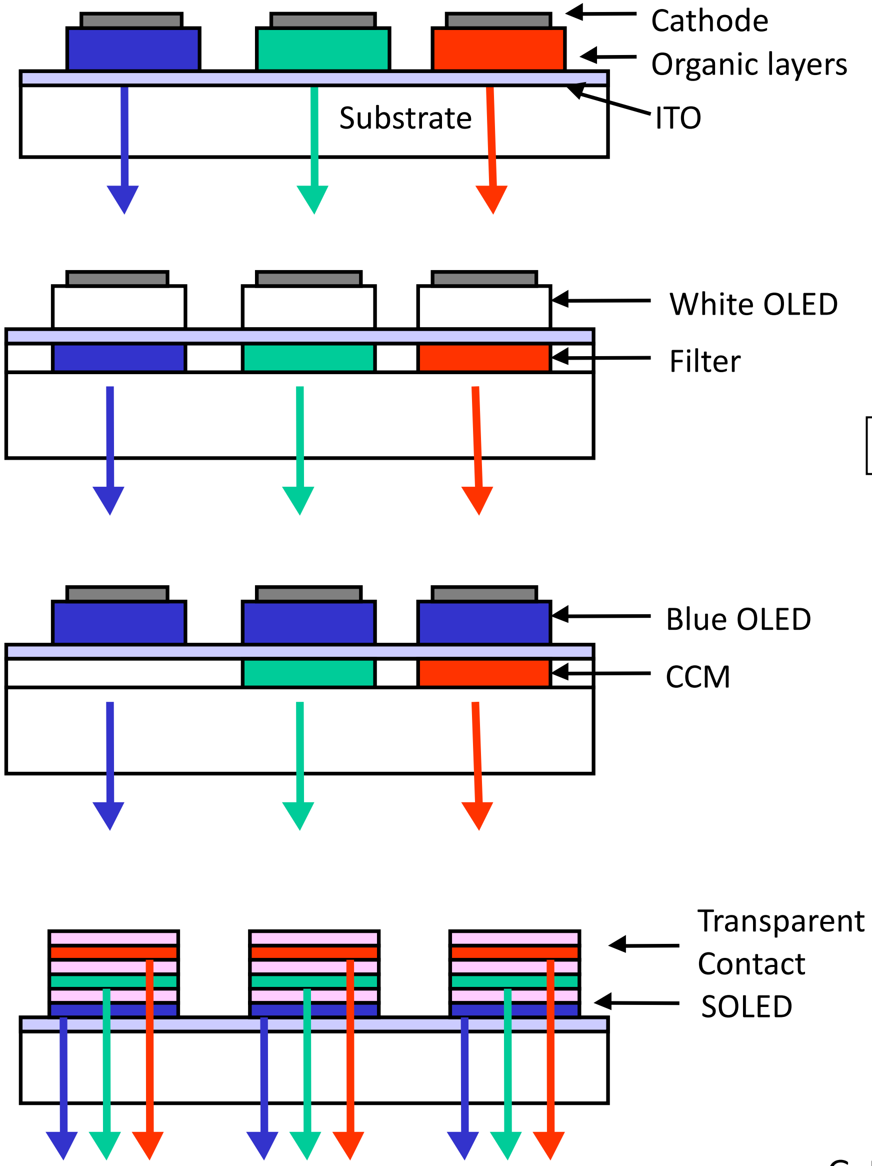


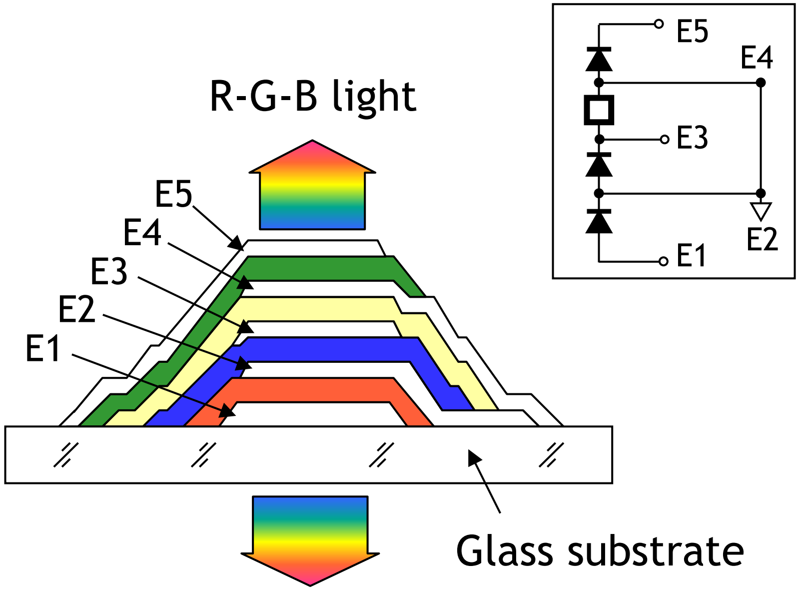
- Color gamuts are geometric shapes (usually triangles) that enclose the color space available to the display
- The vertices are located at the color coordinates of the pixels that comprise the display
- Two common color gamuts
  - NTSC=National Television Standards Committee
  - sRGB= super Red Green Blue
- The arc in the center of the color space is the white, or Planckian locus
  - Defines the color temperatures of ideal black bodies that follow Planck's law of radiation
  - The isoenergetic point is (0.33,0.33)

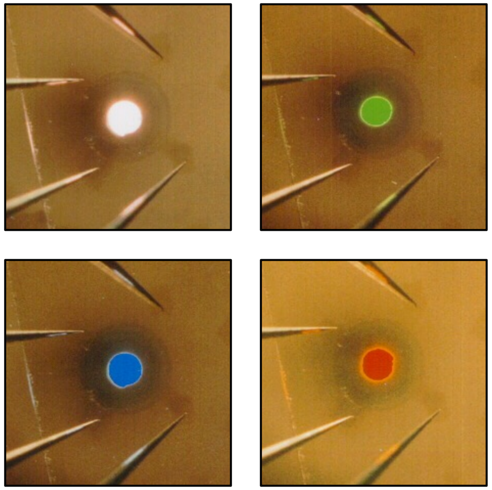
Planck's law for emission of a black body at temperature T

$$B(\lambda,T)=\frac{2hc^2}{\lambda^5}\frac{1}{\exp\left(hc/\lambda k_B T\right)-1}$$

Pixel Arrangements for OLED Displays

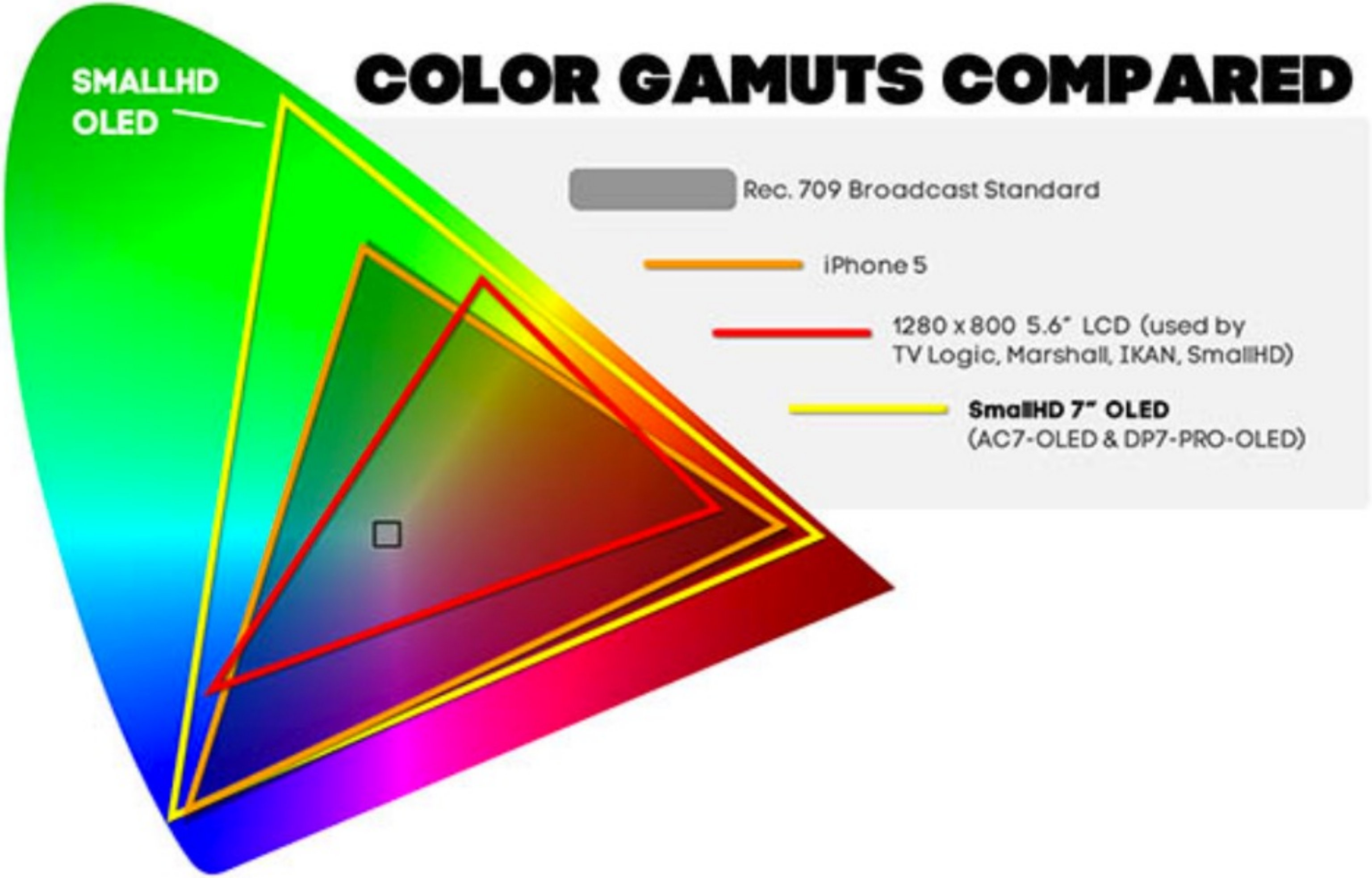






G. Parthasarathy, et al., *Adv. Mater.*, **11**, 907 (1999).

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	$\frac{d\Phi_e}{dSd\Omega\cos\theta}$	W/sr-m^2	Luminance	L	$\frac{d\Phi}{dSd\Omega\cos\theta}$	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

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

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

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

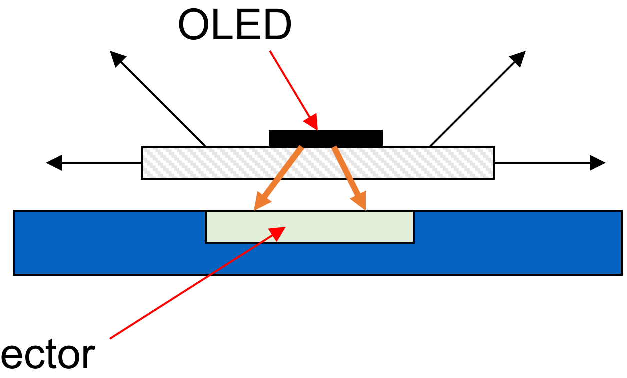
$$\text{Luminance power efficiency} = \frac{\text{Luminance}}{\text{Elect. power injected}} = \frac{L_{meas}}{I_{OLED}V_{OLED}} \quad \text{[lm/W]}$$

