Week 9

Light Emitters 2

OLED Designs

PHOLEDs and TADF

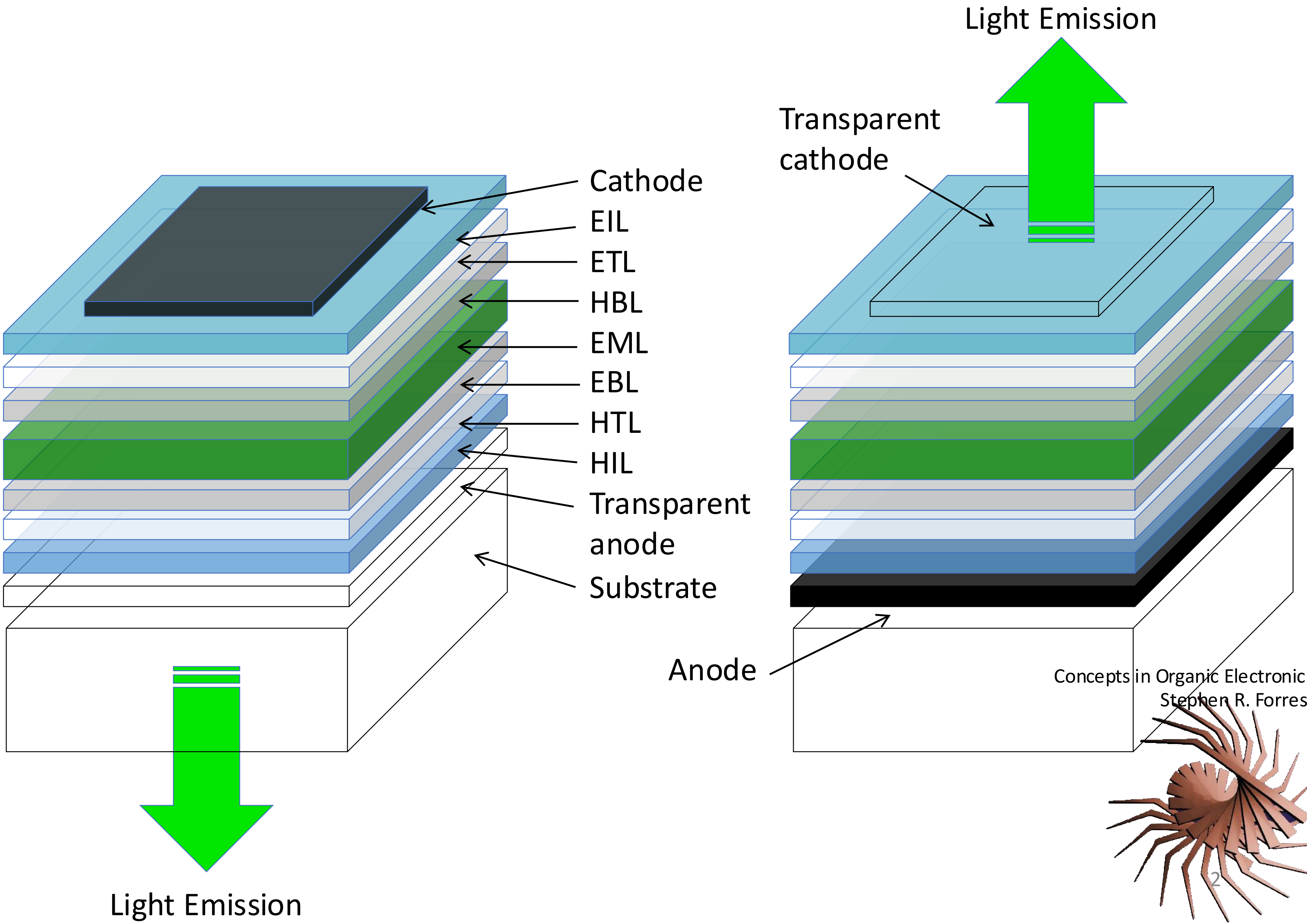
Materials

Displays and Lighting

Chapter 6.4 – 6.8

Concepts in Organic Electronics
Stephen R. Forrest

Today's OLEDs Are Not So Simple



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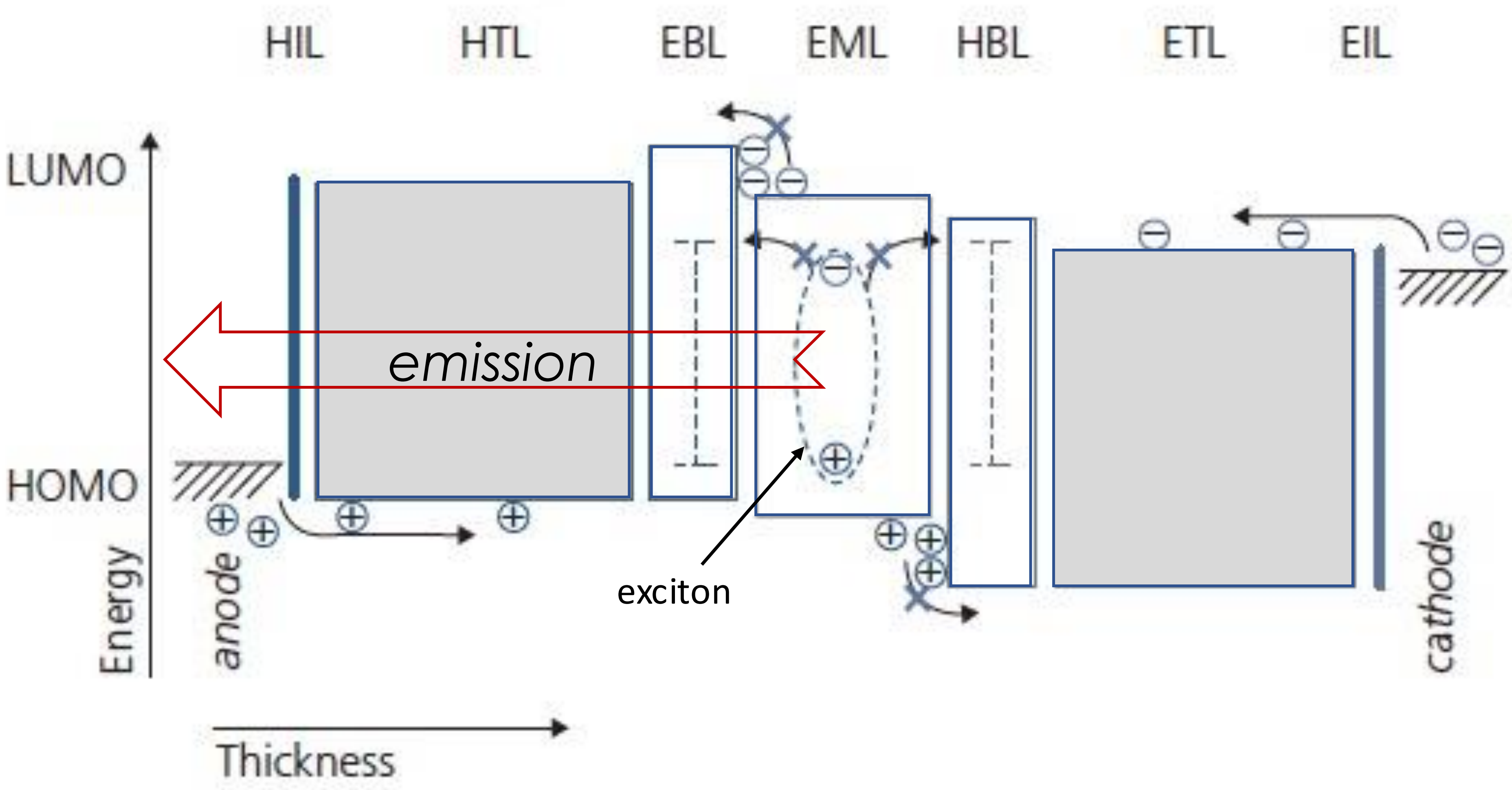
Energy level diagram of an example OLED



S. M. Reineke, et al. 2013. *Rev. Mod. Phys.*, 85, 1245.

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

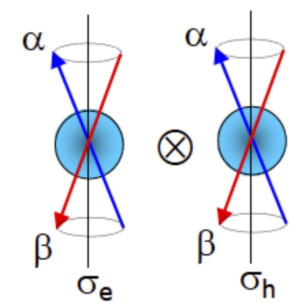
ϕ_p: quantum efficiency of fluorescence

η_{out}: light out-coupling efficiency

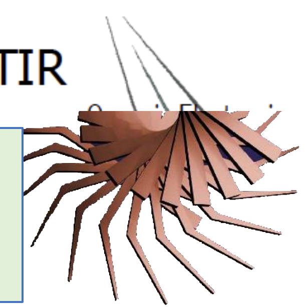
1. Fluorescence is restricted to singlet excitons $\chi_r \sim 25\%$

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

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



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



⇒ Maximum η_{ext} for fluorescent devices: 5%
Maximum η_{ext} for phosphorescent devices: 20%

Bad things happen to good excitons: Sources of roll off at high brightness

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

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

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

Delayed fluorescence
Triplet fusion

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

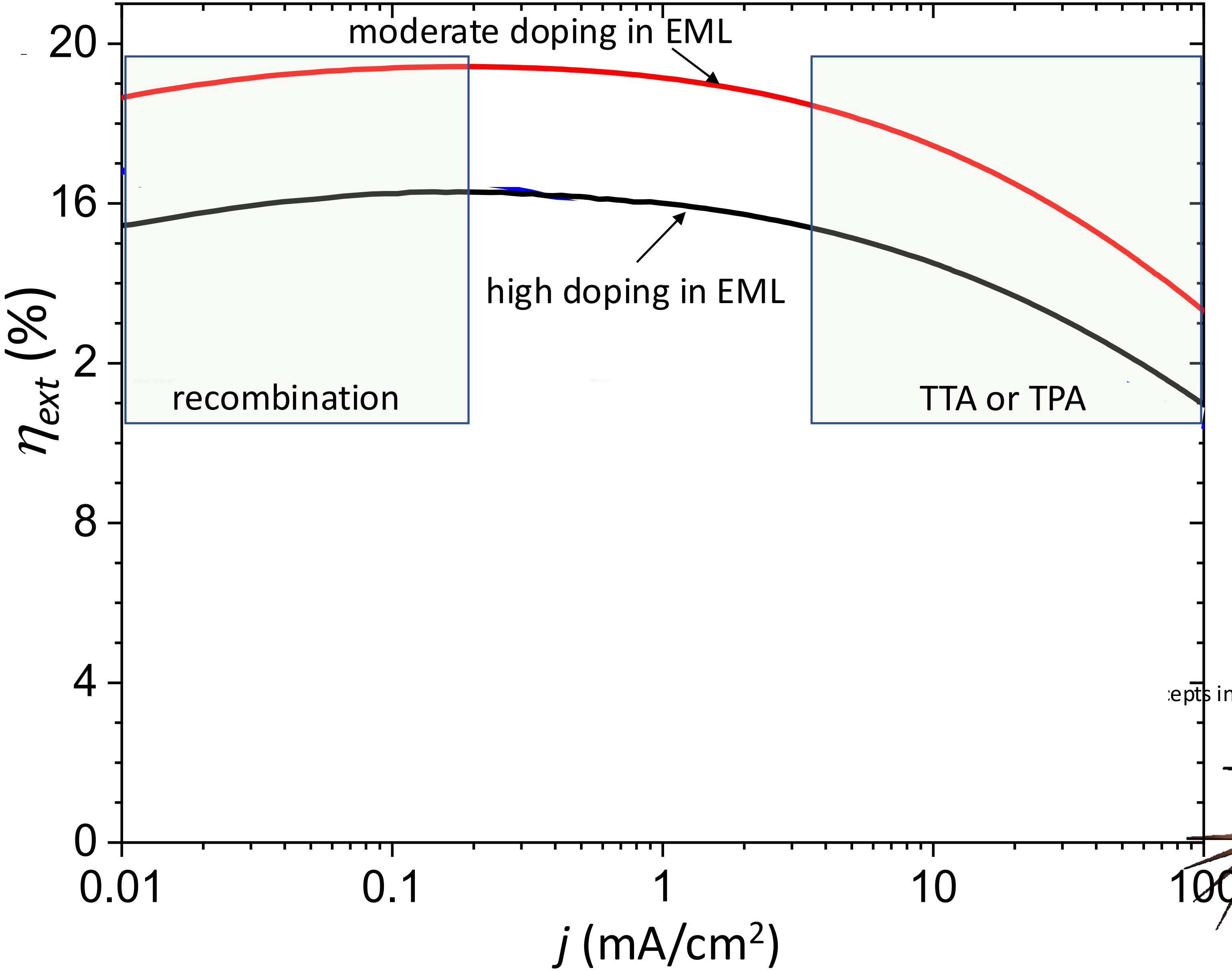
$$T + T \xrightarrow{k_{TTA-T}} T^n + S_0 \xrightarrow{k_{Tn}} T + S_0 \qquad \text{(TTA-T)}$$

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

Singlet fission when
$E_S \geq 2E_T$

$$S \rightarrow 2T$$

Characteristic OLED efficiency vs. current density



S and T Dynamics Describe TTA

Reactions

Reaction	Rate
$S+T \rightarrow T+S_0$	k_{ST}
$T+T \rightarrow T+S_0$	$(1-\alpha)\times k_{TT}$
$T+T \rightarrow S+S_0$	$\alpha \times k_{TT}$

S generation fraction in TTA

Dynamics

STA

$$\frac{dS}{dt} = \gamma \frac{J}{4ed} - k_S S - k_{ST} ST + \alpha k_{TT} T^2$$

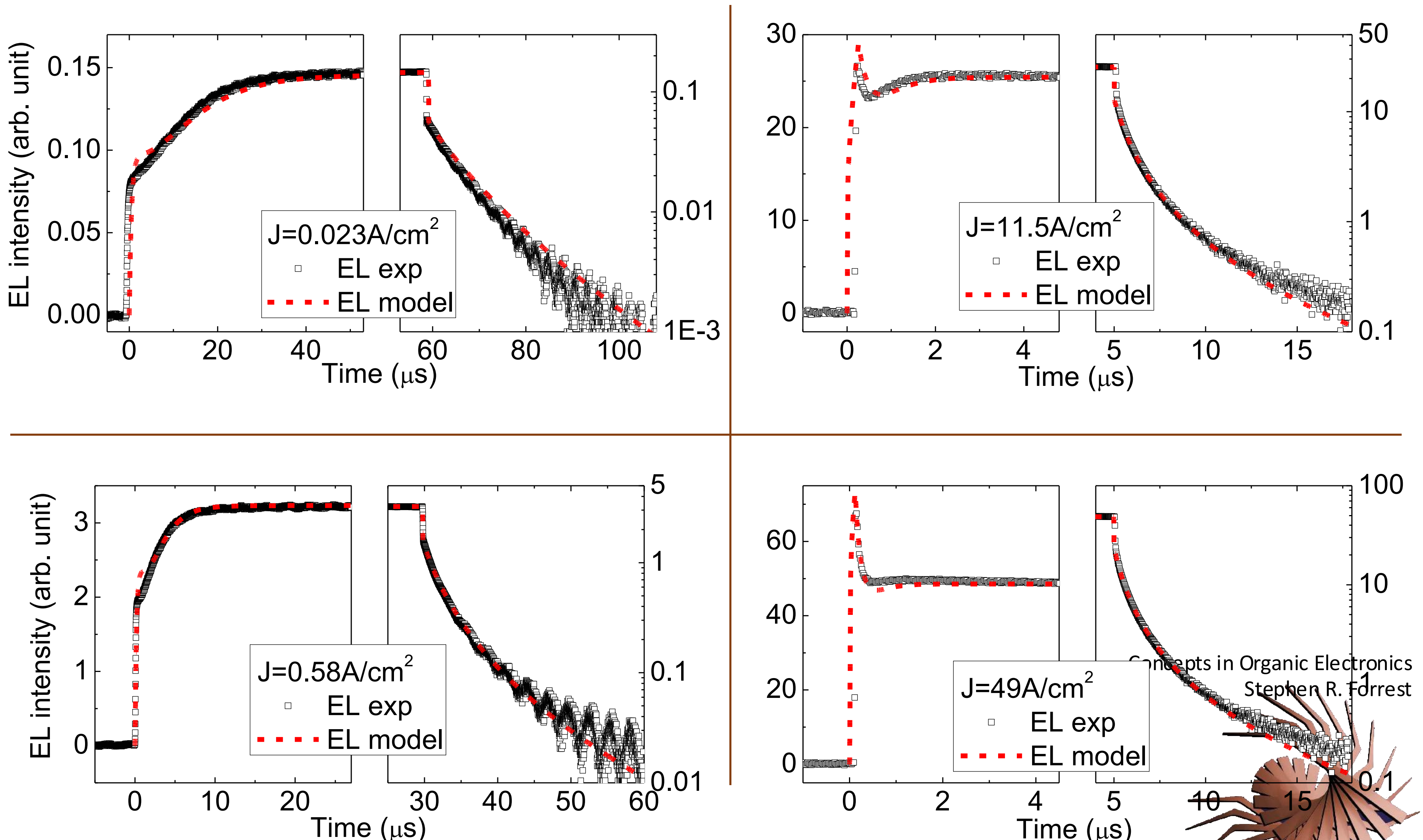
$$\frac{dT}{dt} = \gamma \frac{3J}{4ed} - k_T T - (1+\alpha) k_{TT} T^2$$