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

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

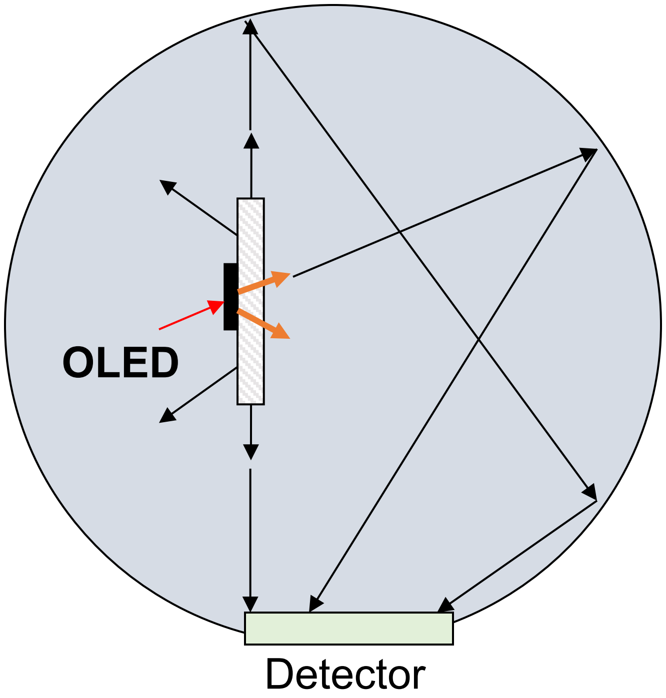
Measuring Quantum Efficiency

External QE



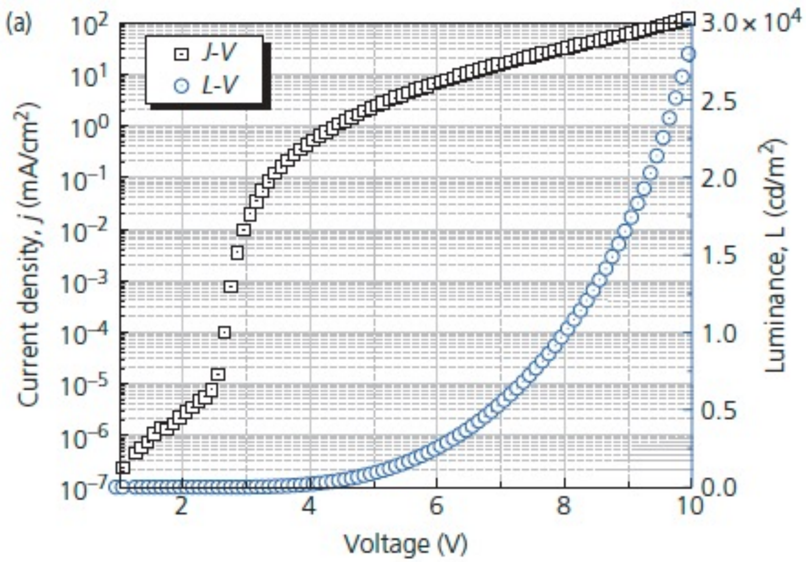
- Measure in forward (viewing) direction only
- Mask waveguided and scattered light
- Place OLED on detector for max. accuracy

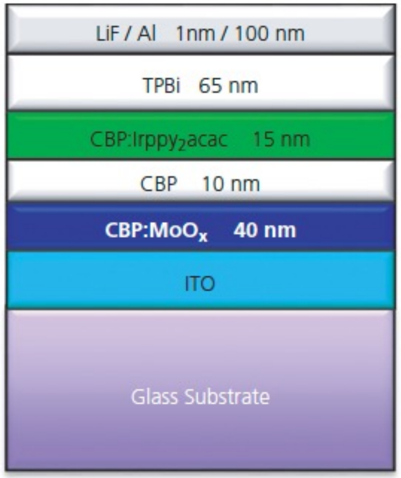
Internal QE



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

Example Data Set for a PHOLED




LiF / Al 1nm / 100 nm

TPBi 65 nm

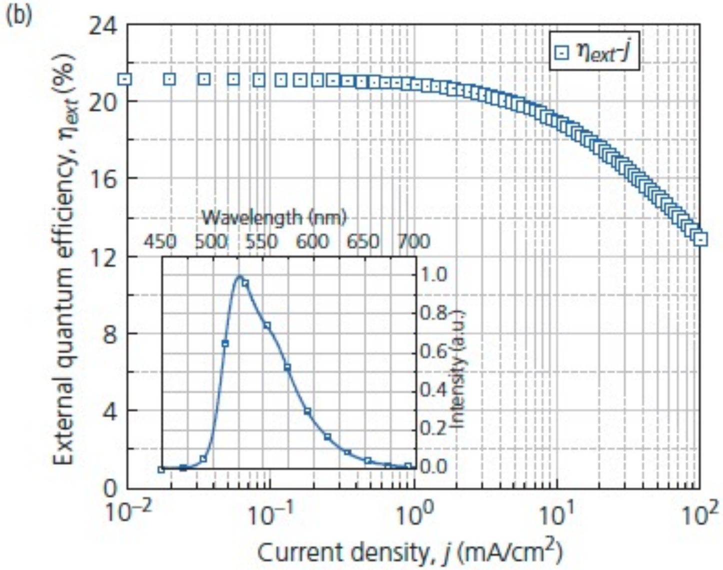
CBP:Irppy$_2$acac 15 nm

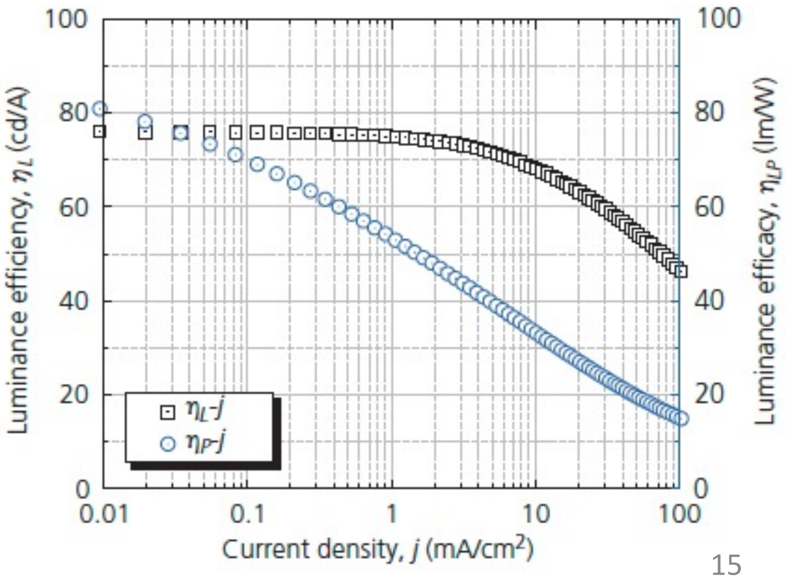
CBP 10 nm

CBP:MoO$_x$ 40 nm

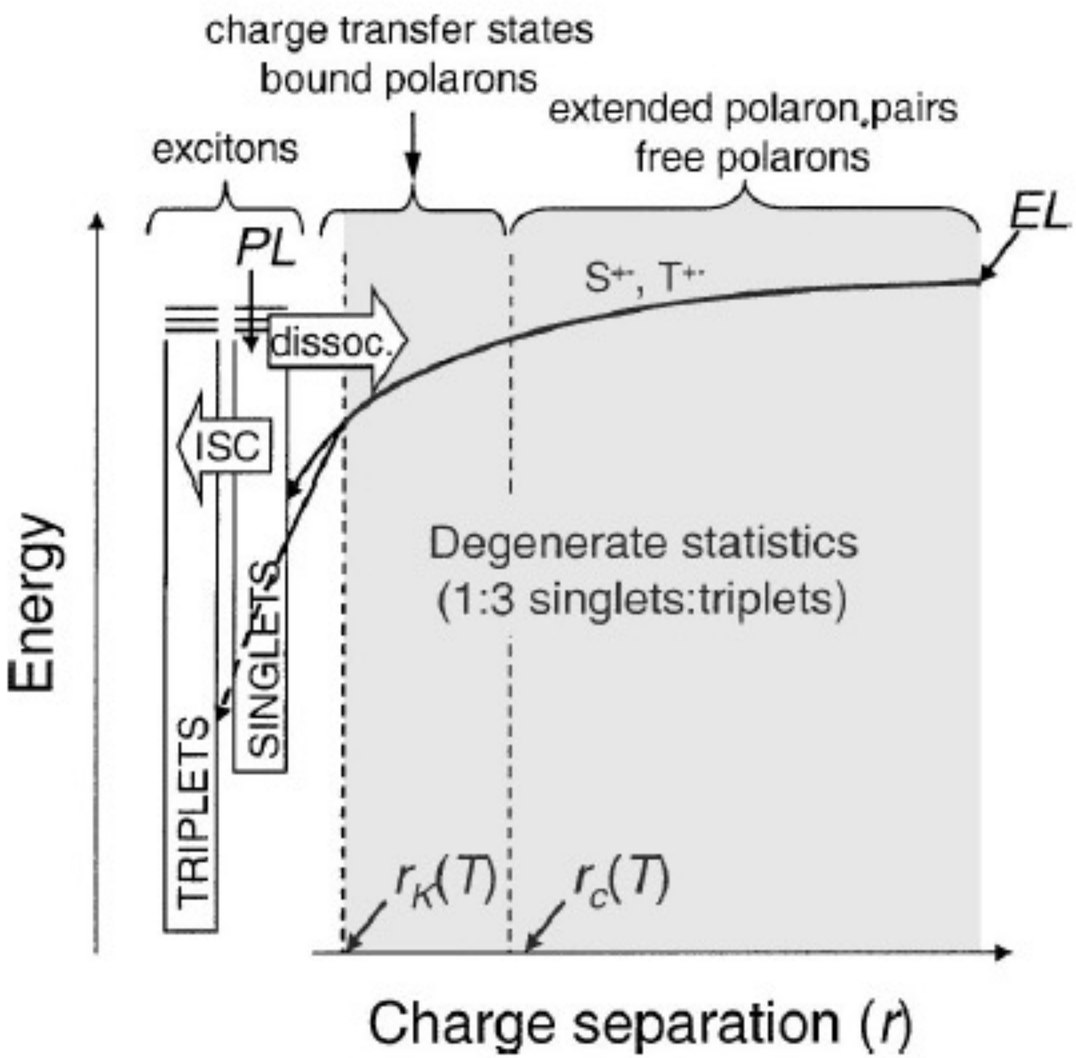
ITO

Glass Substrate





Formation dynamics of singlets and triplets



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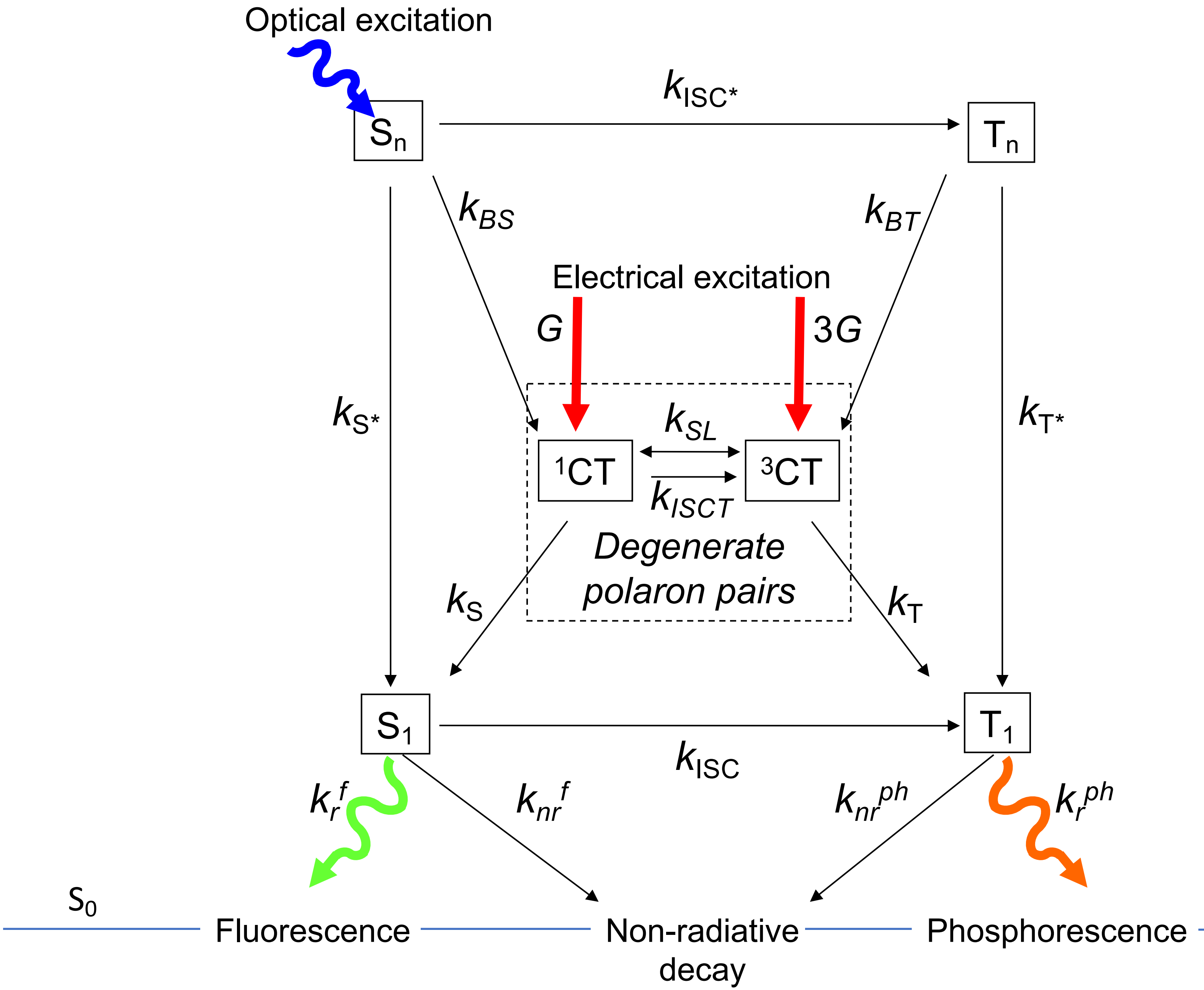
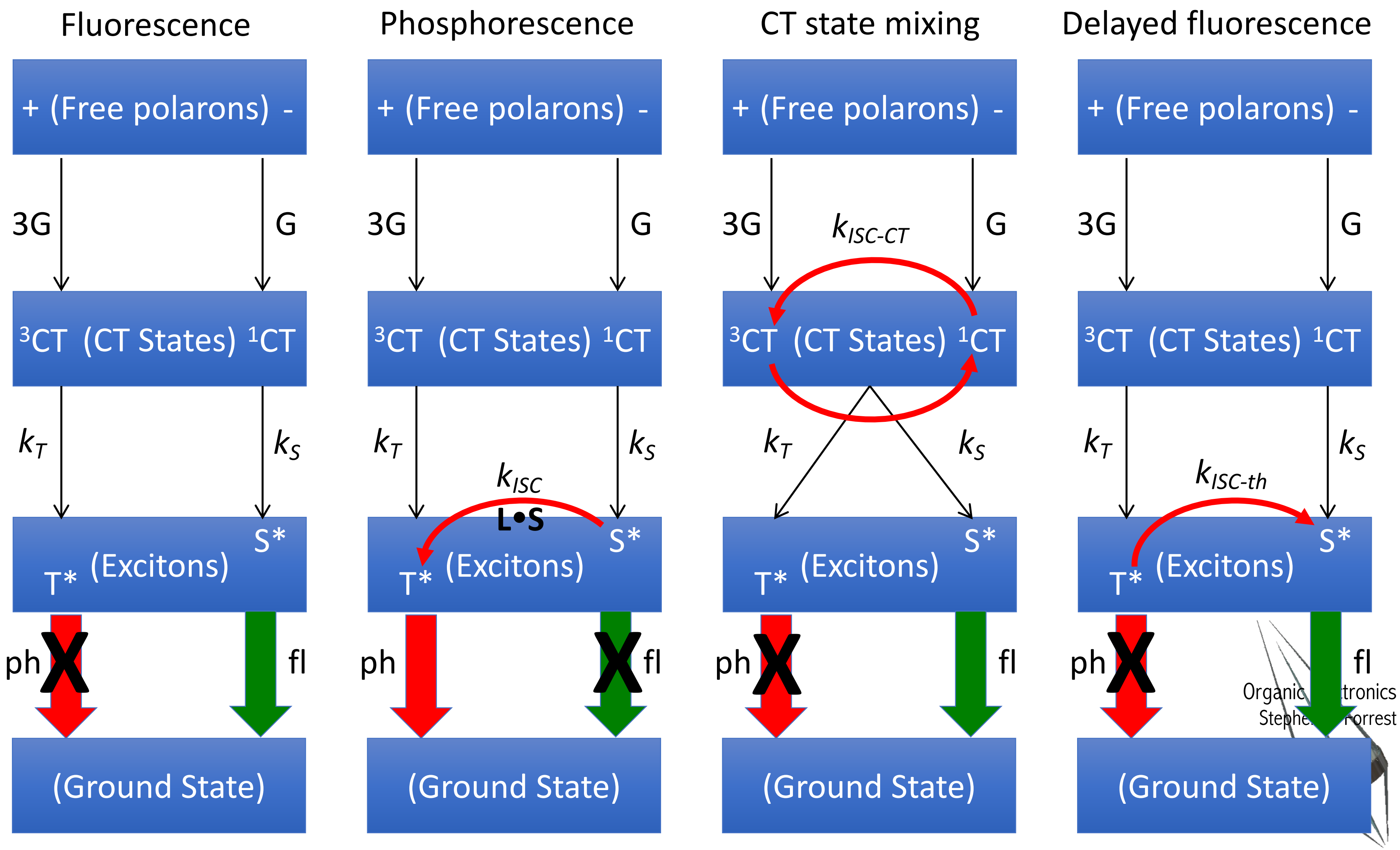
Exciting Dopant Molecules in an OLED



Singlet and triplet formation in OLEDs



Fluorescence

+ (Free polarons) -

3G G

^{3}CT (CT States) ^{1}CT

k_T k_S

T^* (Excitons) S^*

ph fl

(Ground State)

Phosphorescence

+ (Free polarons) -

3G G

^{3}CT (CT States) ^{1}CT

k_T k_S

k_{ISC}

L•S

T^* (Excitons) S^*

ph fl

(Ground State)

CT state mixing

+ (Free polarons) -

3G G

$k_{ISC\text{-}CT}$

^{3}CT (CT States) ^{1}CT

k_T k_S

T^* (Excitons) S^*

ph fl

(Ground State)

Delayed fluorescence

+ (Free polarons) -

3G G

^{3}CT (CT States) ^{1}CT

k_T k_S

$k_{ISC\text{-}th}$

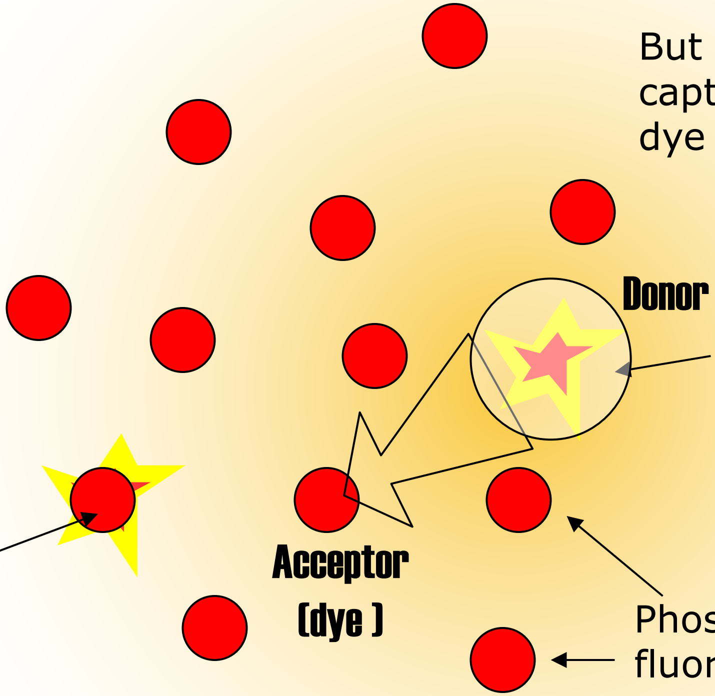
T^* (Excitons) S^*

ph fl

(Ground State)

Efficiency Improves if Dopant Dispersed in Host

C. W. Tang, S. A. Van Slyke, C. H. Chen, C. H. 1989. *J. Appl. Phys.*, 65, 3610.



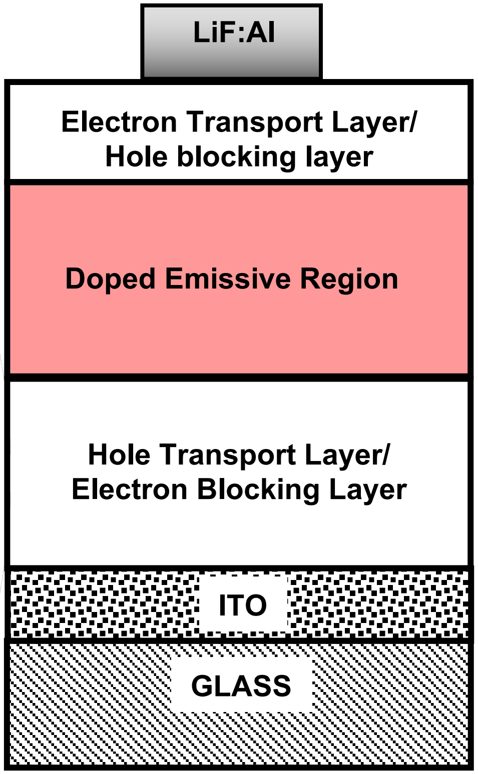
But excitons must be captured by dispersed dye

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


LiF:Al

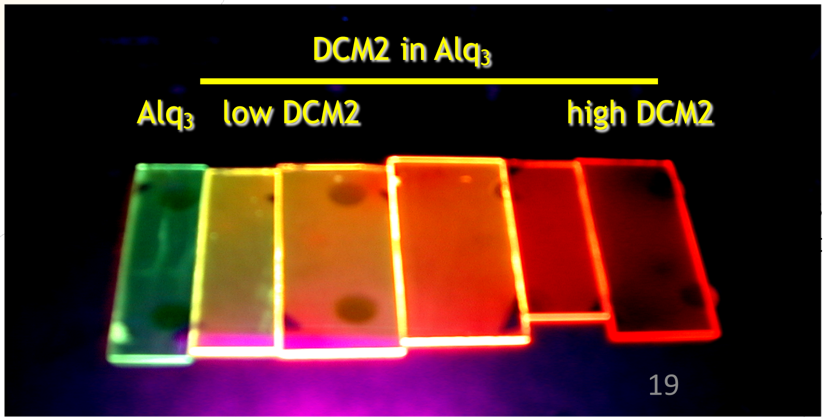
Electron Transport Layer/ Hole blocking layer