TTA

Generation

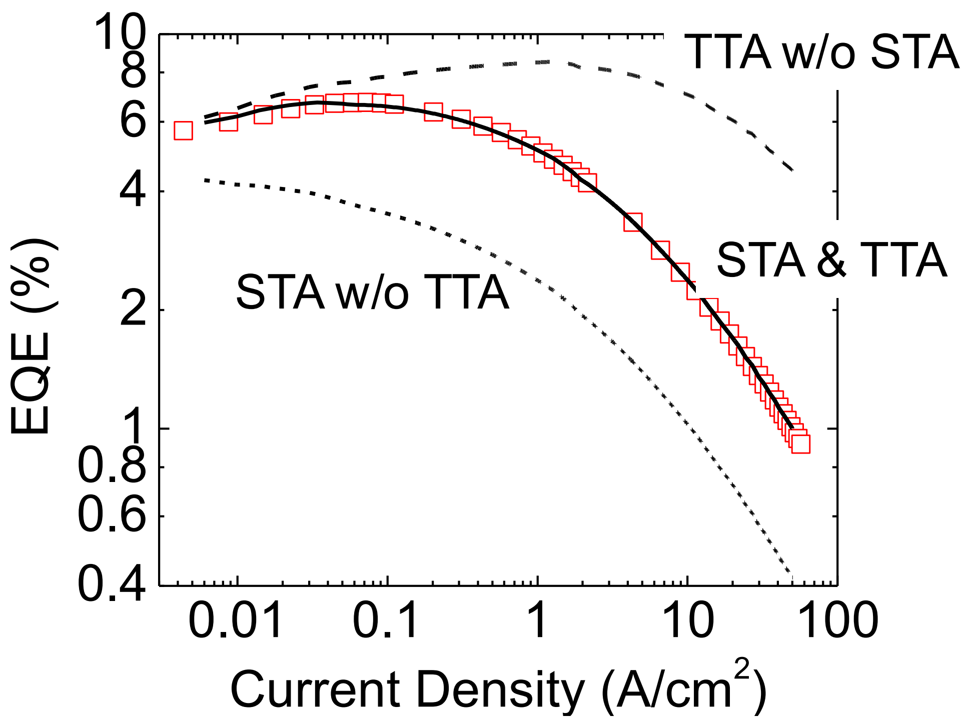
Natural decay

Model fits to experiment



Y. Zhang, S. Forrest *Phys. Rev. Lett.*, **108**, 267474 (2012)

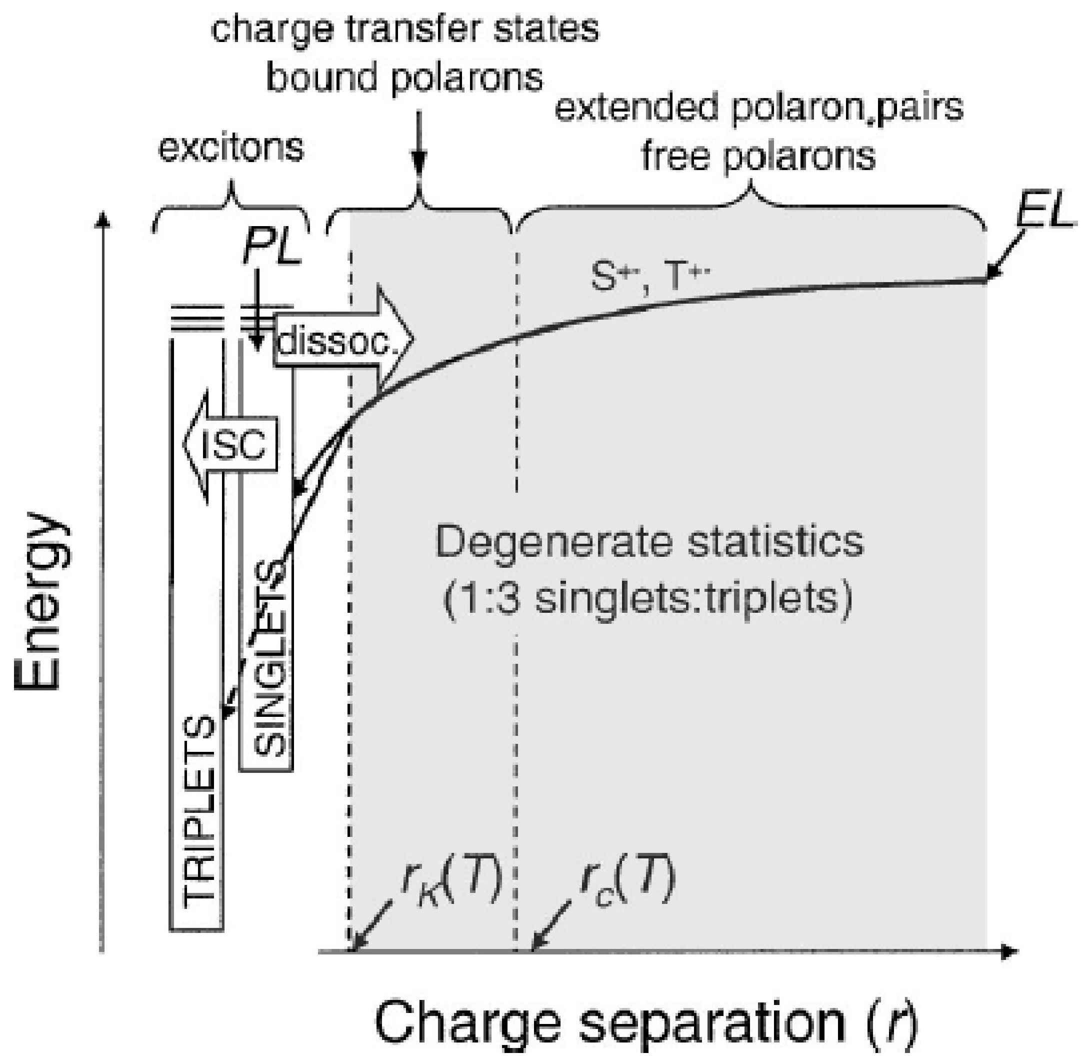
EQE of Rubrene OLEDs



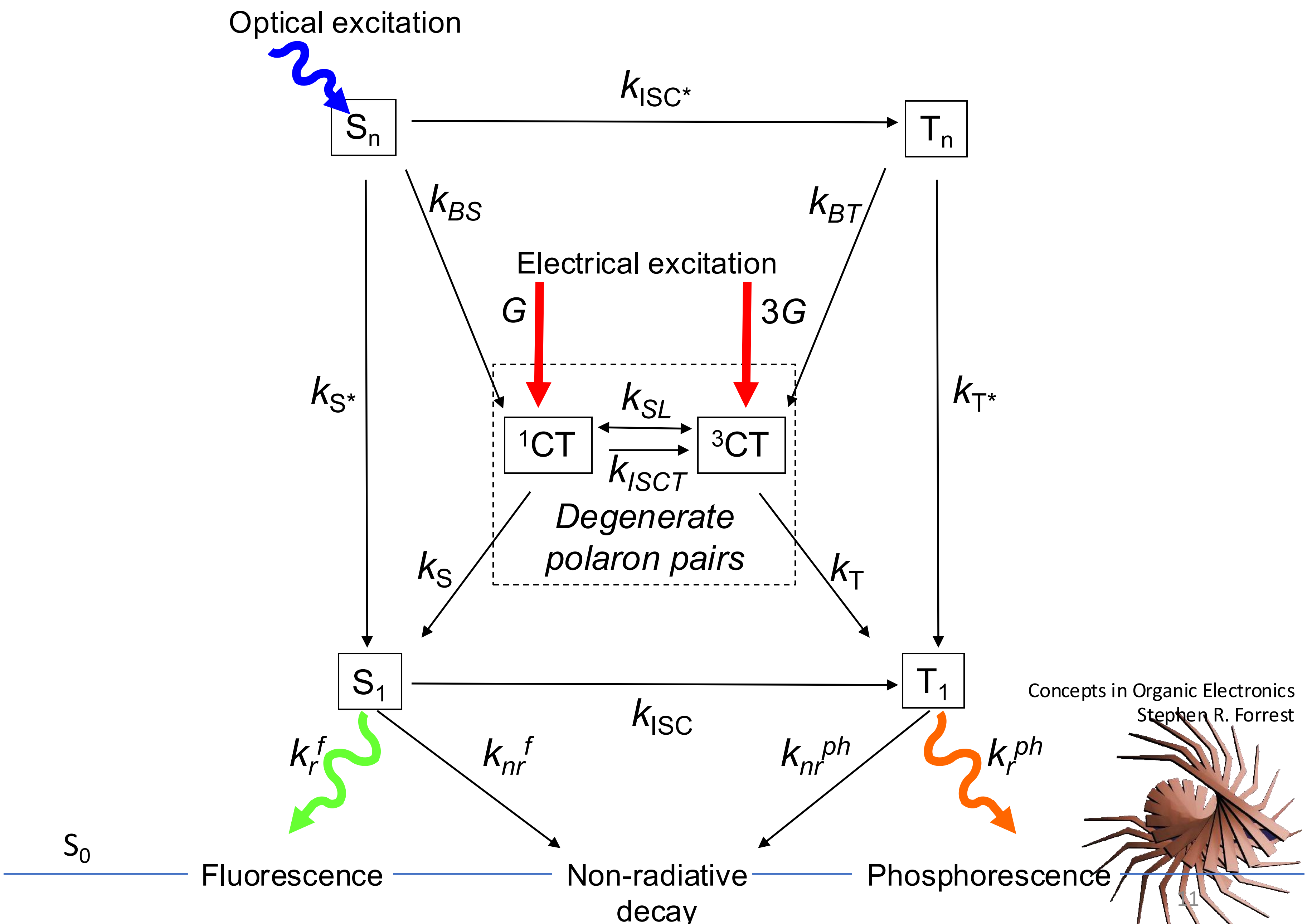
Route to high EQE & brightness in fluorescent OLEDs:

- High S fraction in TTA: α
  - ✓ $2xE_T$ slightly larger than E_S
- High TTA: k_{TT}
  - ✓ Strong triplet diffusion
- Low STA: k_{ST}
  - ✓ Low S emis./T abs overlap

Formation dynamics of singlets and triplets



Exciting Dopant Molecules in an OLED



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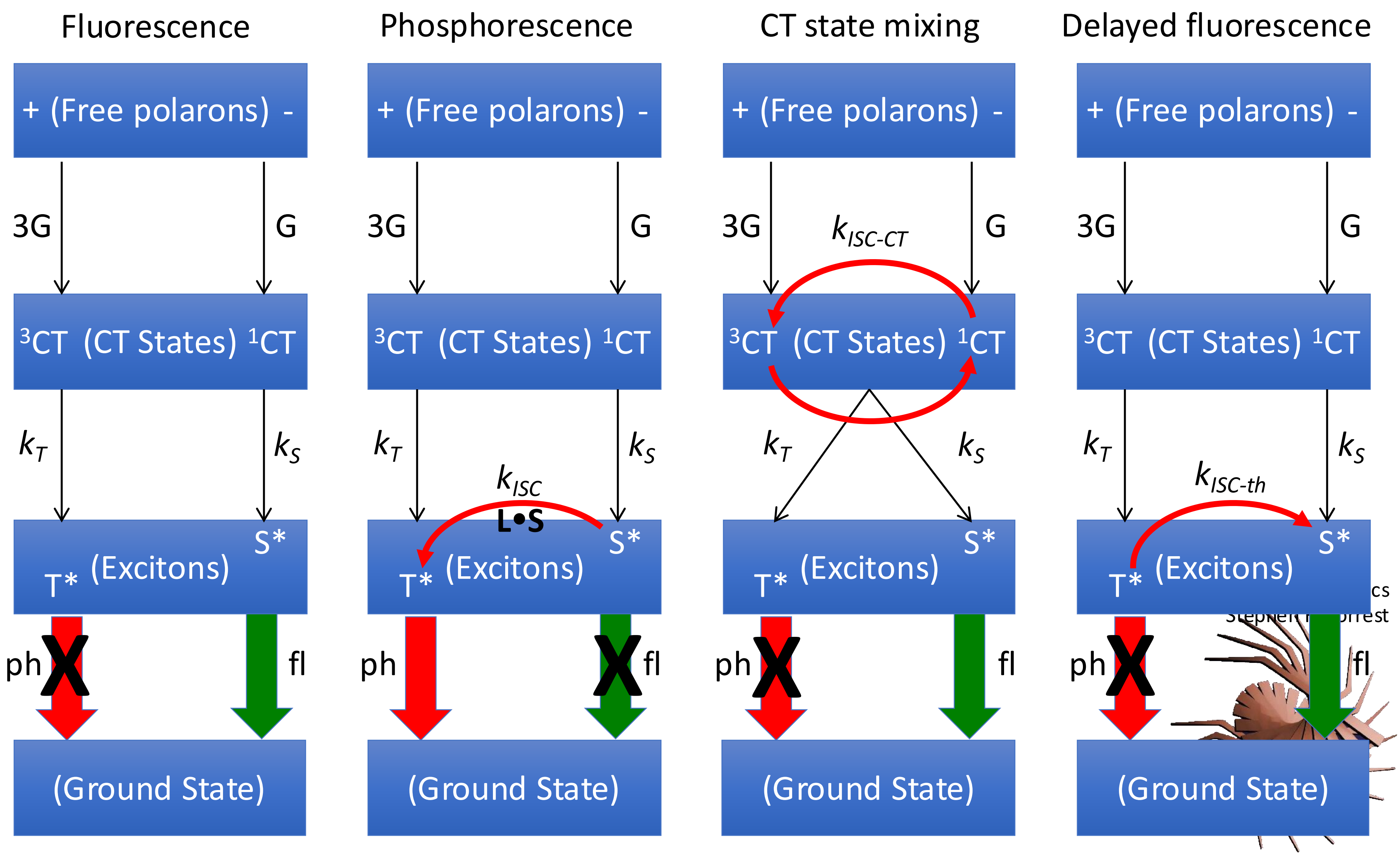
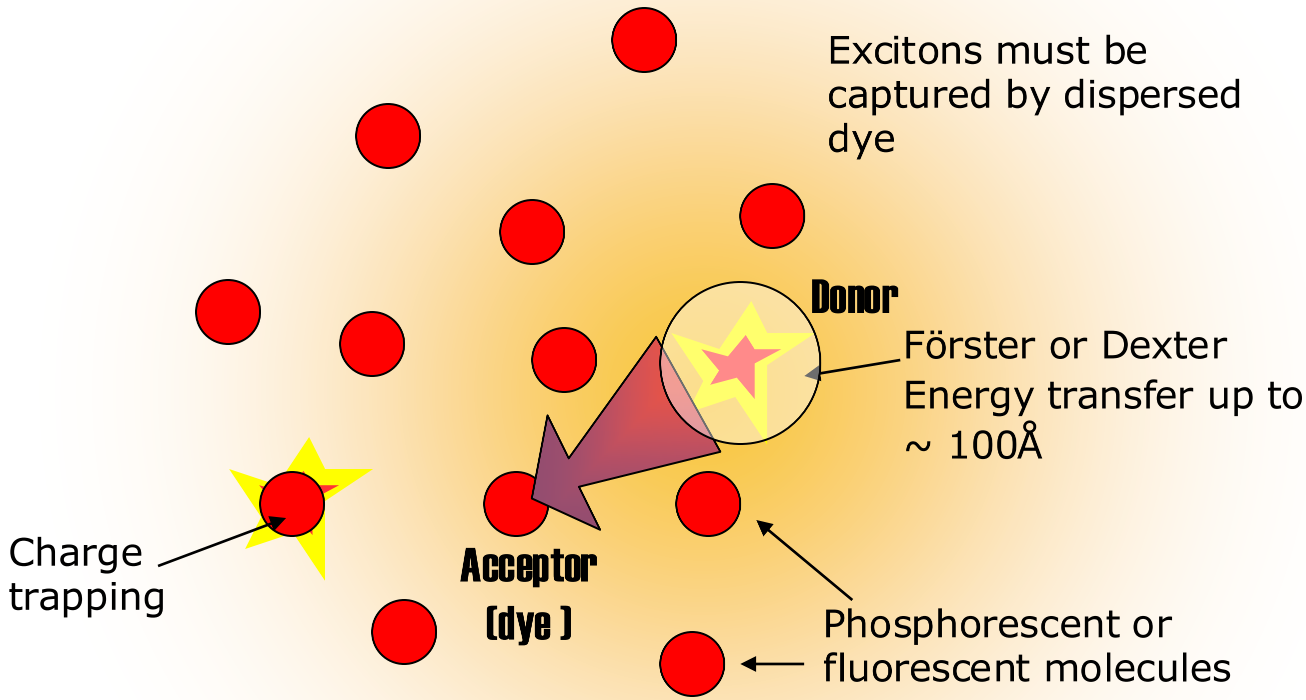
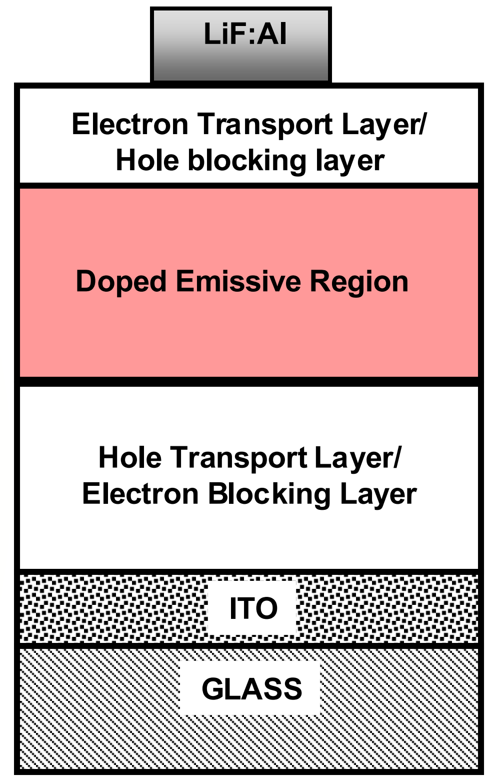
Singlet and triplet formation in OLEDs

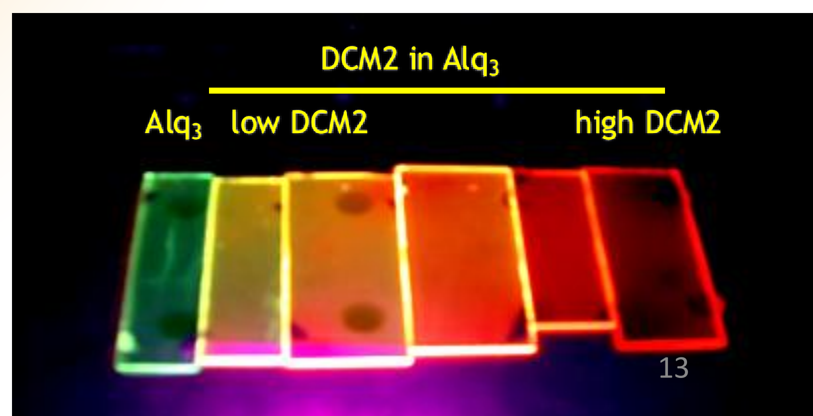


Efficiency Improves if Dopant Dispersed in Host





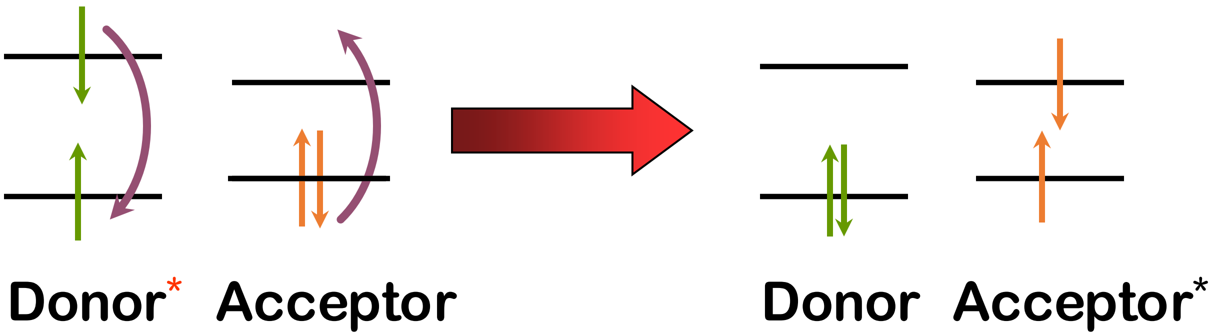
1. Charges trapped on dye molecules
2. Energy transferred from host
3. Effect used to increase color range and efficiency of OLEDs

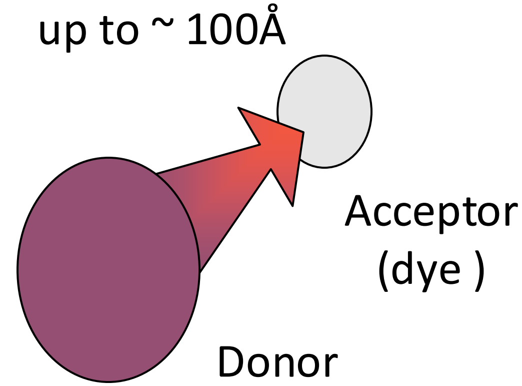


C. W. Tang, et al. *J. Appl. Phys.*, **65,** 3610 (1989).

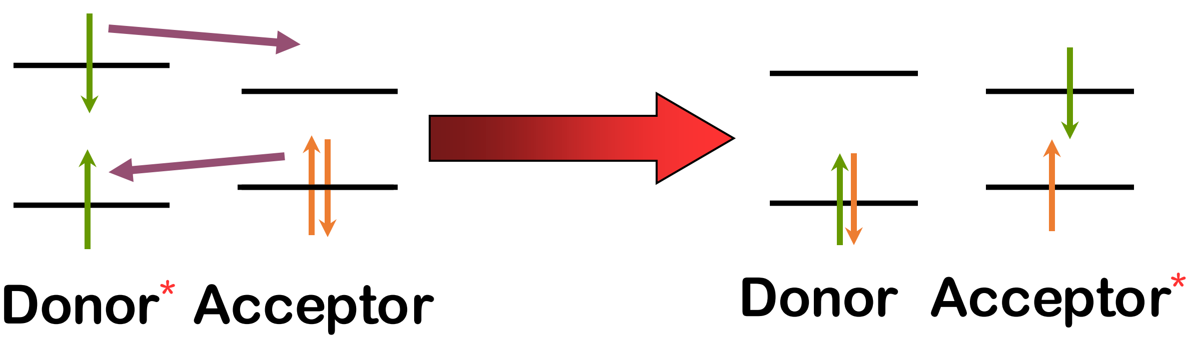
Energy Transfer from Host to Dopant: A Review

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

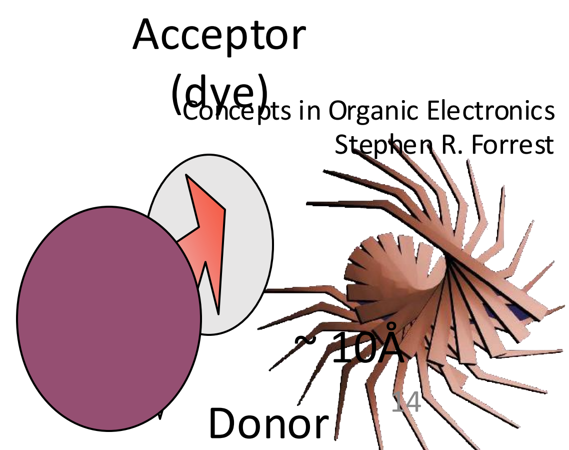




Electron Exchange (Dexter):
- diffusion of excitons from donor to acceptor by simultaneous charge exchange: short range



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



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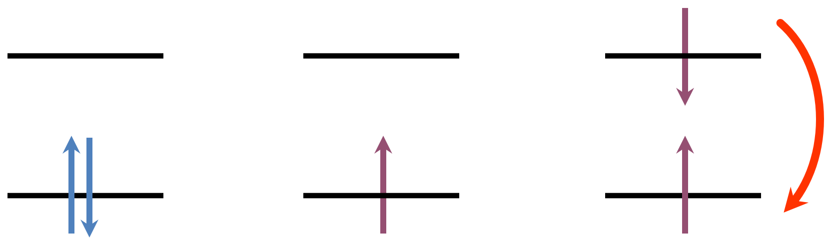
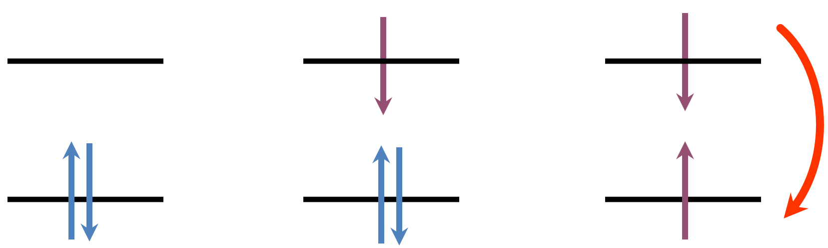
Direct trapping on the lumophore

Cation formation by electrical injection

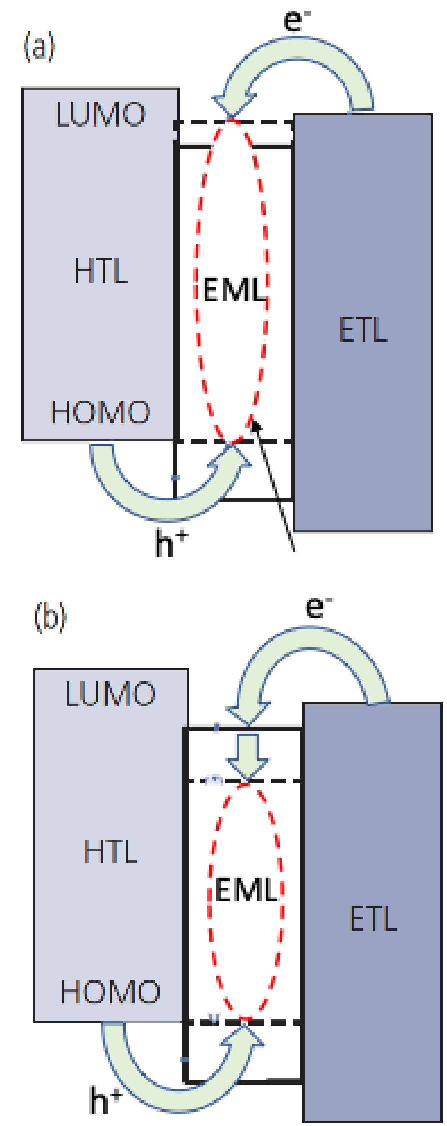


Acceptor^0 Acceptor$^+$ Acceptor* Acceptor^0

Or, anion formation



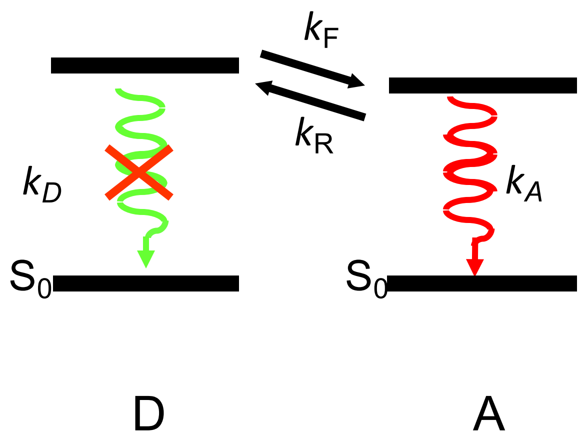
Acceptor^0 Acceptor$^-$ Acceptor* Acceptor^0



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

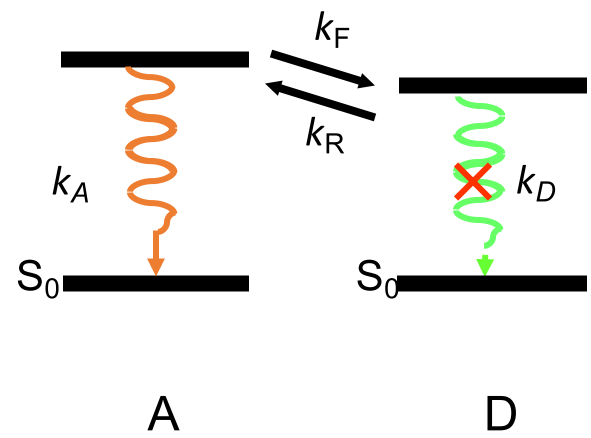
Energy transfer rates and directions

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

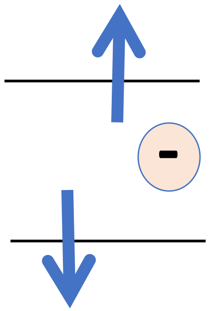


- Acceptor energy ~ Donor energy
- $k_F \sim k_R > k_A > k_D$
- Radiative rate determined by k_A, k_R
- Route for green and blue emission
- Similar to TADF, delayed fluorescence

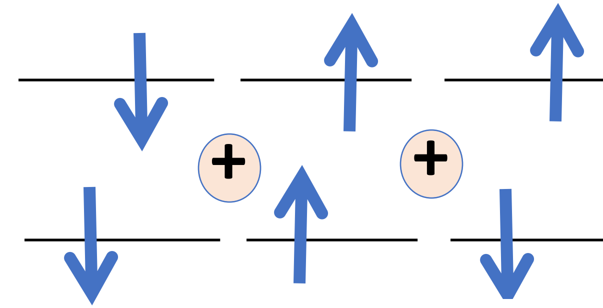
100% Internal Efficiency via Spin-Orbit Coupling