Doped Emissive Region

Hole Transport Layer/ Electron Blocking Layer

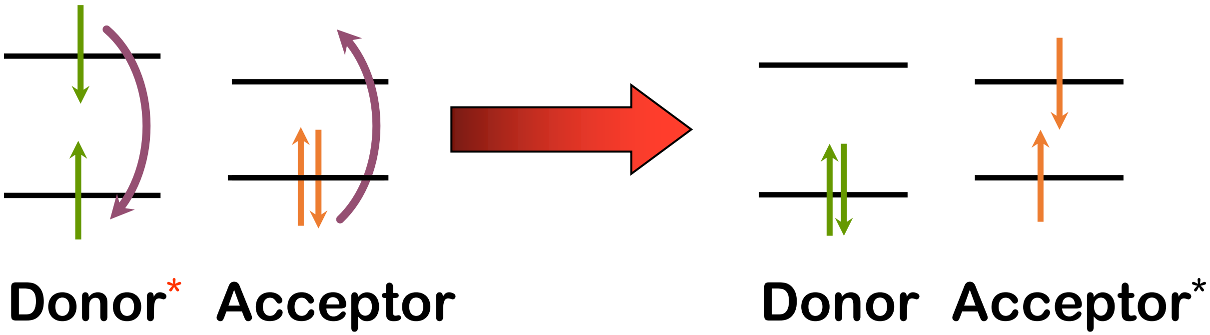
ITO

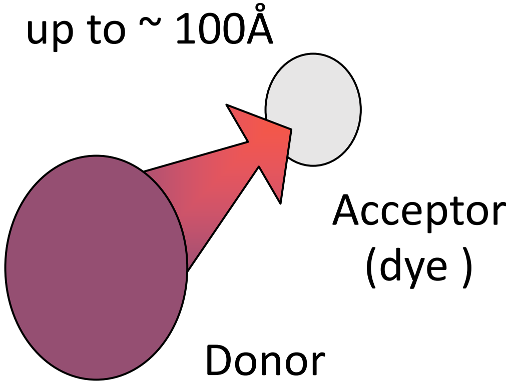
GLASS



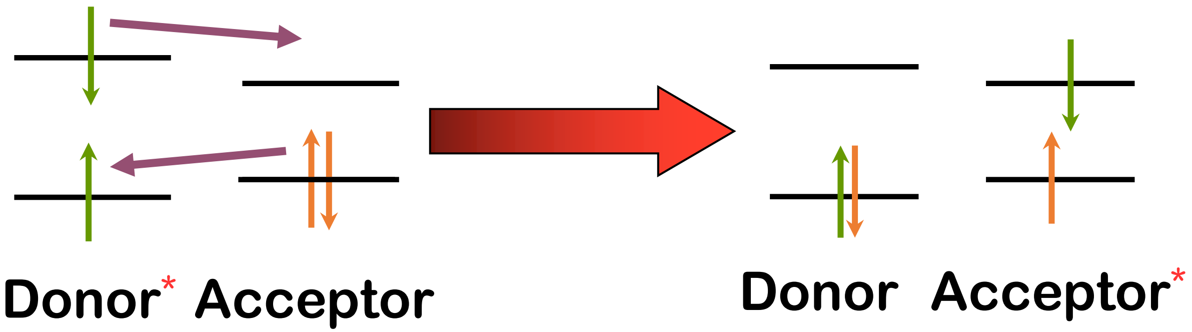
Energy Transfer from Host to Dopant: A Review

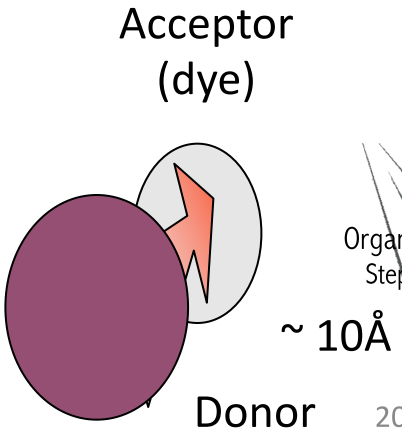
Förster:
- resonant dipole-dipole coupling
- donor and acceptor transitions must be allowed





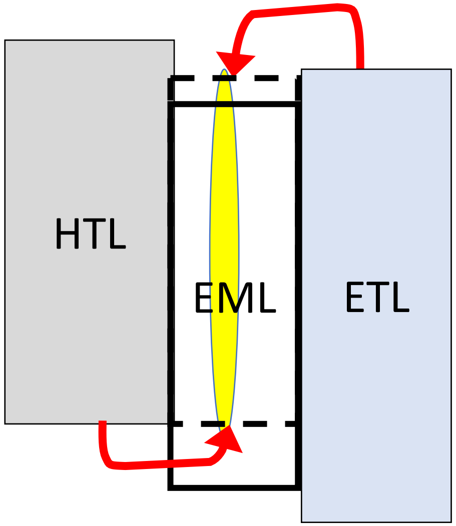
Electron Exchange (Dexter):
- diffusion of excitons from donor to acceptor by simultaneous charge exchange: short range



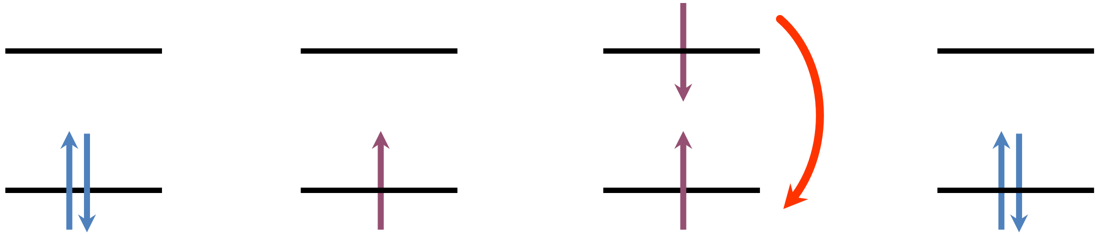


spin is conserved: e.g. singlet-singlet or triplet-triplet

Direct trapping on the lumophore

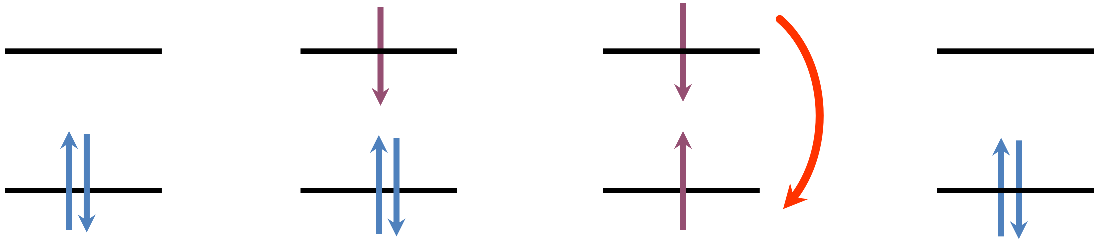


Cation formation by electrical injection

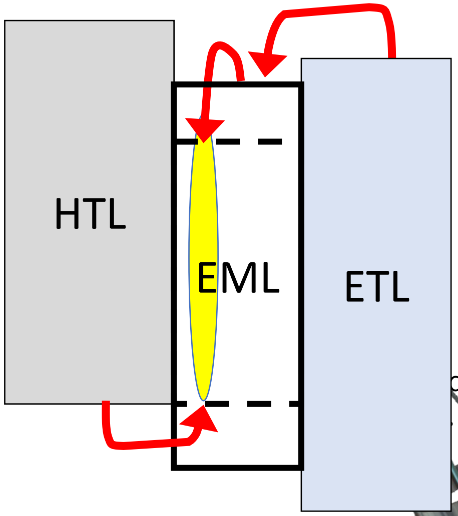


Acceptor^0 Acceptor$^+$ Acceptor* Acceptor^0

Or, anion formation



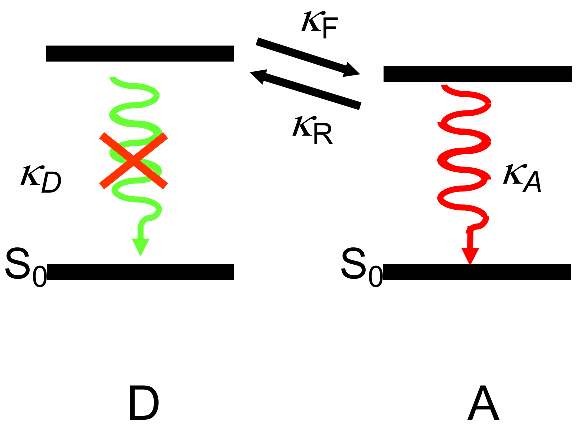
Acceptor^0 Acceptor$^-$ Acceptor* Acceptor^0



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

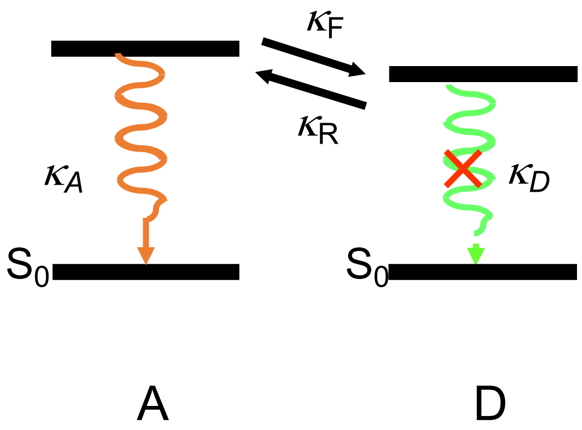
Energy transfer rates and directions

Forward (exothermic) transfer



- Donor energy > Acceptor energy
- $k_F \sim k_A > k_R, k_D$
- Radiative rate determined by k_A
- Route for red and green emission