Heavy metal induced electrophosphorescence ~100% QE

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



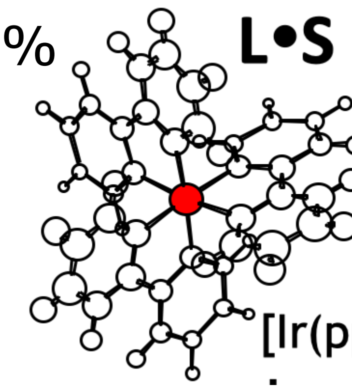
MOLECULAR EXCITED STATES
AFTER ELECTRICAL EXCITATION



Singlet 25%
spin anti-symmetric

75% **Triplet**
spin symmetric

100% **L•S**



$[Ir(ppy)_3]$

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

Relaxation disallowed
slow, inefficient
'Phosphorescence'

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

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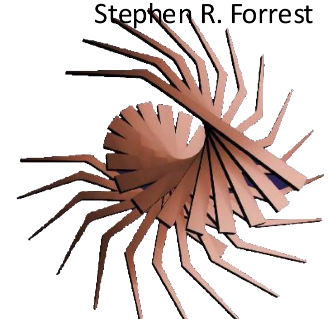
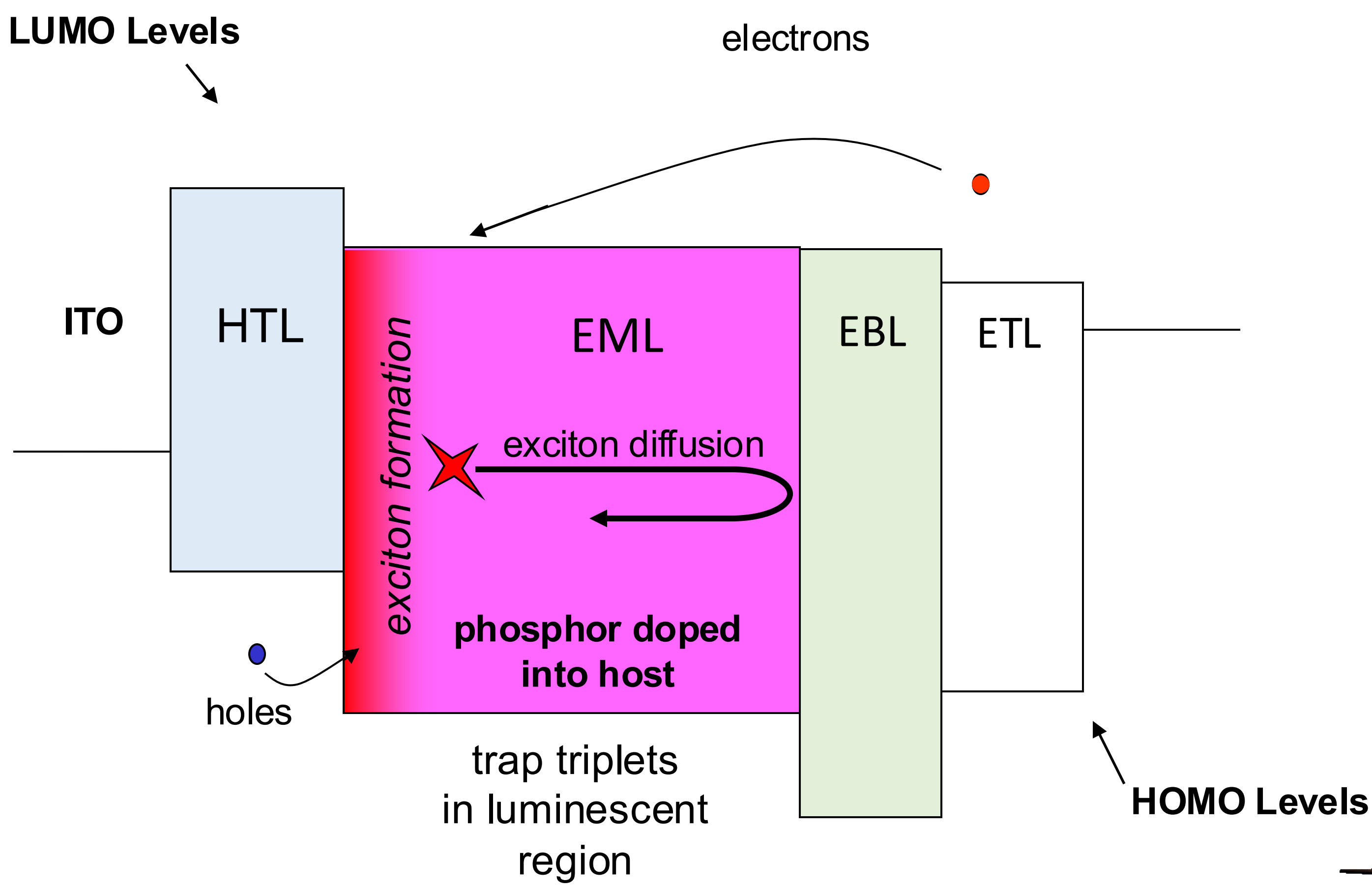
Relaxation allowed
not so slow, efficient
'Phosphorescence'



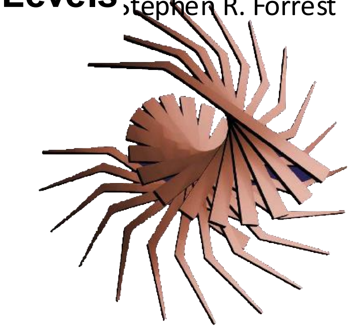
GROUND STATE
spin anti-symmetric

Electrophosphorescent (PHOLED) Device Structure



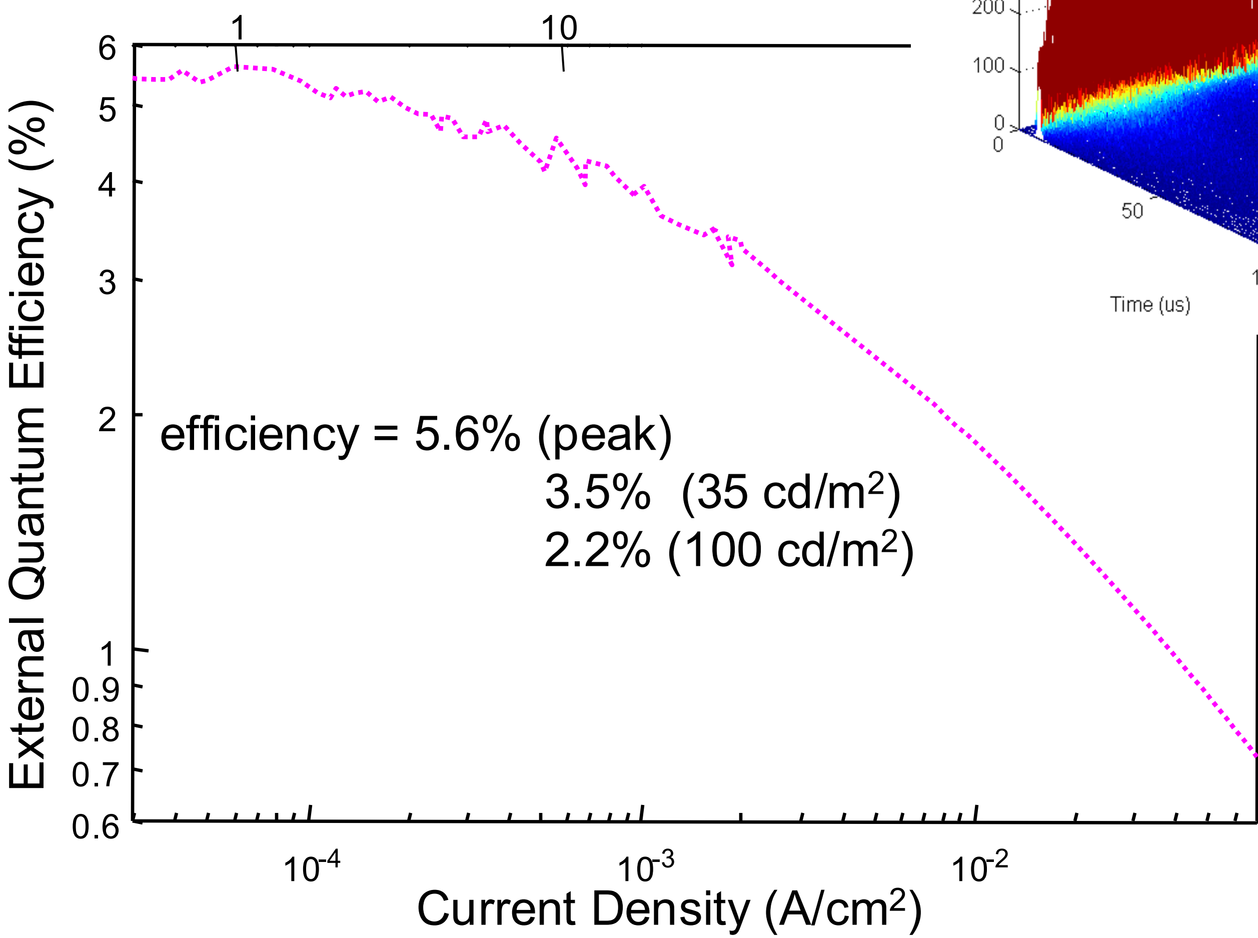
EBL = exciton/electron blocking layer.

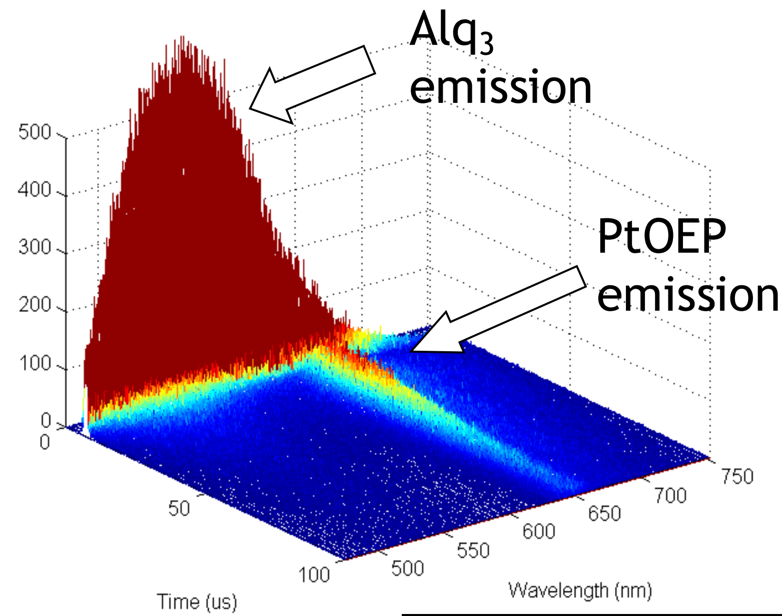
- Increases charge balance factor
- Prevents quenching of excitons at ETL and cathode

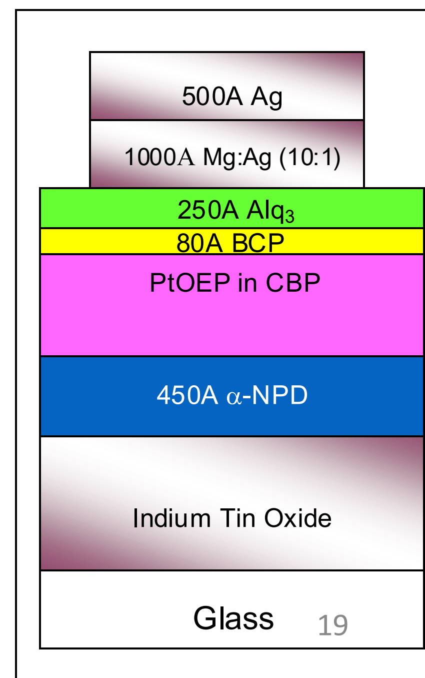


6% PtOEP in CBP: The first PHOLED

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



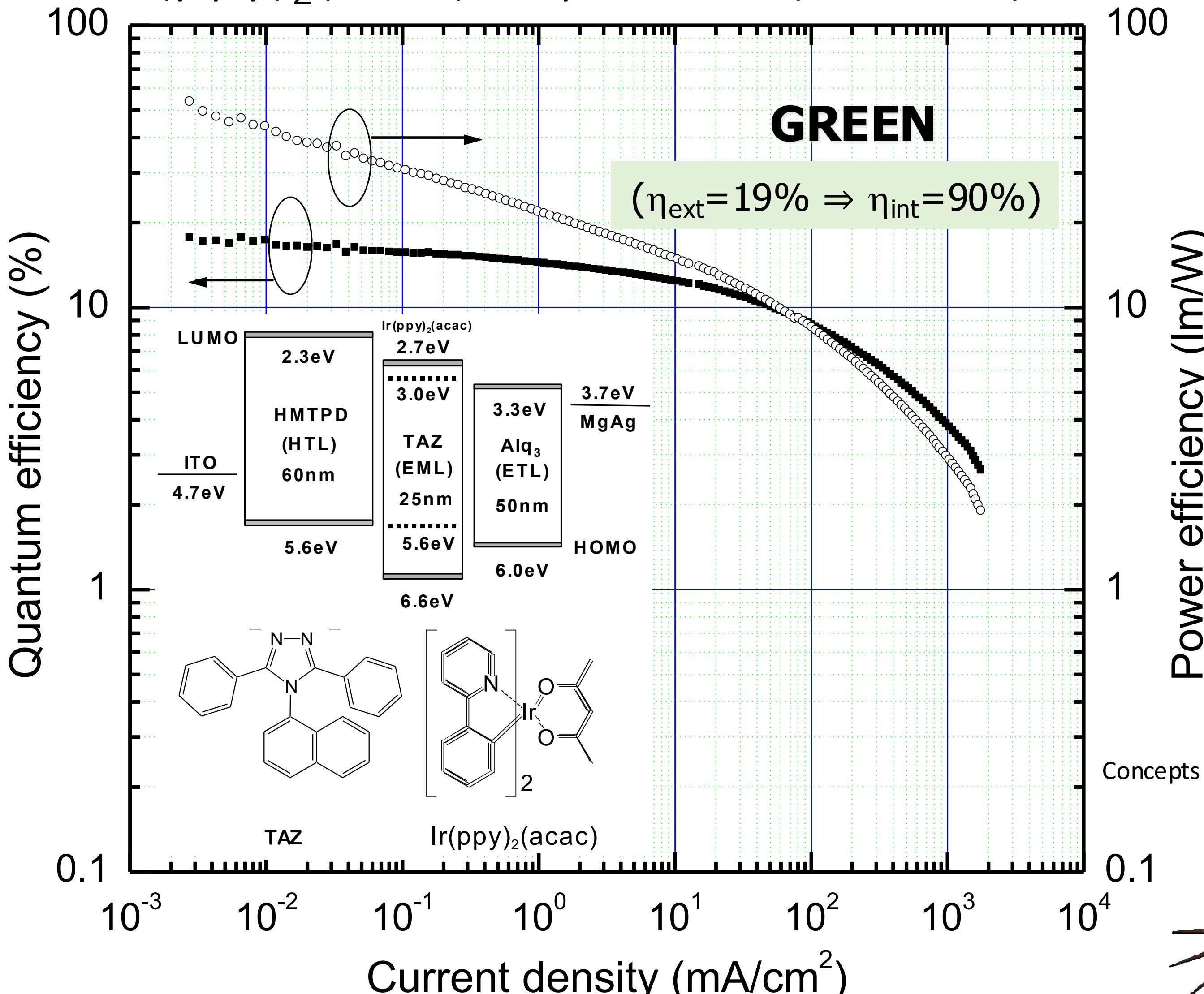




Baldo, et al., Nature **395**, 151 (1998)