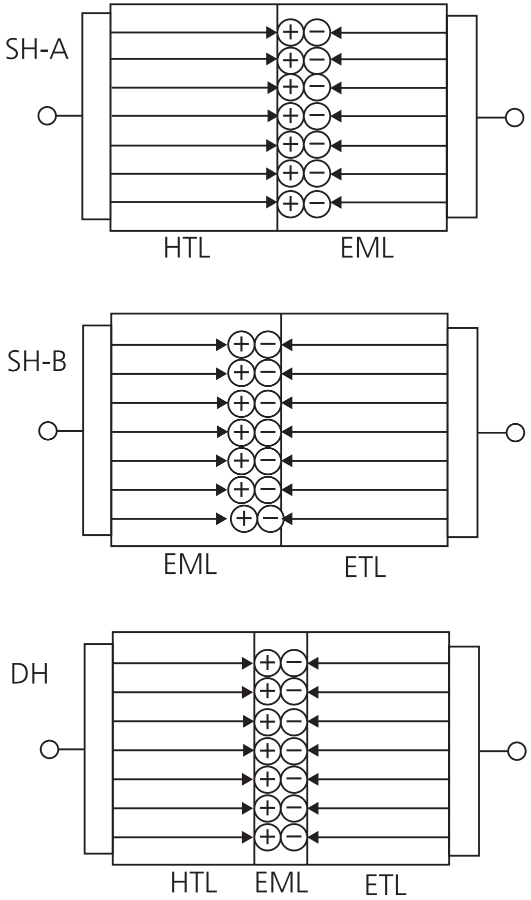
Reverse (endothermic) transfer

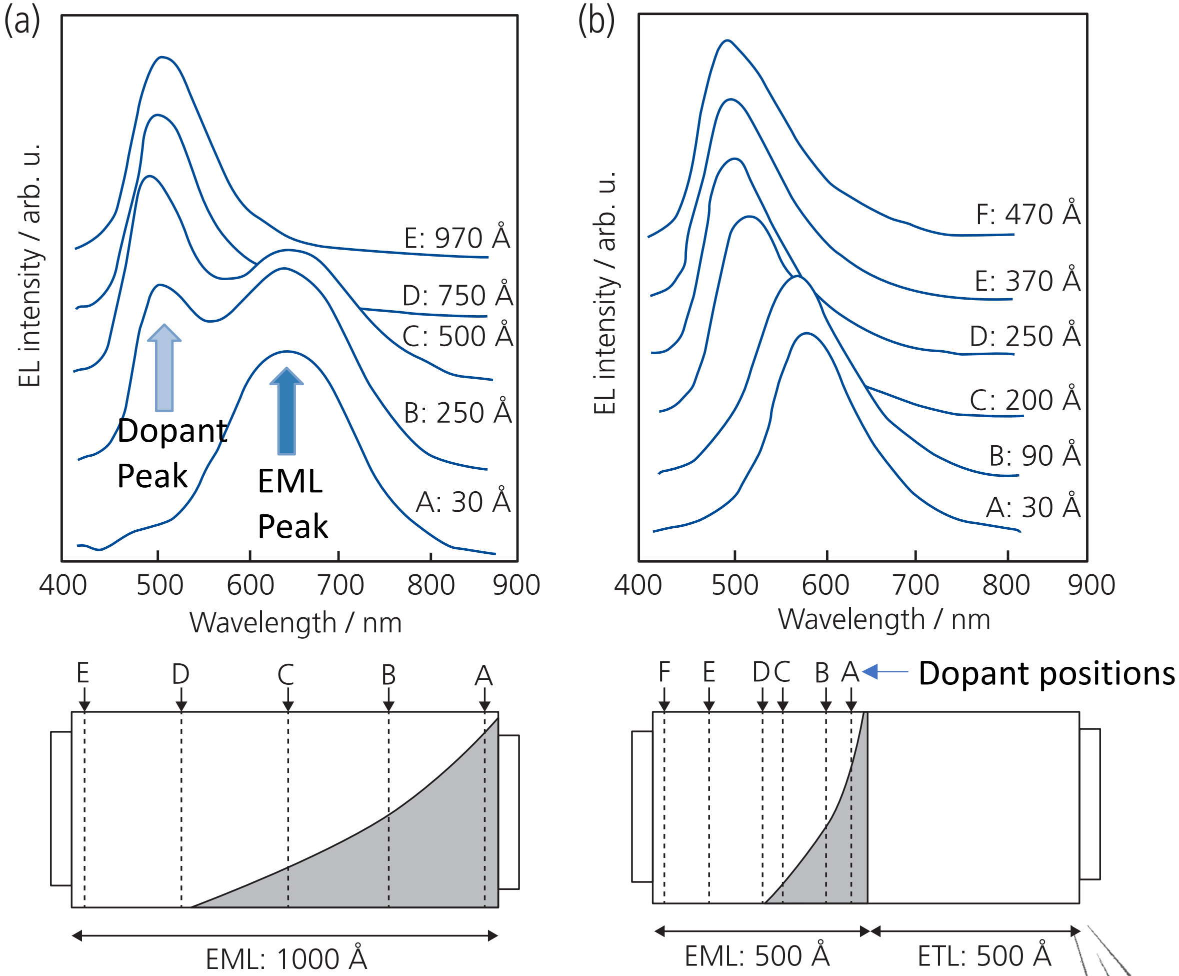


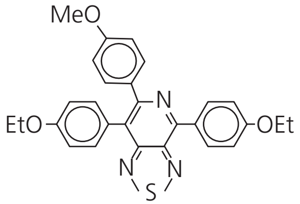
- Acceptor energy ~ Donor energy
- $k_F \sim k_R > k_A > k_D$
- Radiative rate determined by k_A, k_R
- Route for green and blue emission
- Similar to TADF, delayed fluorescence

Where Excitons Form in an OLED

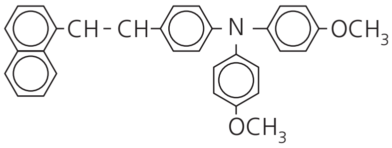
(Closest to the point at which electrons are injected)







Dopant



EML (NSD)

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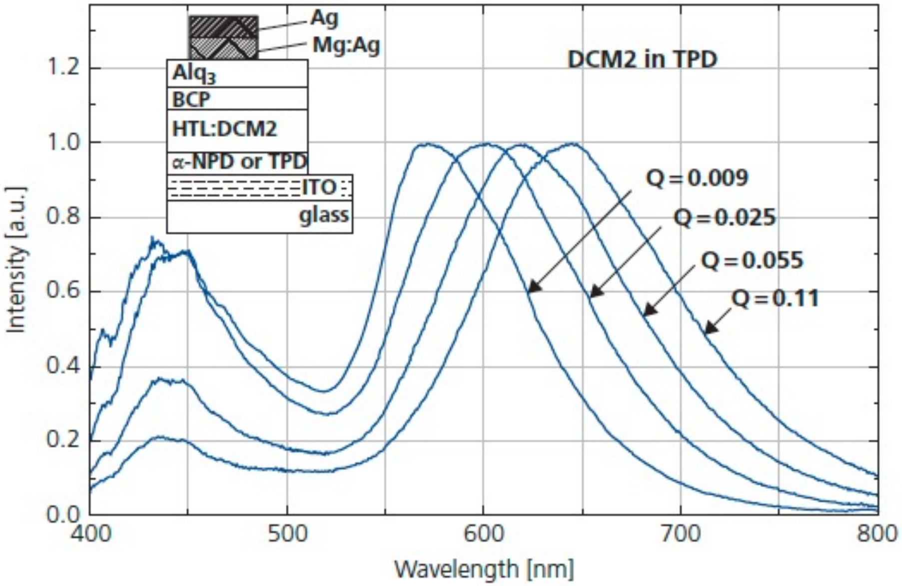
Adachi et al., Optoelec. Dev. Tech. 6, 25 (1991)

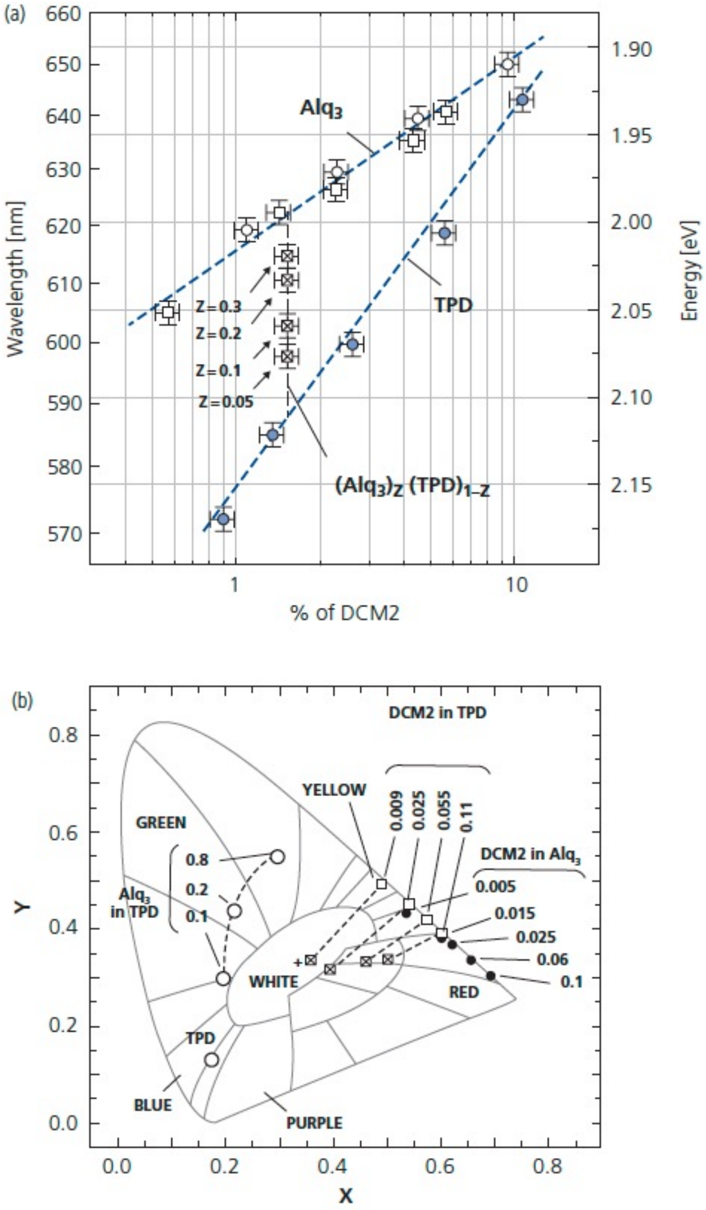
Dopant Emission Shifted By Polarization in the Thin Film

Solid state solvation effect (SSSE) – see Ch. 3

DCM2 (red dopant) has dipole moment 11D
TPD HTL dipole moment: 1.5D
DCM2 self-polarizes (red shifts) with concentration, Q



Bulovic et al., Chem. Phys. Lett., 308 317 (1999)



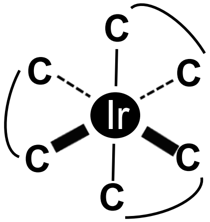
Color shift from red to yellow to white

Another Way to Shift Color: Isomerism

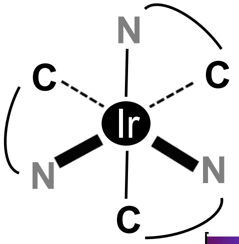
N-Heterocyclic carbene (NHC) ligand for blue

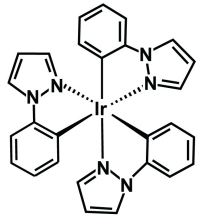
NHC Ir (III) complex = **Ir(C^C:)$_3$**

Conventional design = Ir(C^N)$_3$

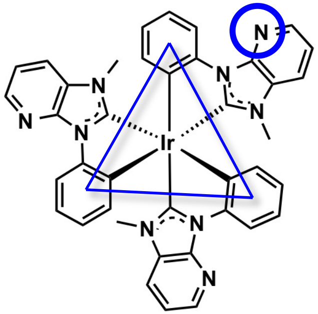


vs.



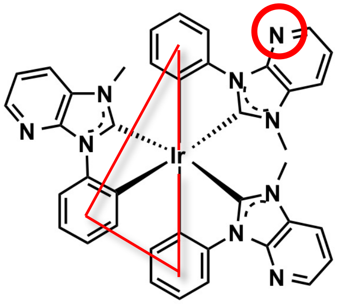


fac-Ir(*ppz*)$_3$



fac-Ir(***pmP***)$_3$

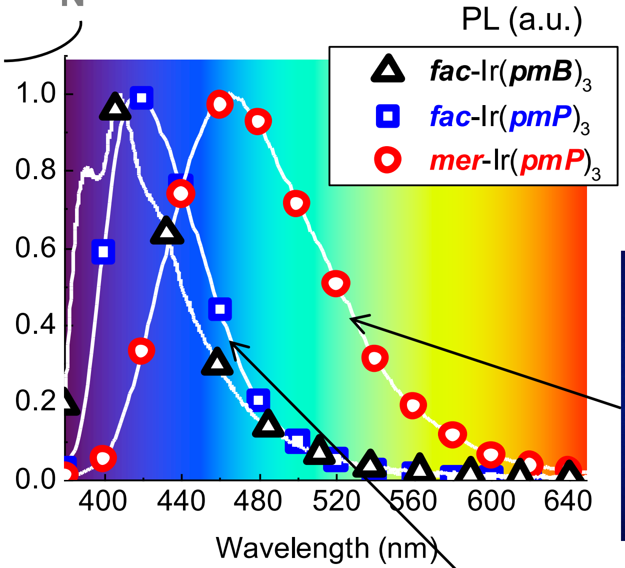
Type I: ^{3}LC



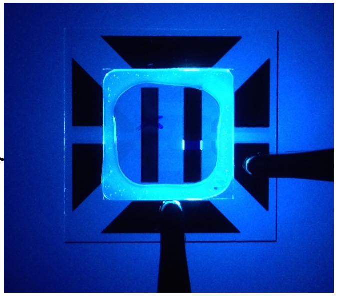
mer-Ir(***pmP***)$_3$

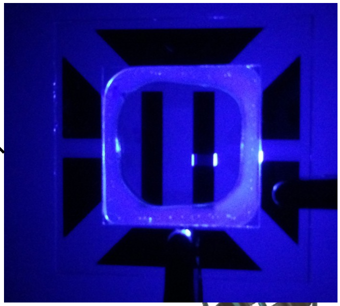
Type II: (^{3}MLCT)

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



mer





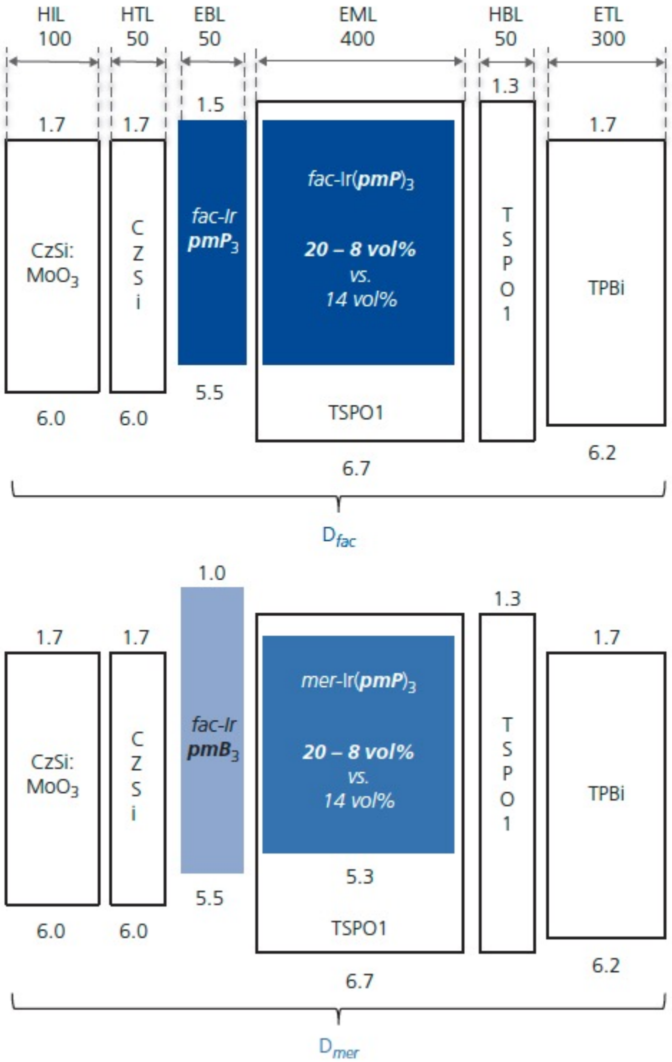
fac

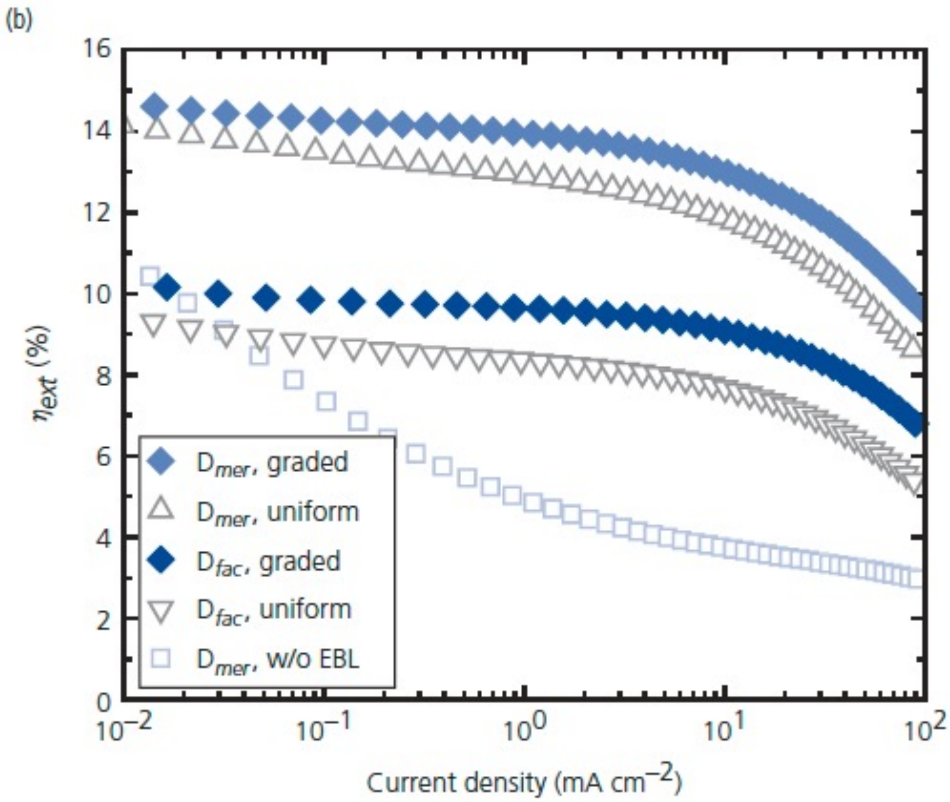
fac

Property	***fac***-Ir(***pmp***)$_3$	***mer***-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)

Higher Energy of *fac*-isomer leads to reduced exciton confinement

⇒ reduced quantum efficiency





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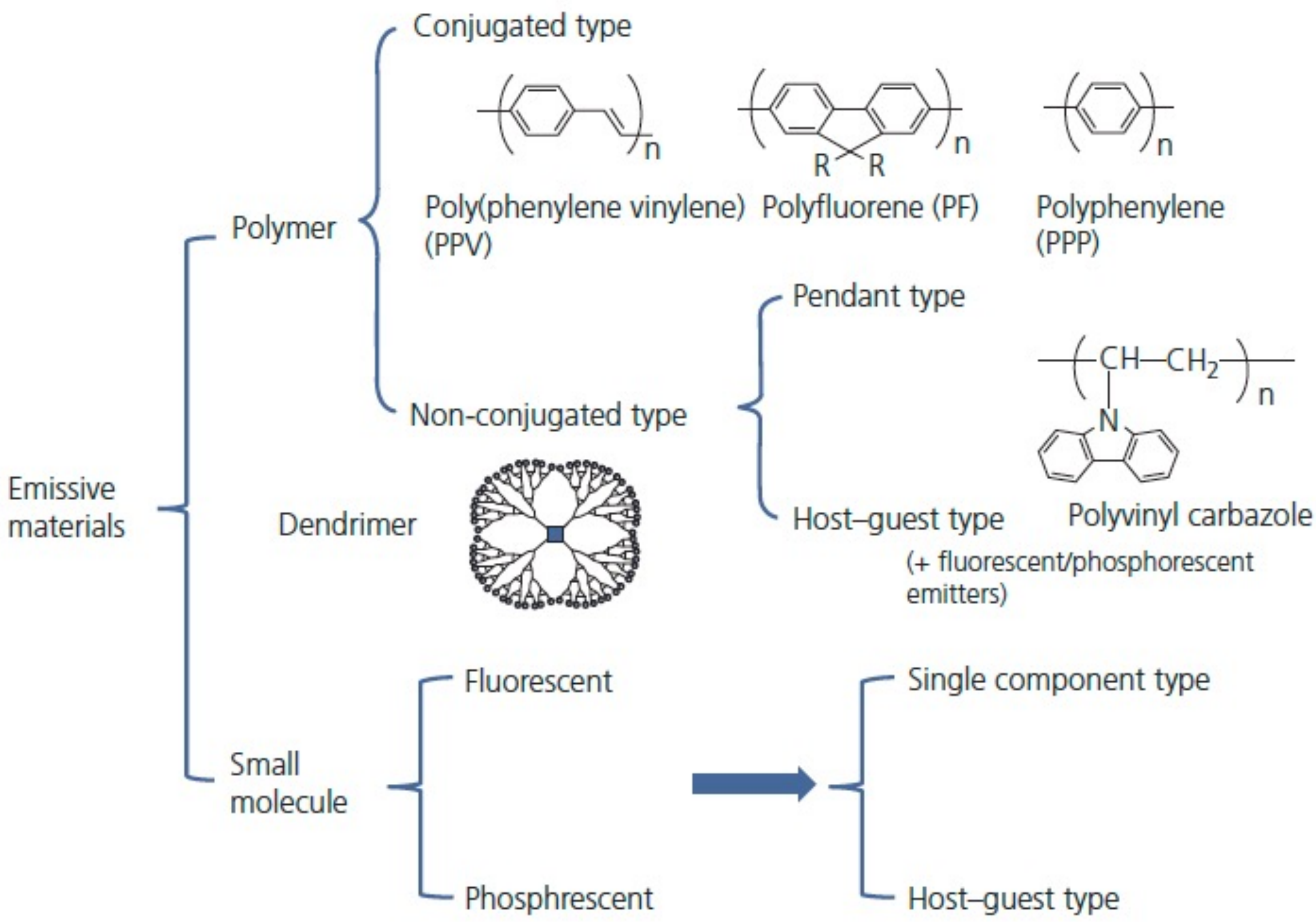
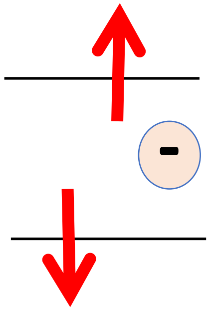
Strategies for Designing Light Emitting Polymers and Small Molecules

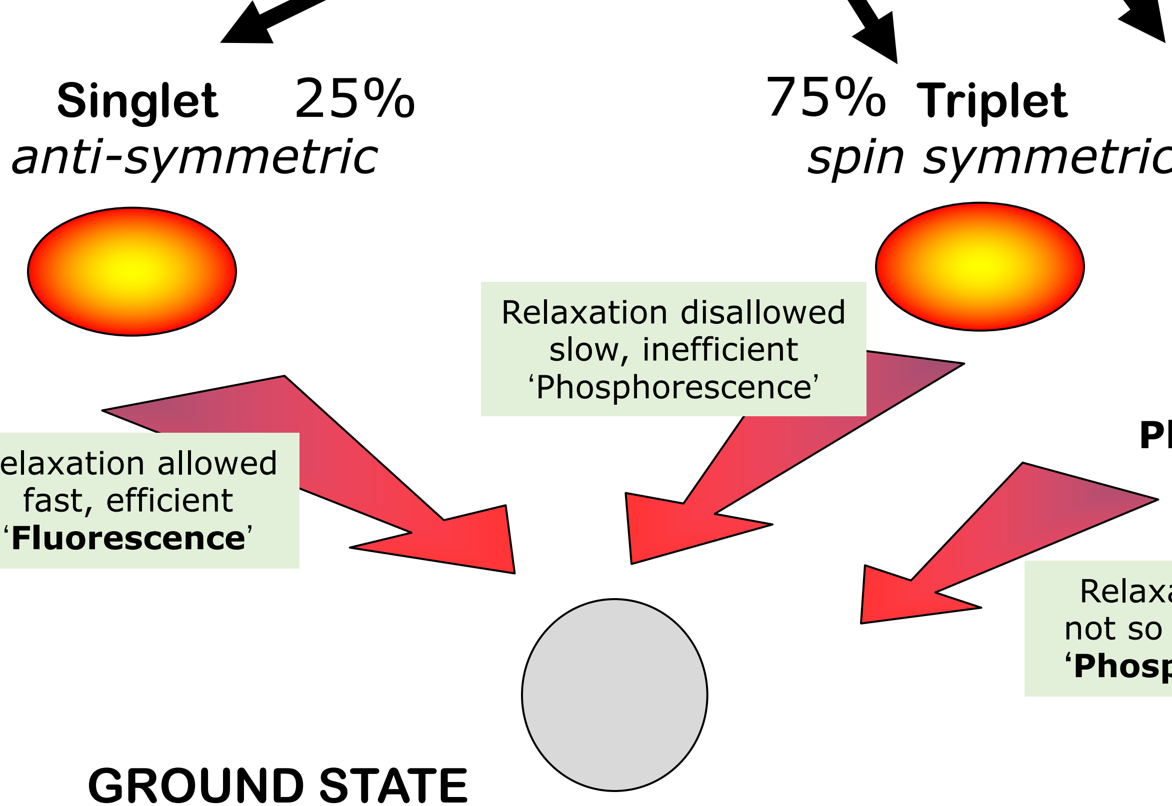


100% Internal Efficiency via Spin-Orbit Coupling

Heavy metal induced electrophosphorescence ~100% QE

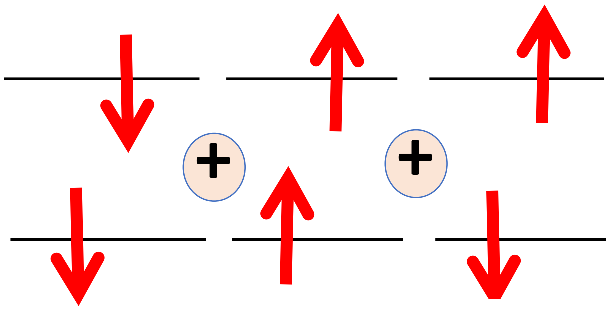


MOLECULAR EXCITED STATES AFTER ELECTRICAL EXCITATION

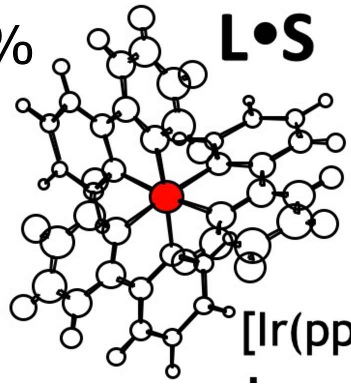


Singlet 25%
spin anti-symmetric

75% **Triplet**
spin symmetric



100%



[Ir(ppy)$_3$]