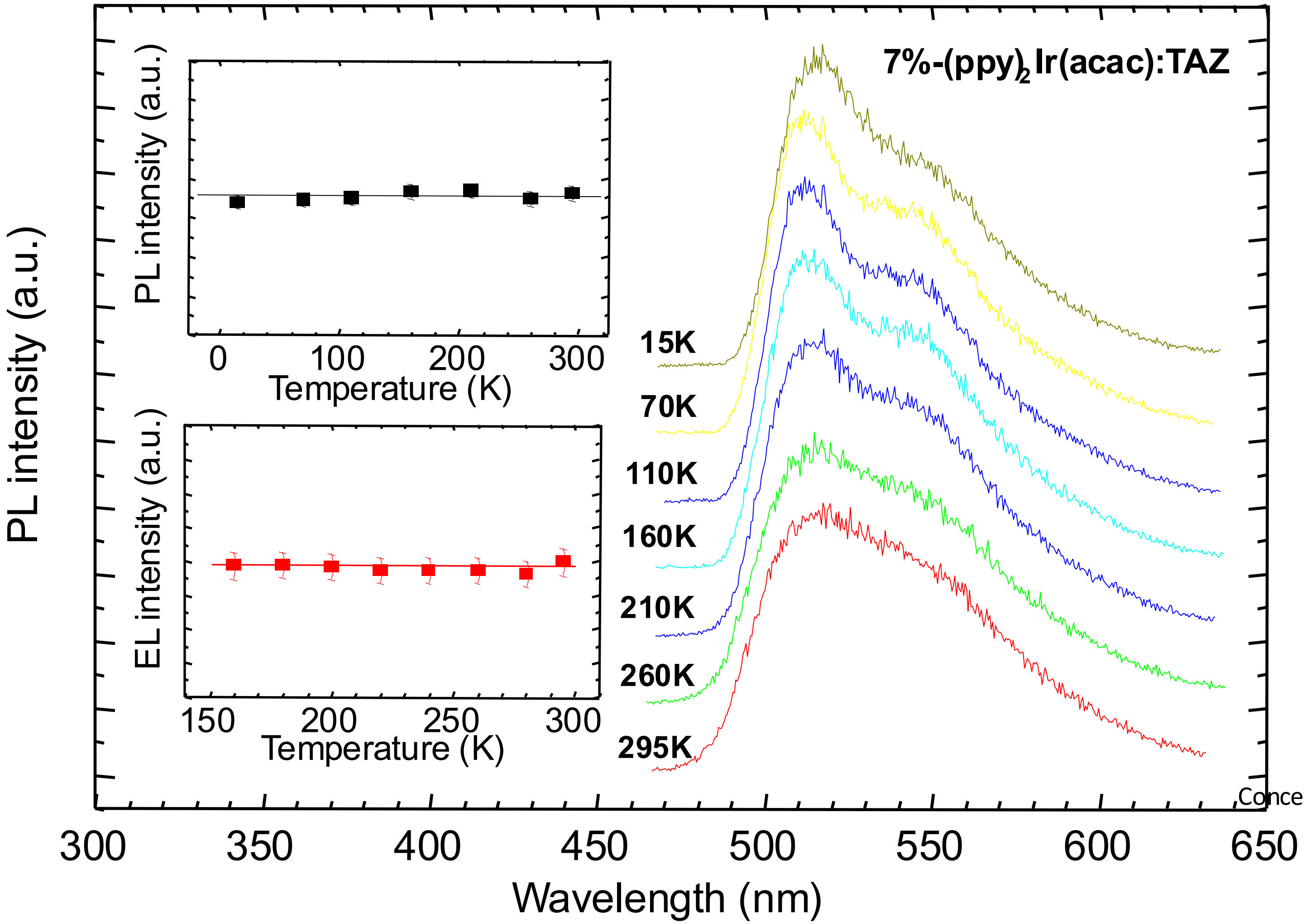
100% Efficient PHOLEDs

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



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

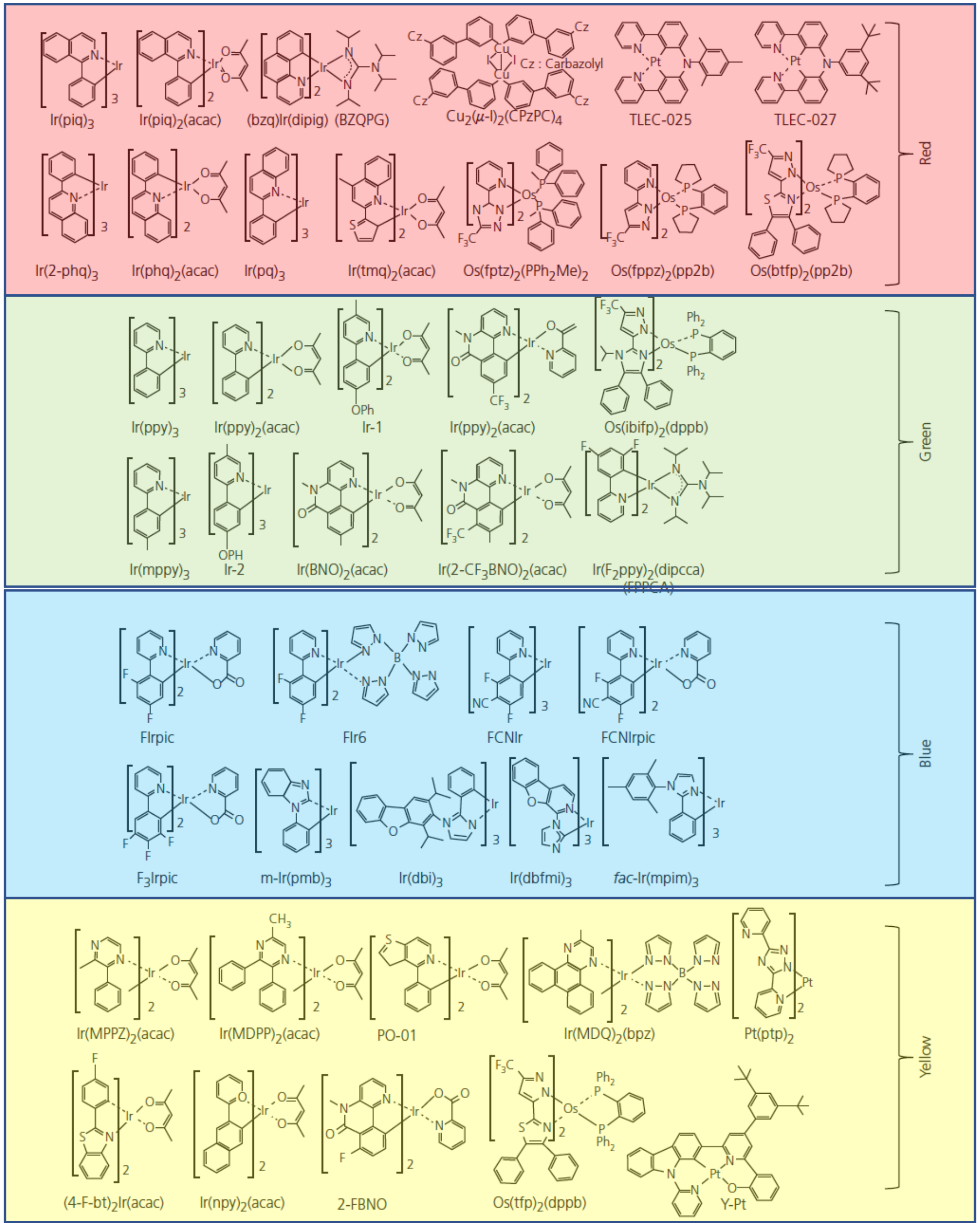
Temperature Independent PL and EL



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

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

Got Color? A few metalorganic complexes emitting in the visible



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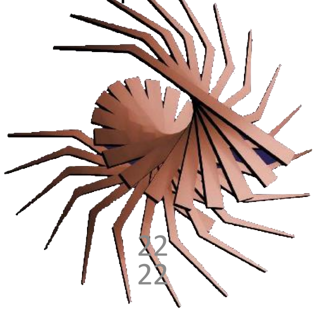
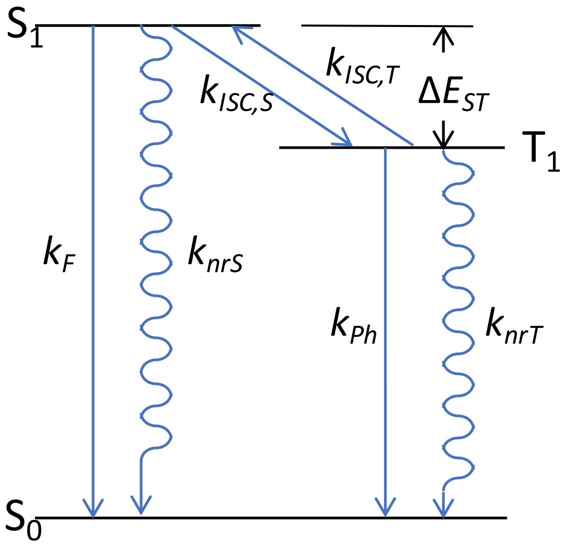


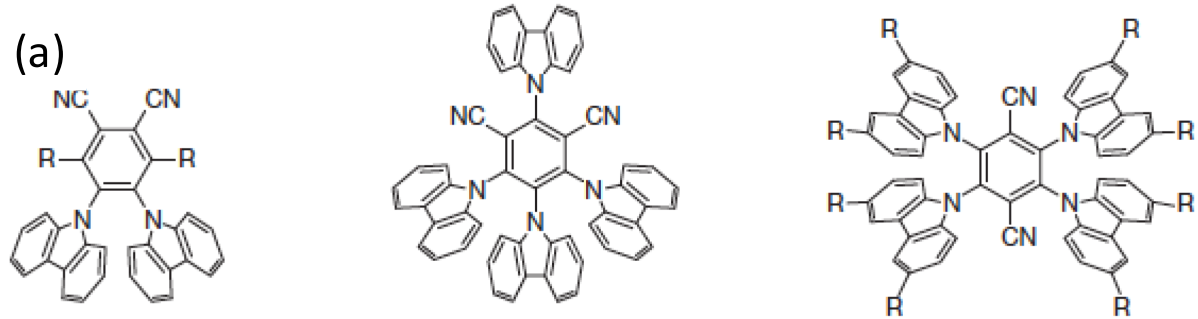
TADF: Another approach to high efficiency

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



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

b (a)

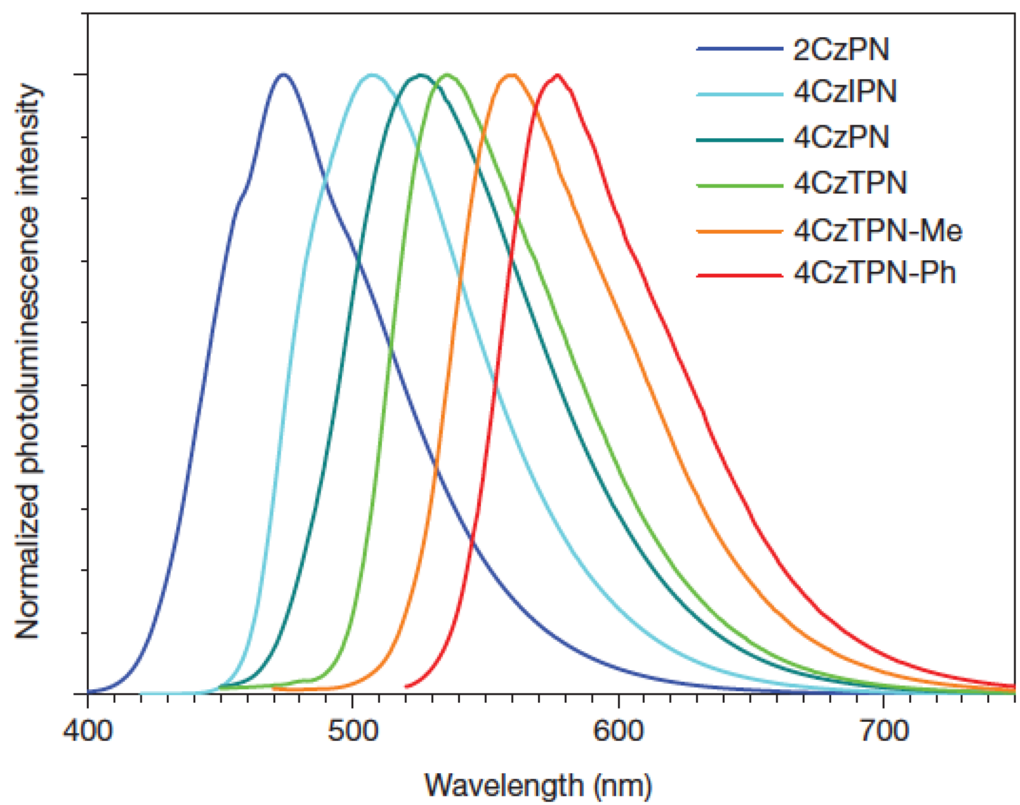


4CzPN: R = carbazolyl
2CzPN: R = H

4CzIPN

4CzTPN: R = H
4CzTPN-Me: R = Me
4CzTPN-Ph: R = Ph

(b)



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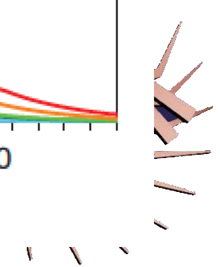
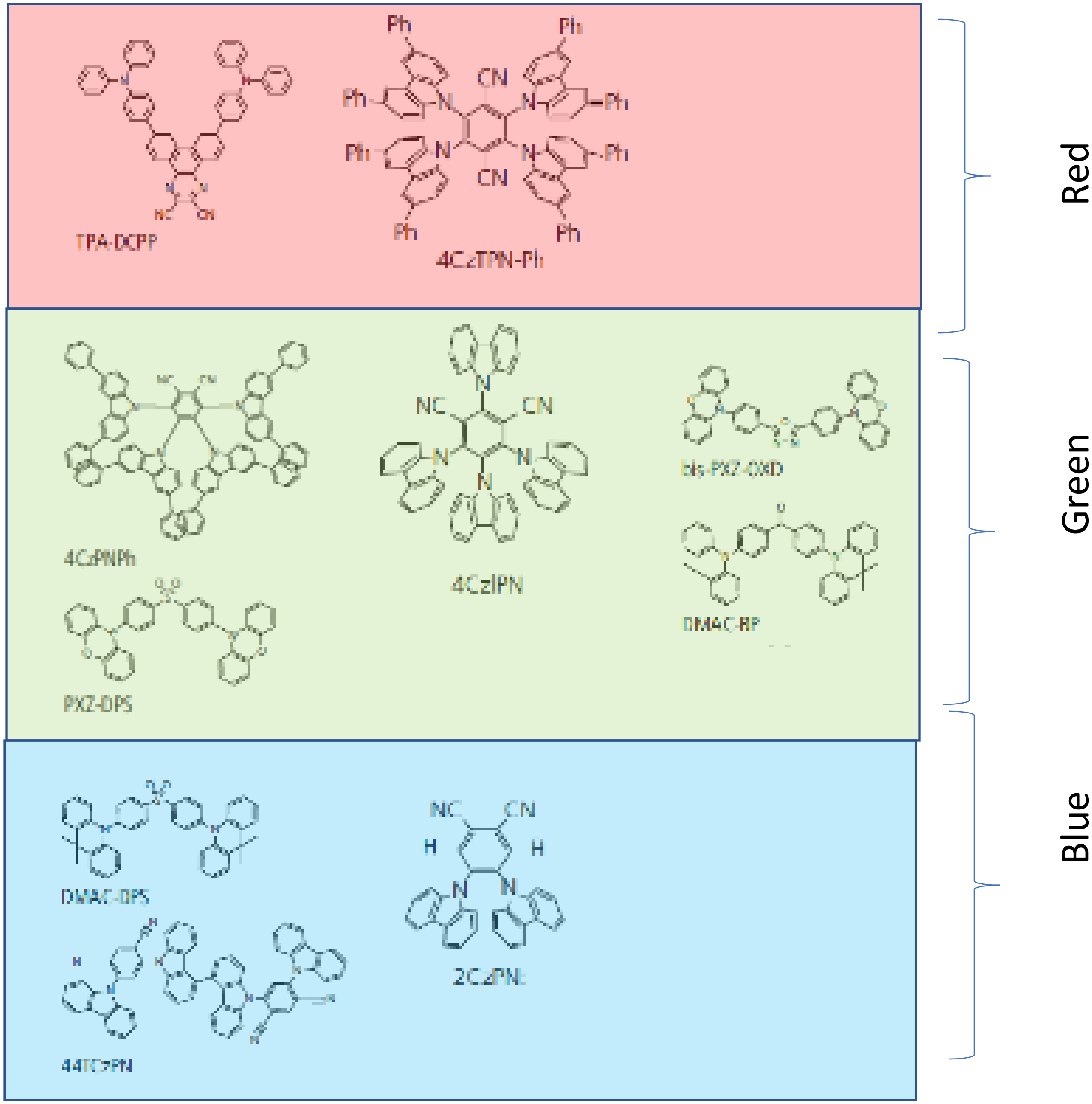
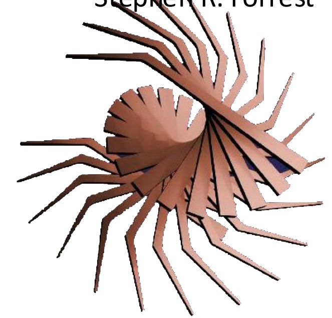