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

Relaxation disallowed
slow, inefficient
'Phosphorescence'

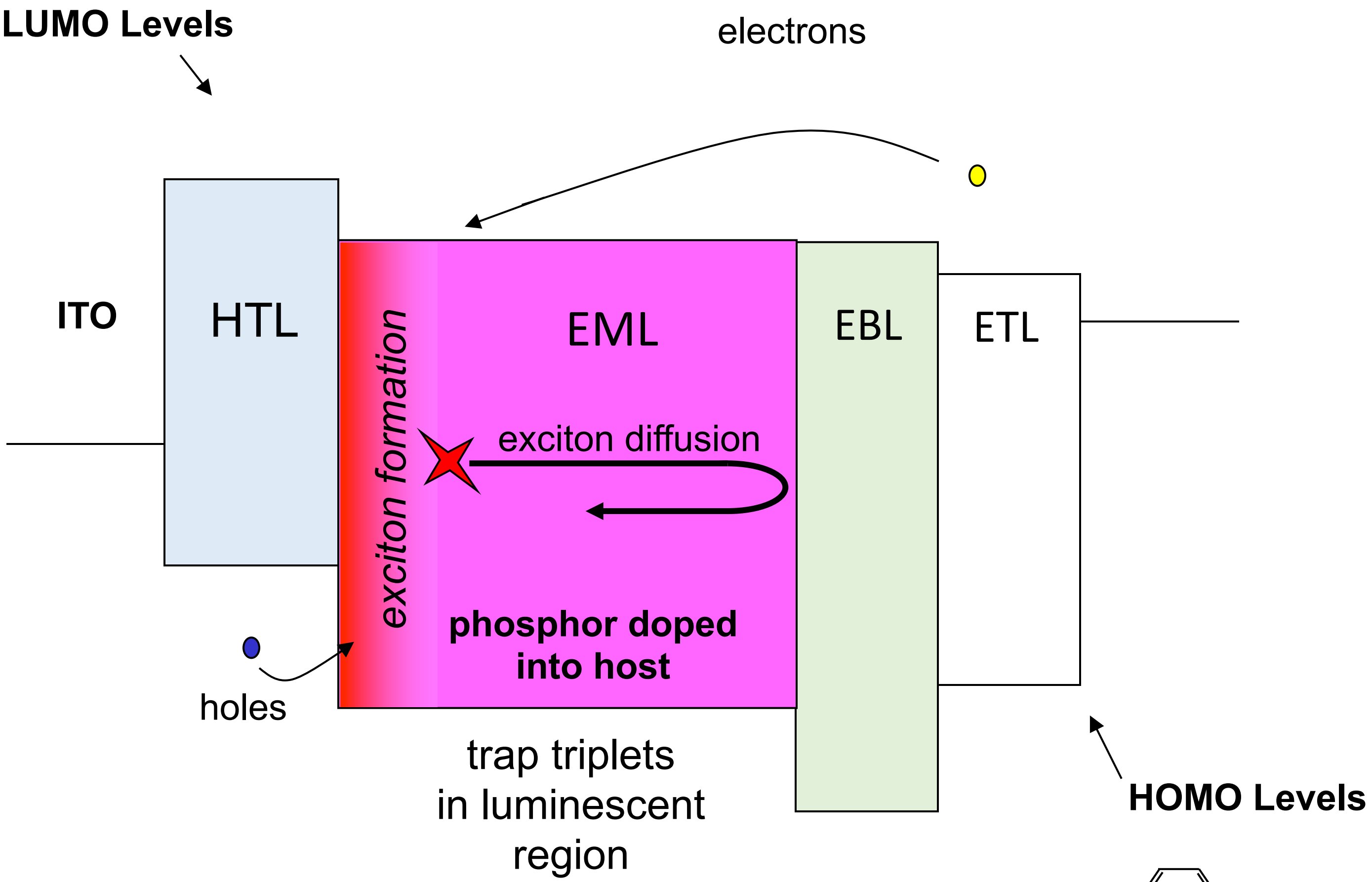
Phosphorescence enhanced by mixing S+T eg: spin-orbit coupling via heavy metal atom

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

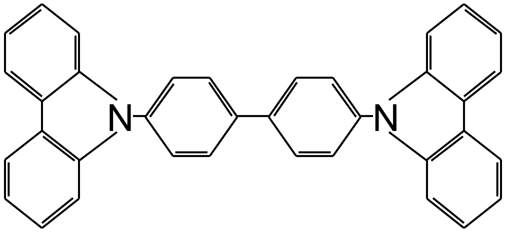
GROUND STATE
spin anti-symmetric

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

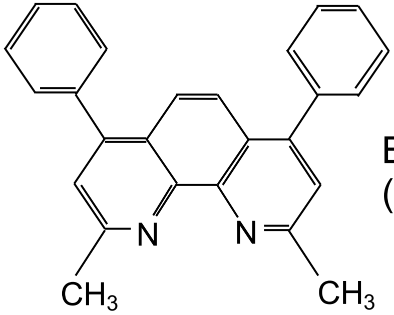
Electrophosphorescent (PHOLED) Device Structure



trap triplets
in luminescent
region



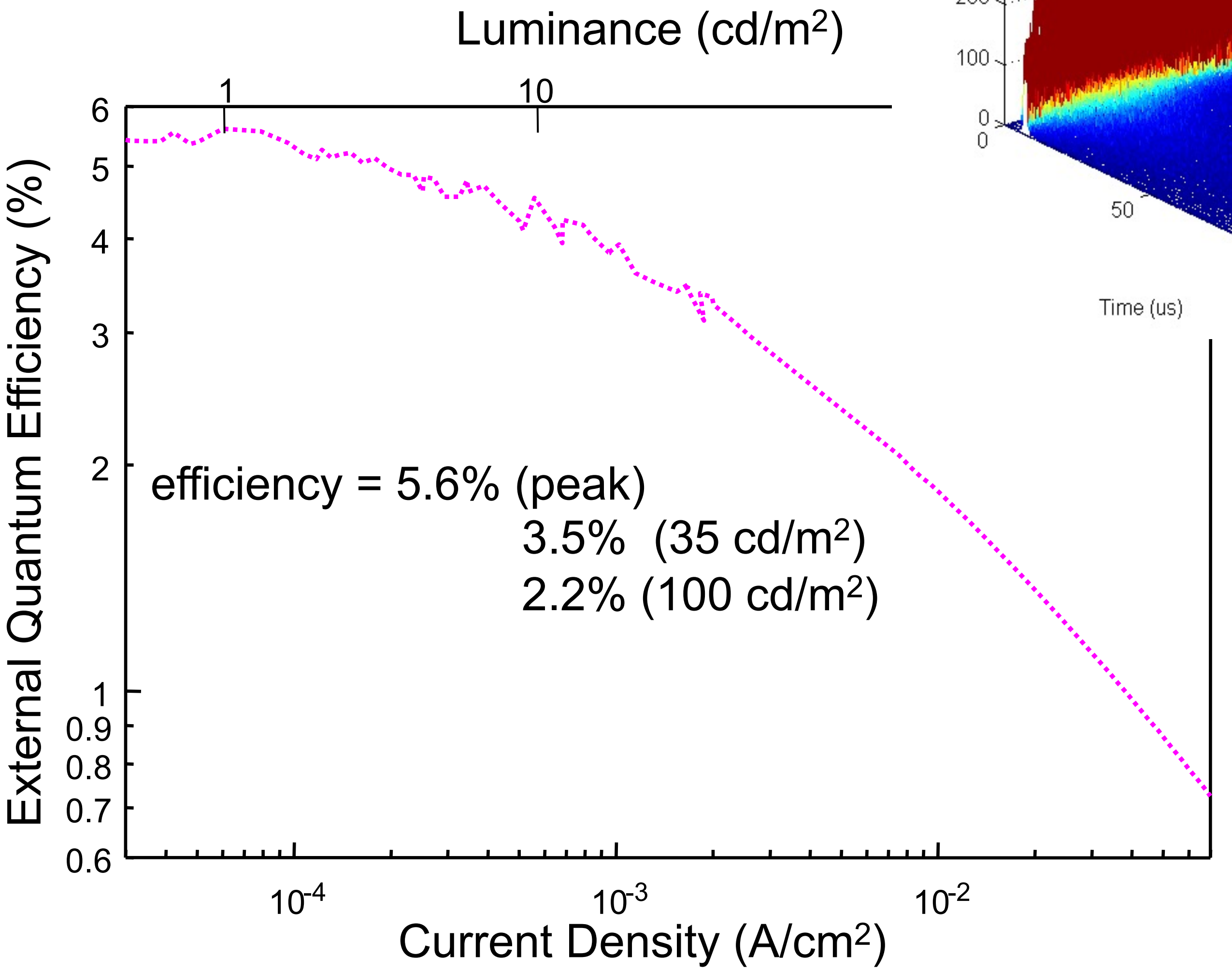
CBP
(common G,B host)



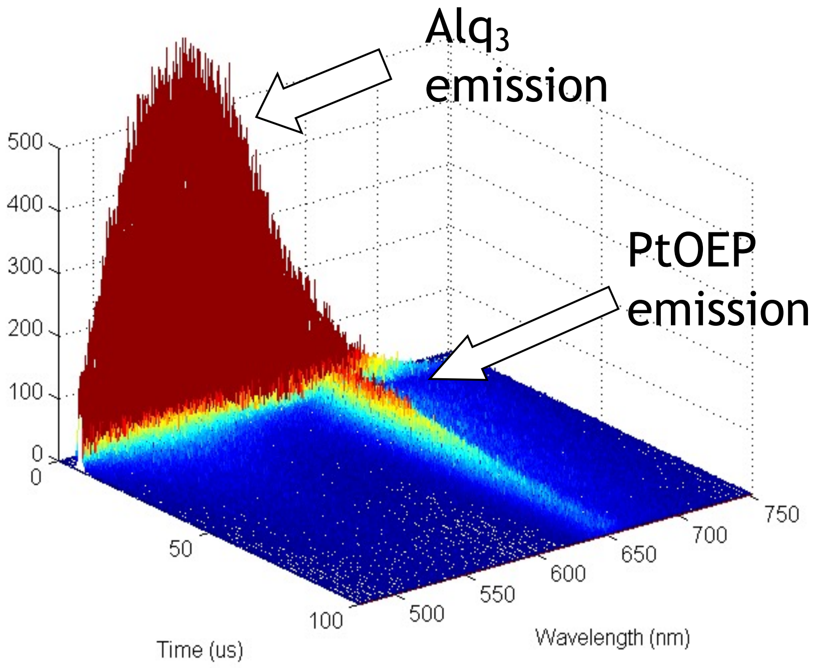
BCP
(common EBL)

6% PtOEP in CBP

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

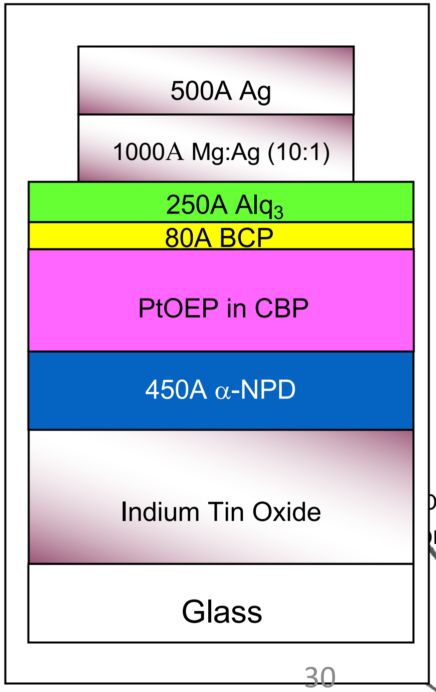


efficiency = 5.6% (peak)
3.5% (35 cd/m^2)
2.2% (100 cd/m^2)



Alq$_3$ emission

PtOEP emission



500A Ag

1000A Mg:Ag (10:1)

250A Alq$_3$

80A BCP

PtOEP in CBP

450A α-NPD

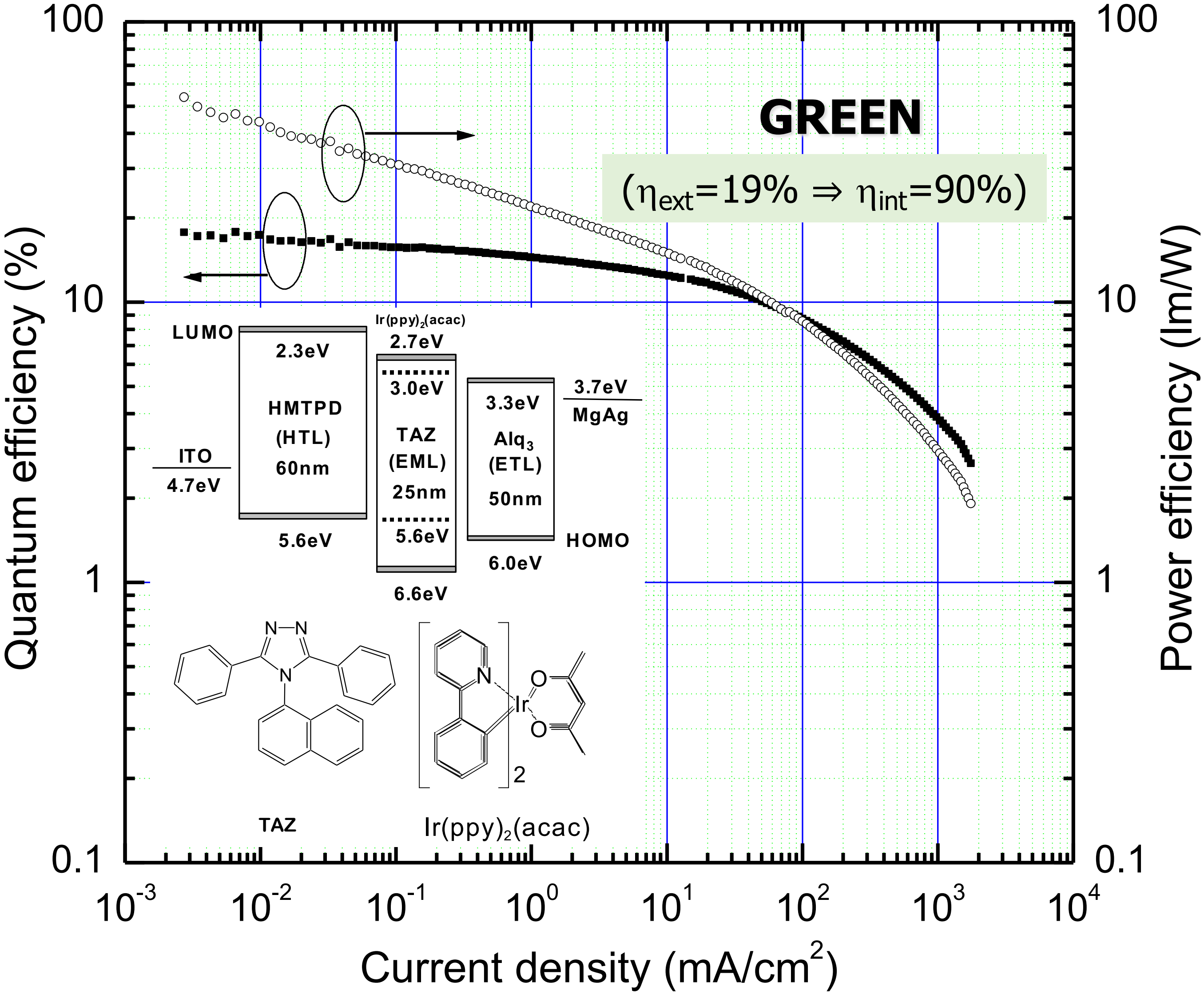
Indium Tin Oxide

Glass

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

100% Efficient PHOLEDs

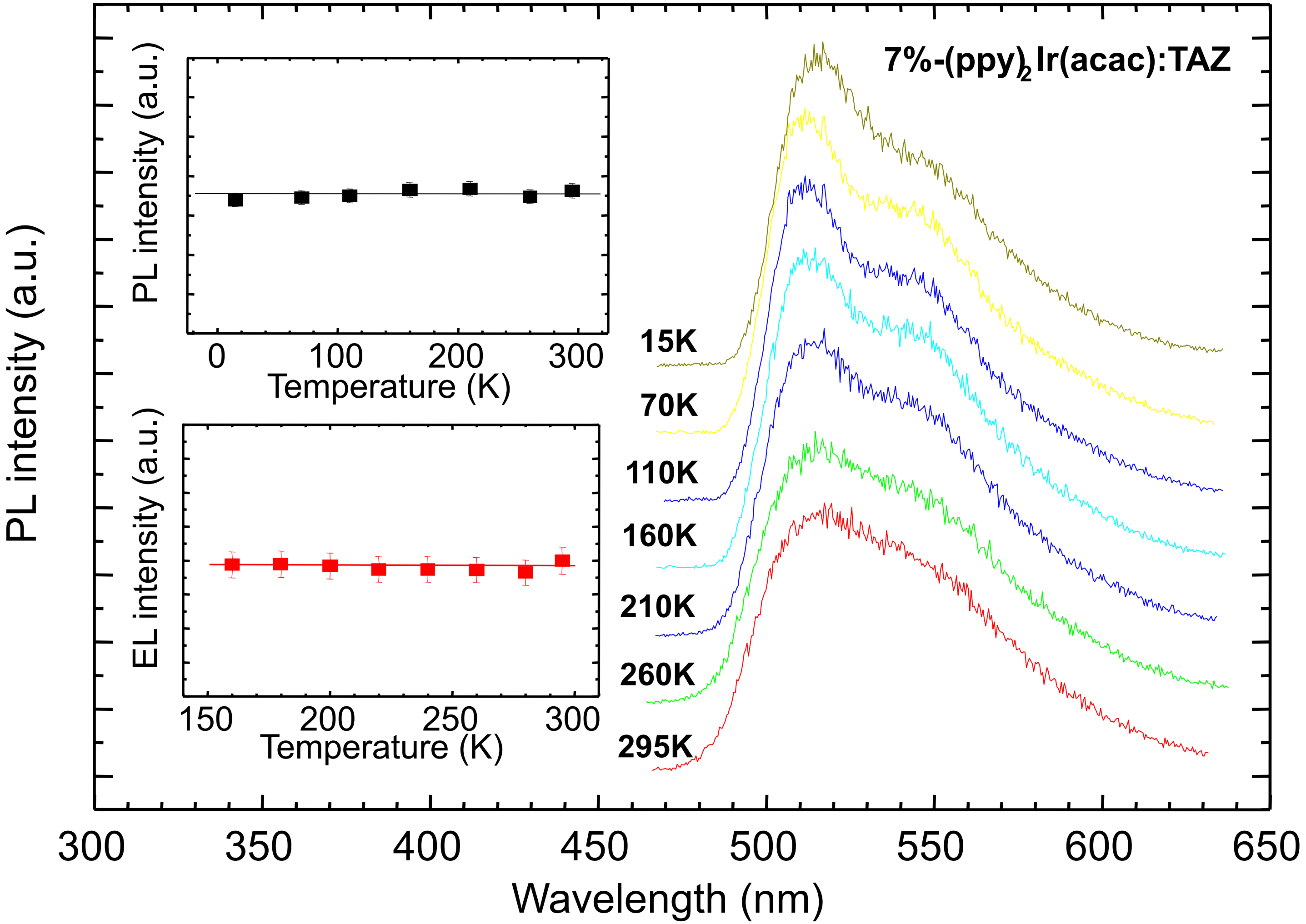
$Ir(ppy)_2(acac)$ doped ETL (Triazole)



$(\eta_{ext}=19\% \Rightarrow \eta_{int}=90\%)$

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

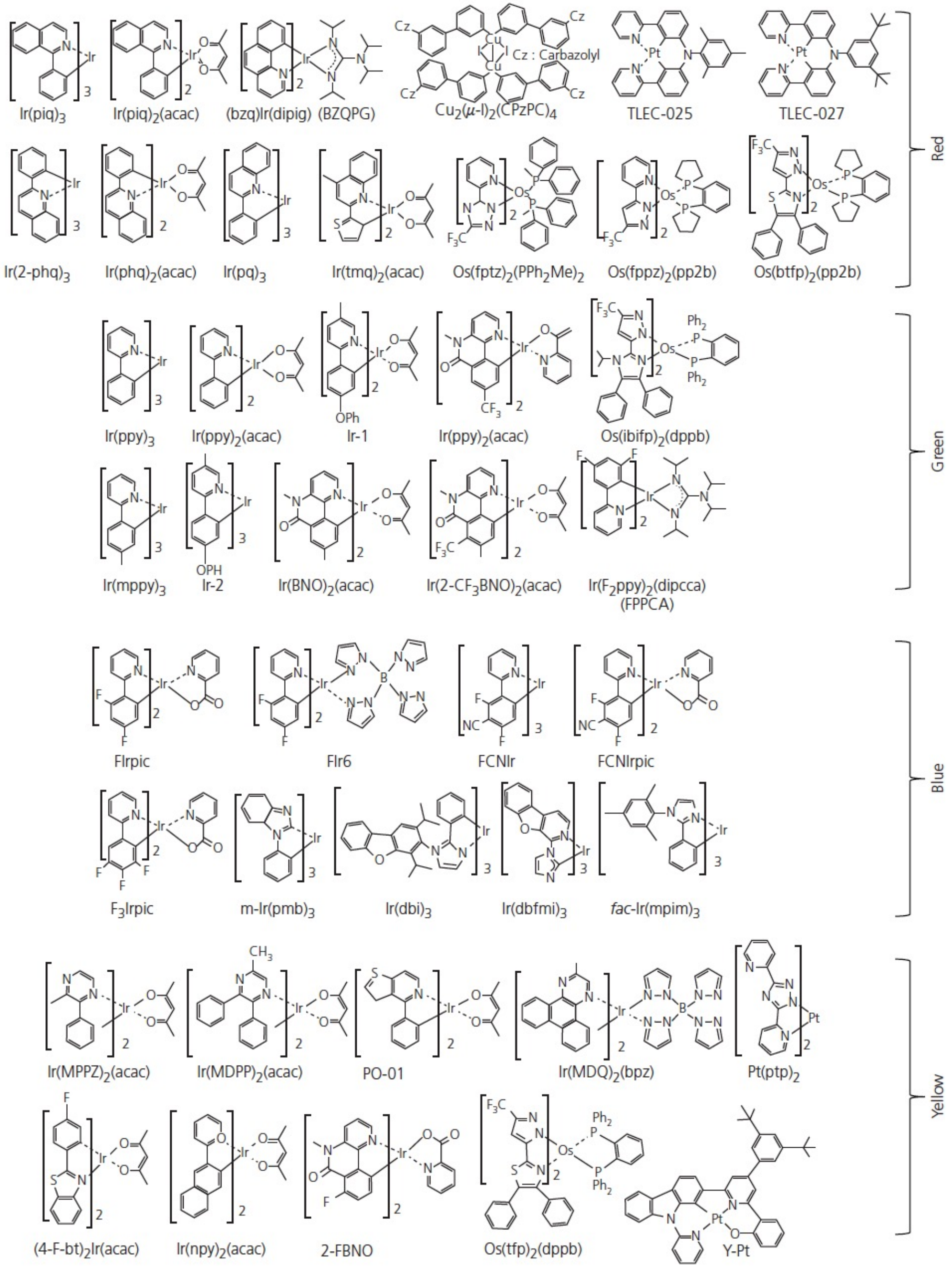
Temperature Independent PL and EL



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



Organic Electronics
Stephen R. Forrest