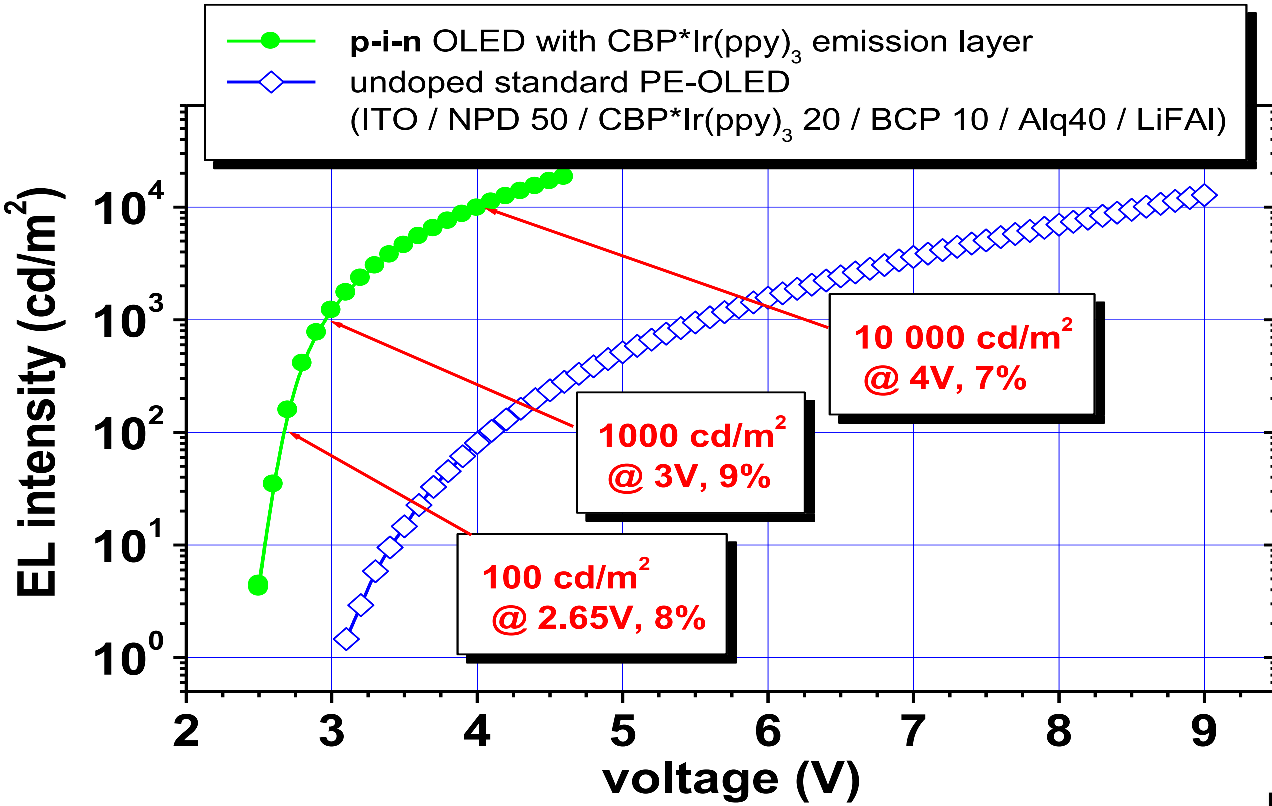
Example organic TADF molecules

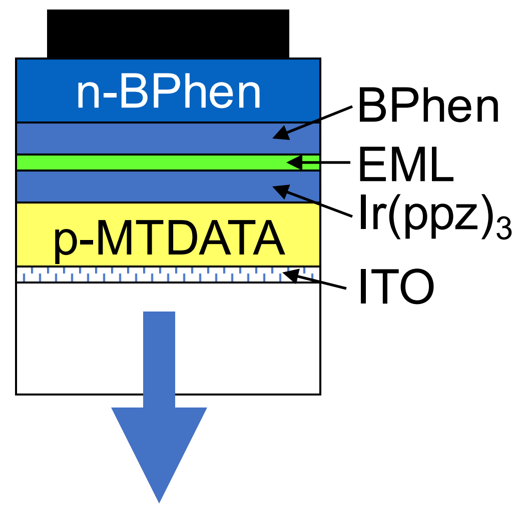




Low voltage high efficiency p-i-n PHOLEDs

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



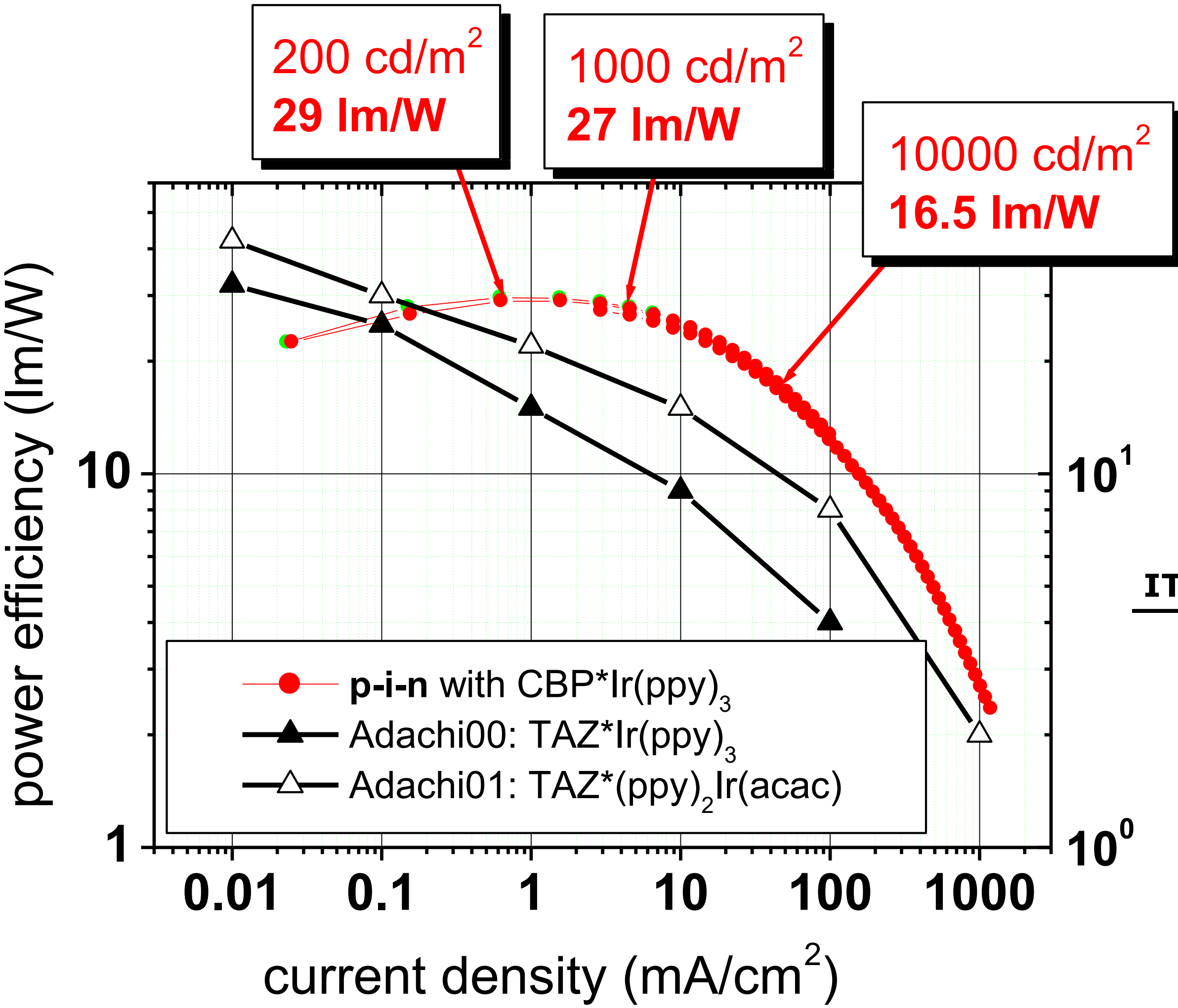


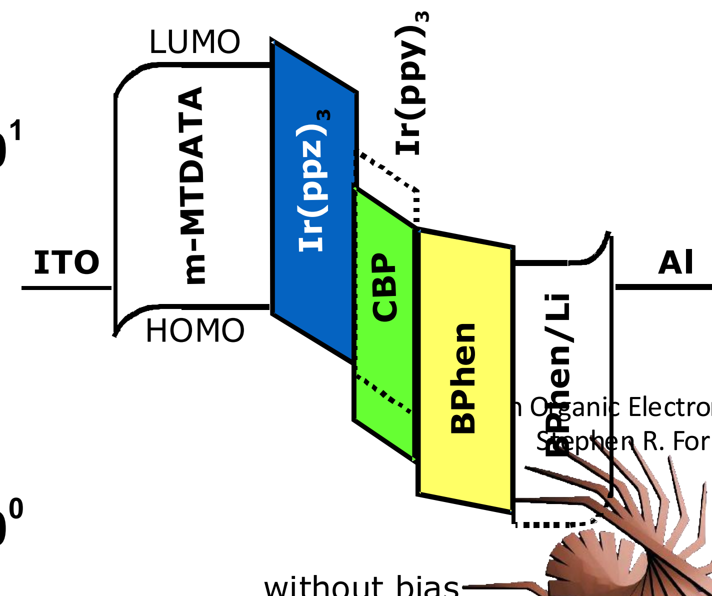
p-i-n PHOLED Structure

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

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

Low voltage high efficiency p-i-n PHOLEDs

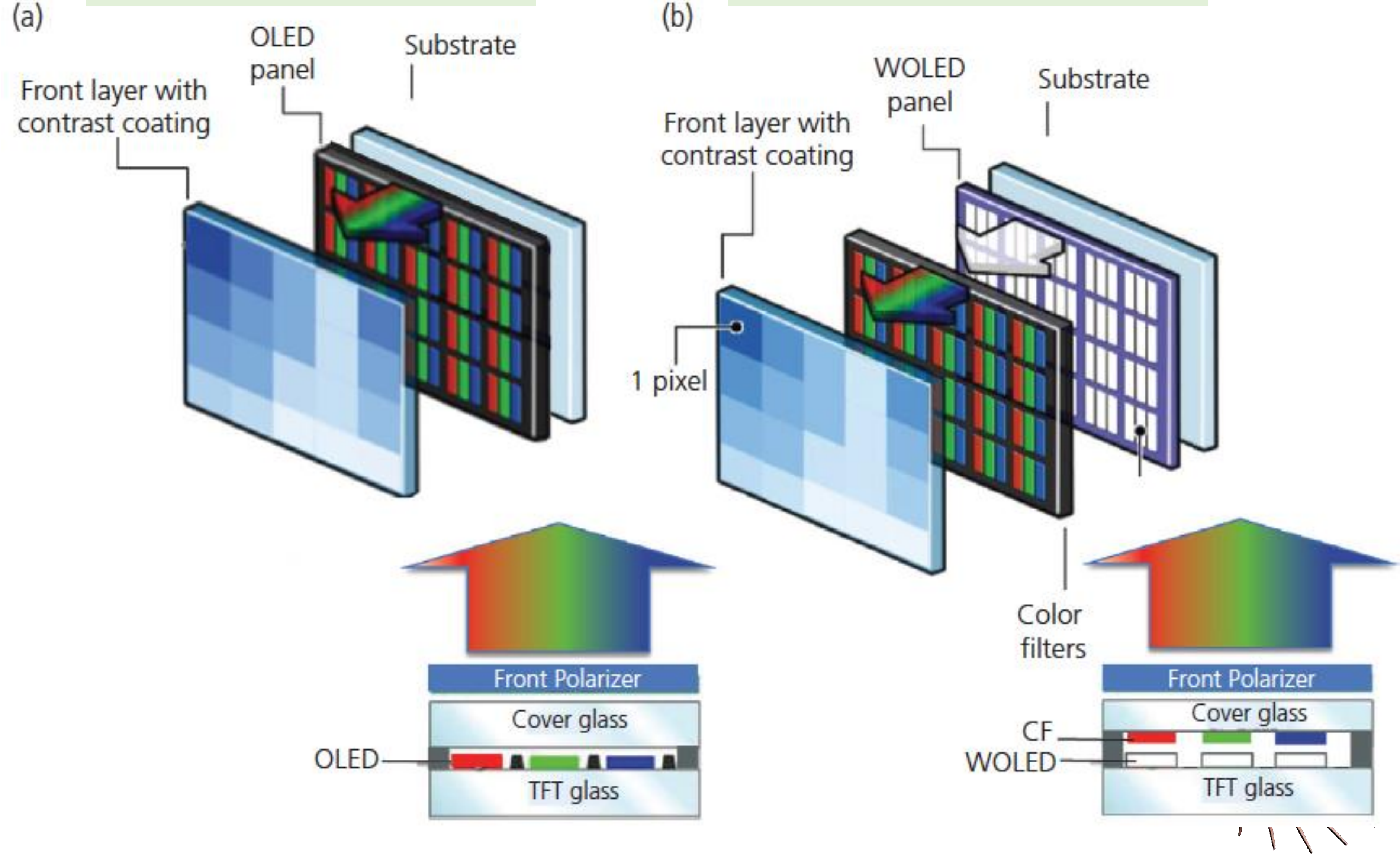




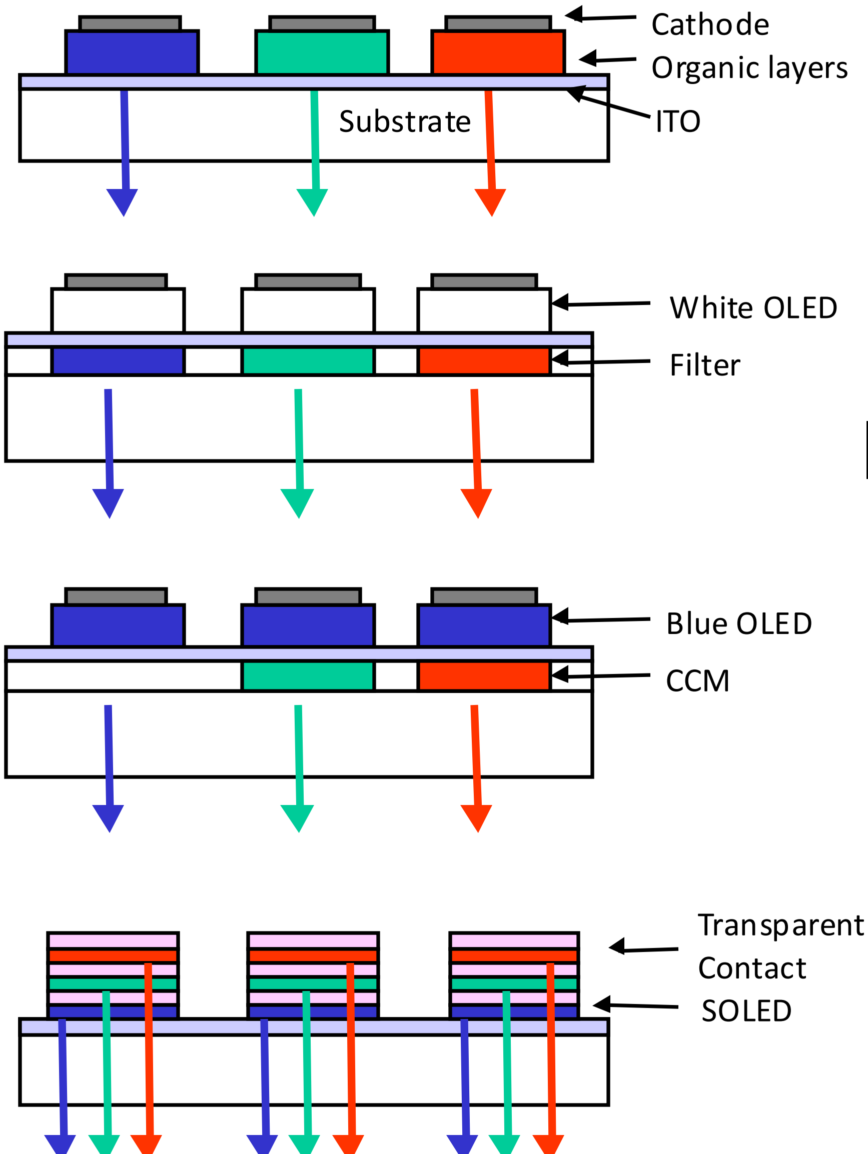
Pfeiffer, M., et al. *Org. Electron.*, **4,** 89 (2003).

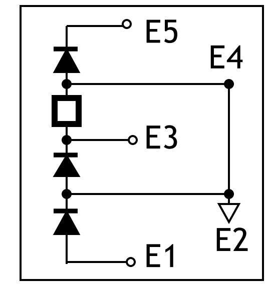
Two OLED Display Architectures

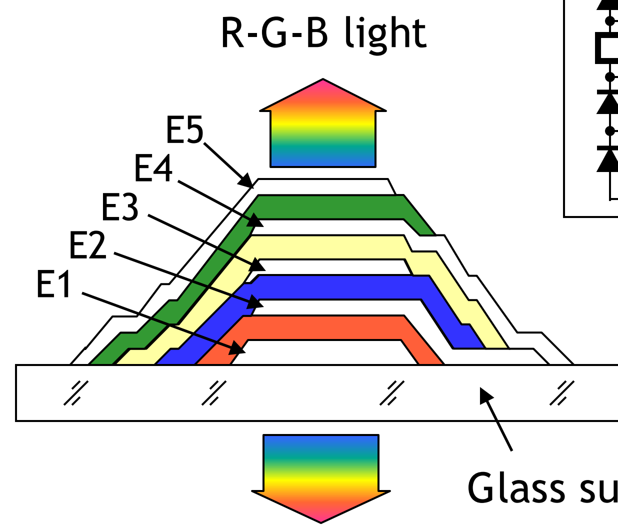
Separate RGB pixellation Preferred for mobile displays	WOLED + Color Filters Preferred for TVs and monitors

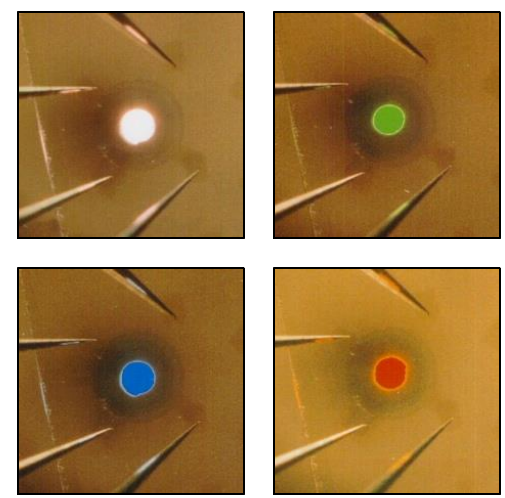


Pixel Arrangements for OLED Displays



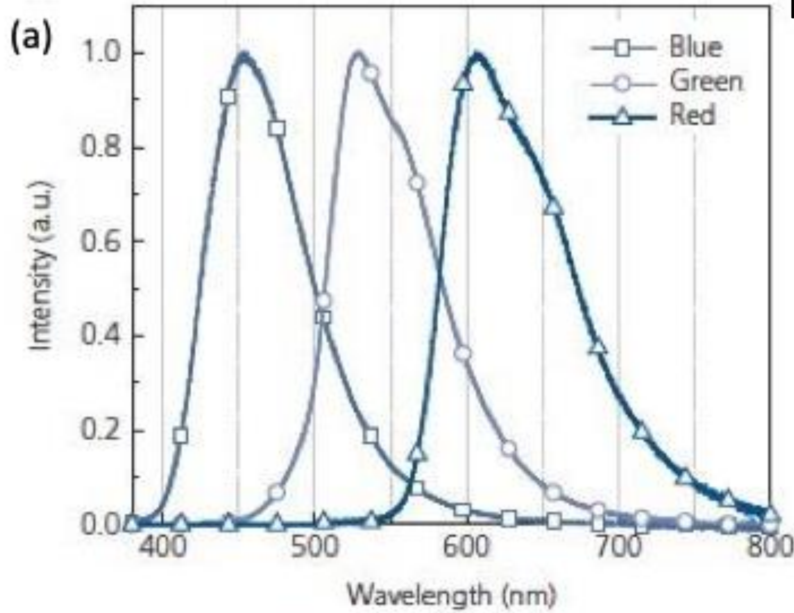




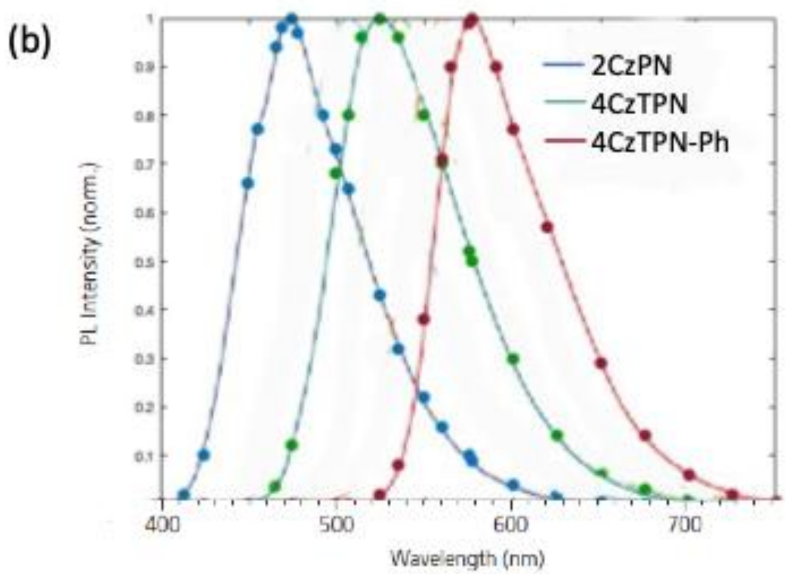


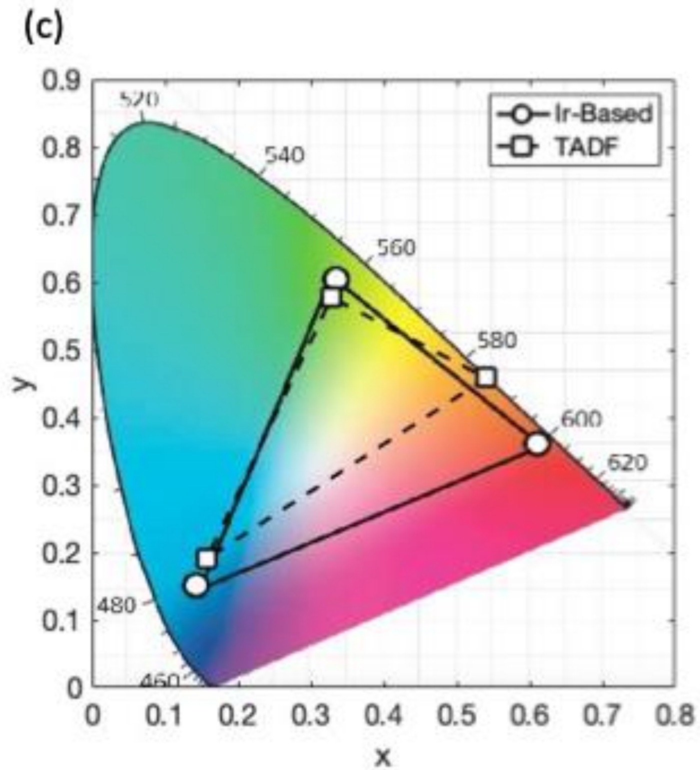
G. Parthasarathy, et al., *Adv. Mater.*, **11**, 907 (1999).

Example Color Gamuts for PHOLEDs and TADF OLEDs



R,G, B PHOLEDs





TADF OLEDs

Note: these are examples. Larger gamuts can be achieved using different chromophores

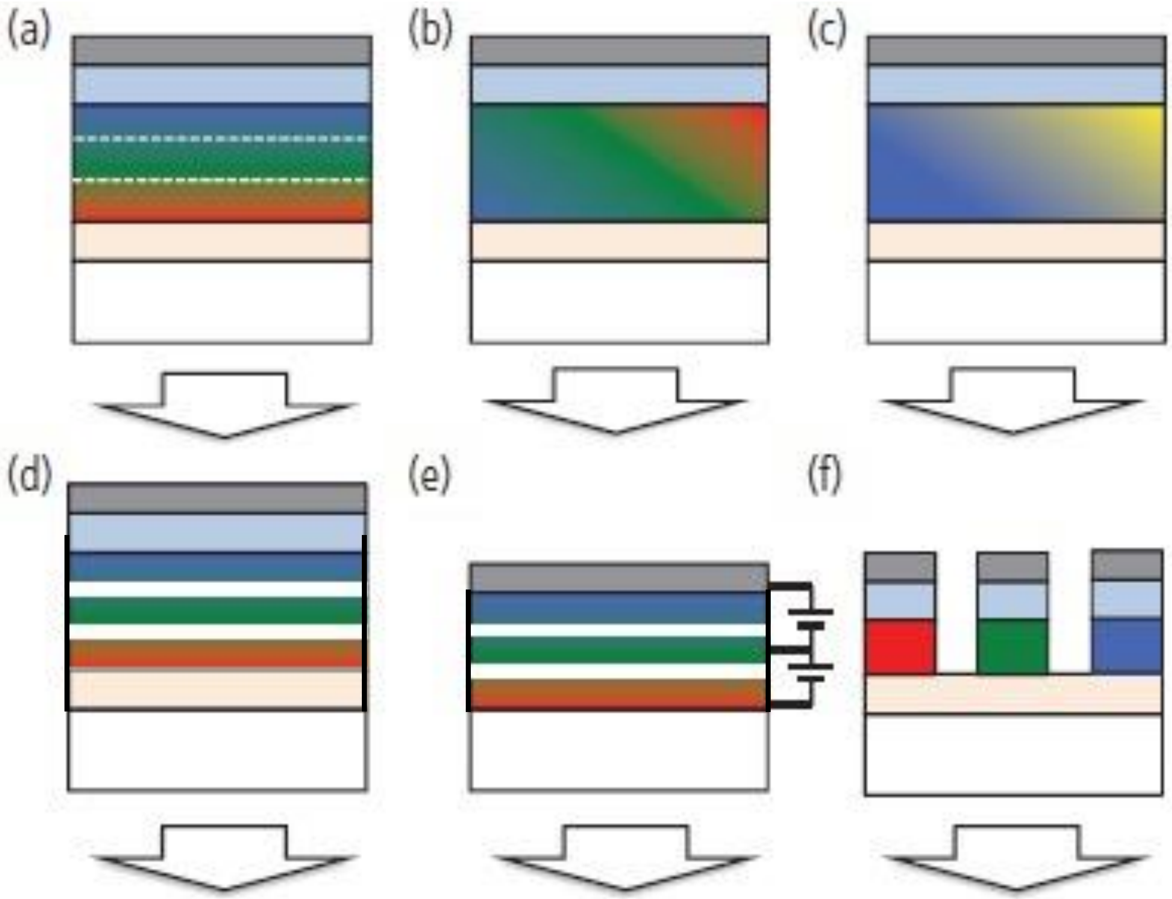
WOLED Challenges

- Good color rendering (high CRI) at the desired CCT
- High efficiency at high intensity
  - Managing triplets
  - Outcoupling
- Long-lived blue
  - Managing triplets
- Thermal management
- Cost reduction

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

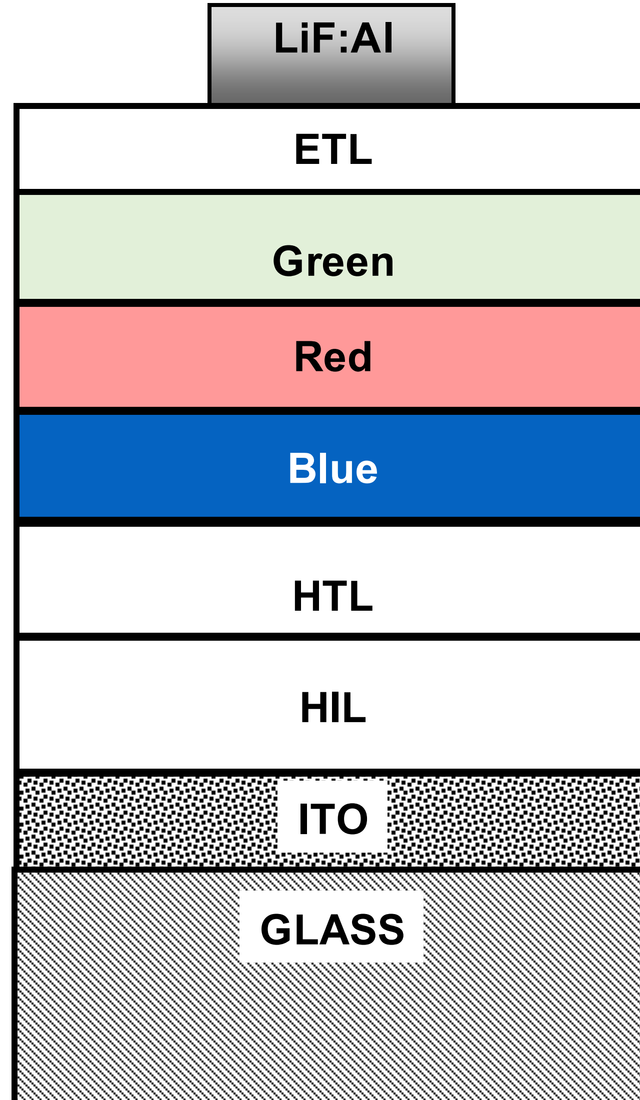
Generating white light by blending combinations of R, Y, G, B



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



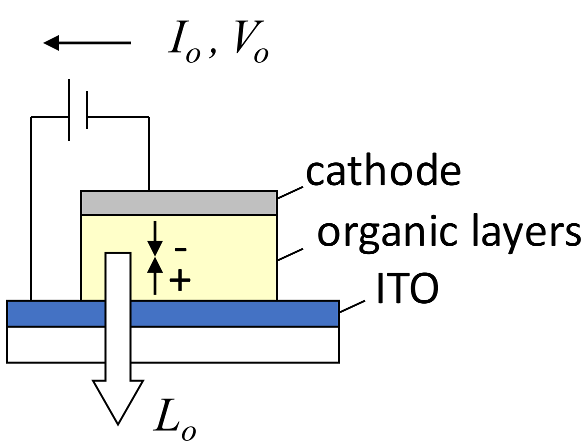
Why does it work?

- Triplets can diffuse much further than singlets (measured ~100 nm)
- Good control over diffusion of excitons using interface blocking layers and layer thickness

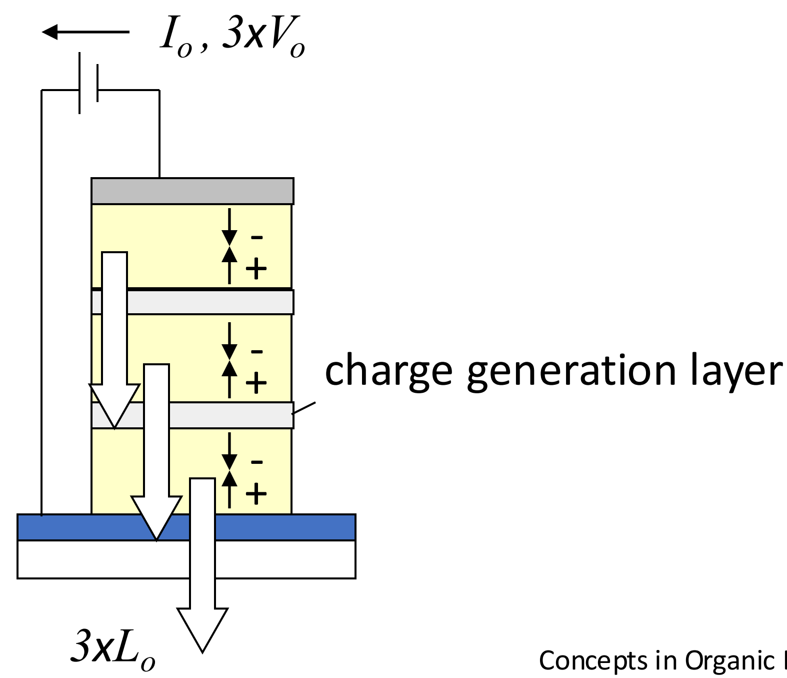
White Stacked OLEDs

Requires less current for same luminance as a single unit device

- Longer lifetime at same luminance
- Less current for a given luminance = reduced resistive power losses and heating



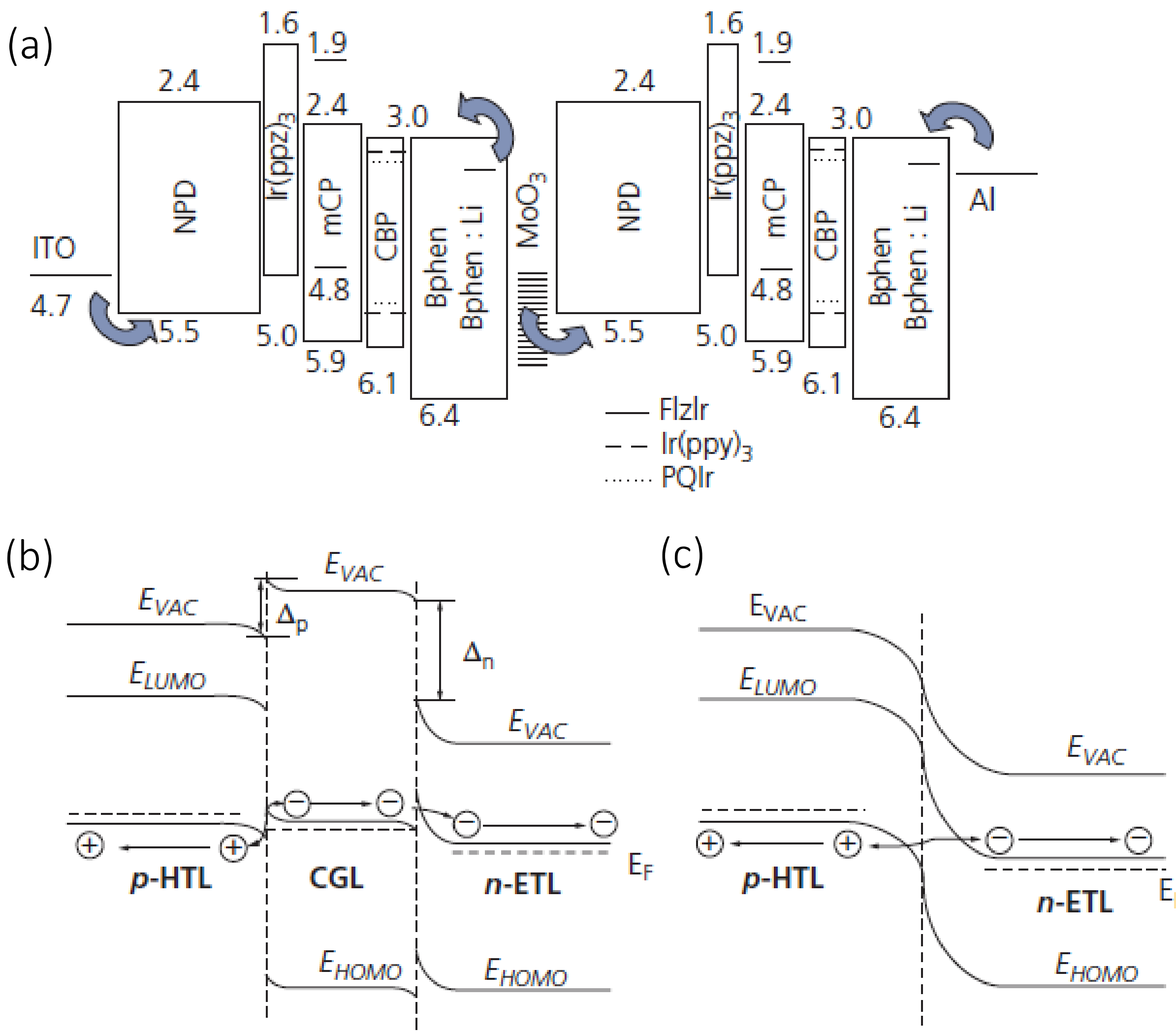
Conventional OLED



Stacked OLED (SOLED)

Lifetime and efficiency of OLEDs can be increased by vertically stacking multiple OLED units in series

Transparent Charge Generation Layers Required for SOLED Efficiency

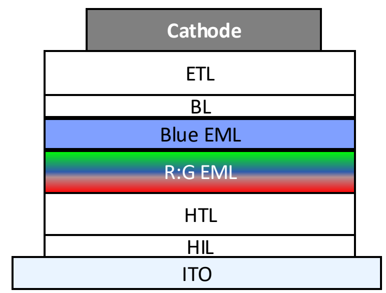


Concepts in Organic Electronics
Stephen R. Forrest

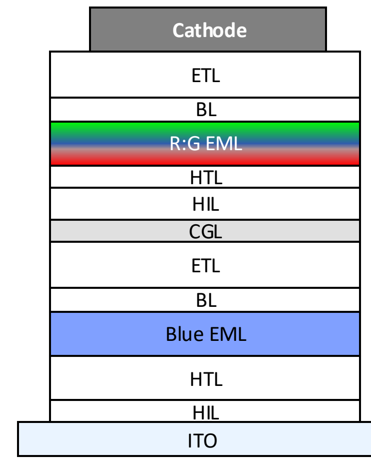
Phosphorescent WOLED vs. SOLED Panel Comparison

Panel 15 cm x 15 cm 82% fill factor	Single Unit WOLED*	2 Unit WSOLED
Luminance [cd/m^2]	**3,000**	**3,000**
Efficacy [lm/W]	**49**	**48**
CRI	**83**	**86**
Luminous Emittance [lm/m^2]	7,740	7,740
Voltage [V]	4.3	7.4
1931 CIE	(0.471, 0.413)	(0.454, 0.426)
Duv	0.000	0.006
CCT [K]	2,580	2,908
Temperature [^{o}C]	**27.2**	**26.2**
LT_{70} [hrs]	**4,000**	**13,000**

P.Levermore et al, SID Digest, 72.2, 1060, (2011).



WOLED

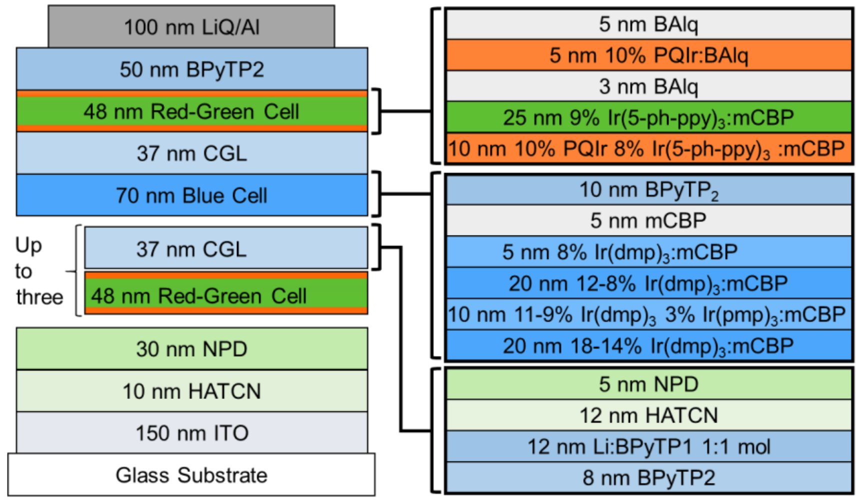


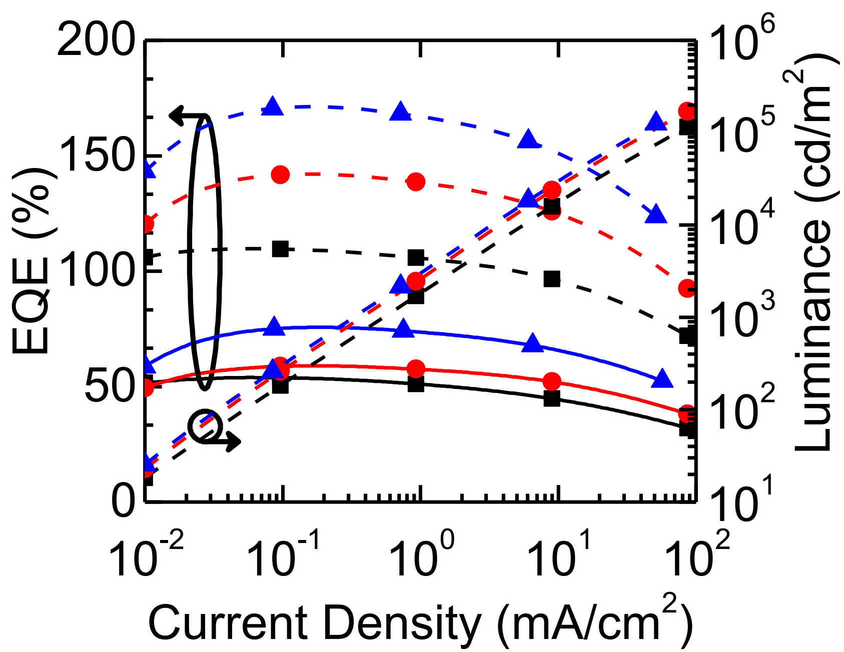
SOLED

Con lectronics
R. Forrest

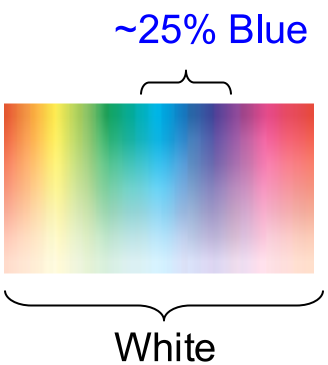
SOLED architecture: ~ 3x LT_{70} improvement vs. single unit WOLED with similar color and power efficacy

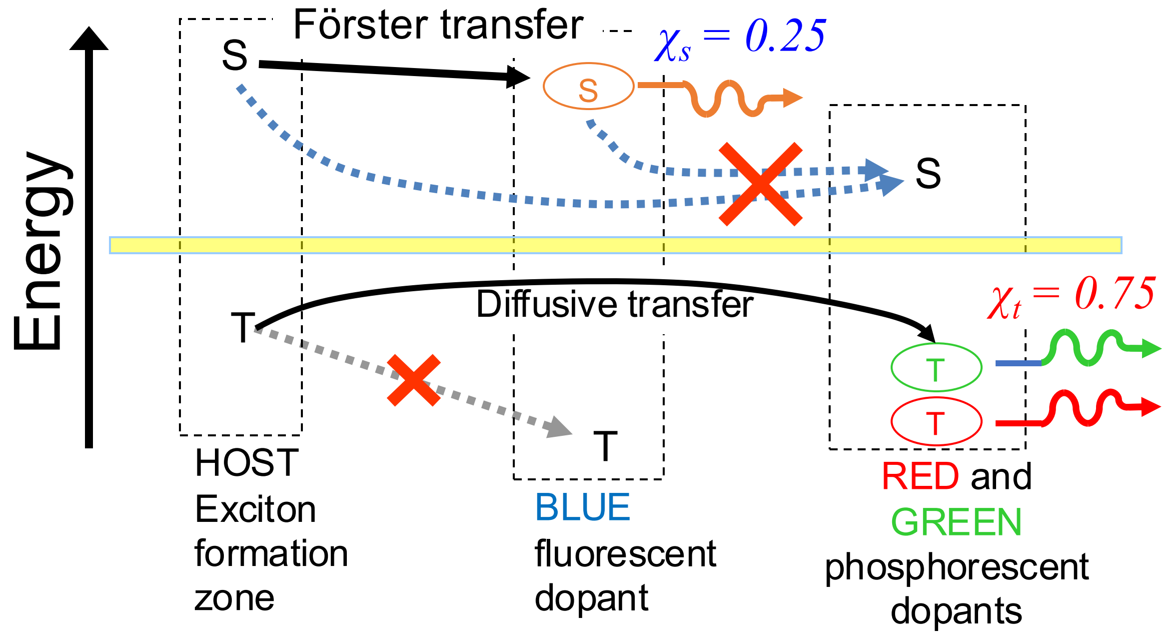
Brightness and lifetime increased using multistage PHOLEDs





Fluorescent/Phosphorescent WOLED





- Singlet and triplet excitons harvested along independent channels ➡ Resonant transfer of both excitonic species is independently optimized:
  - High energy singlet excitons for **blue** emission
  - Remainder of lower-energy triplet excitons for **green** and **red** emission

Minimizing exchange energy losses	Potential for 100% IQE
More stable color balance	Enhanced stability

(Y. Sun, et al., *Nature*, **440**, 908, 2006)