Week 9

Light emitters 2

Efficiency Rolloff
White OLEDs (WOLEDs)
Outcoupling Basics

Chapter 6.5-6.6.1

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
$E_S \geq 2E_T$

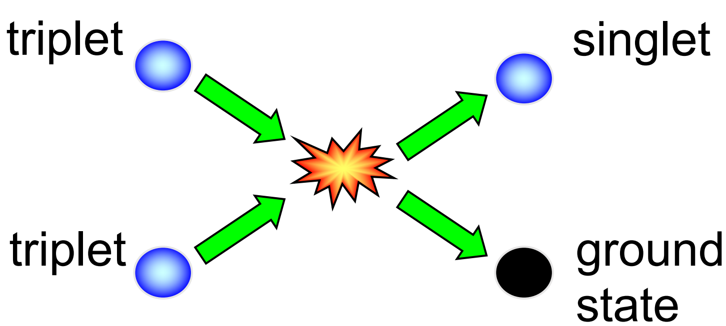
$$S \rightarrow 2T$$

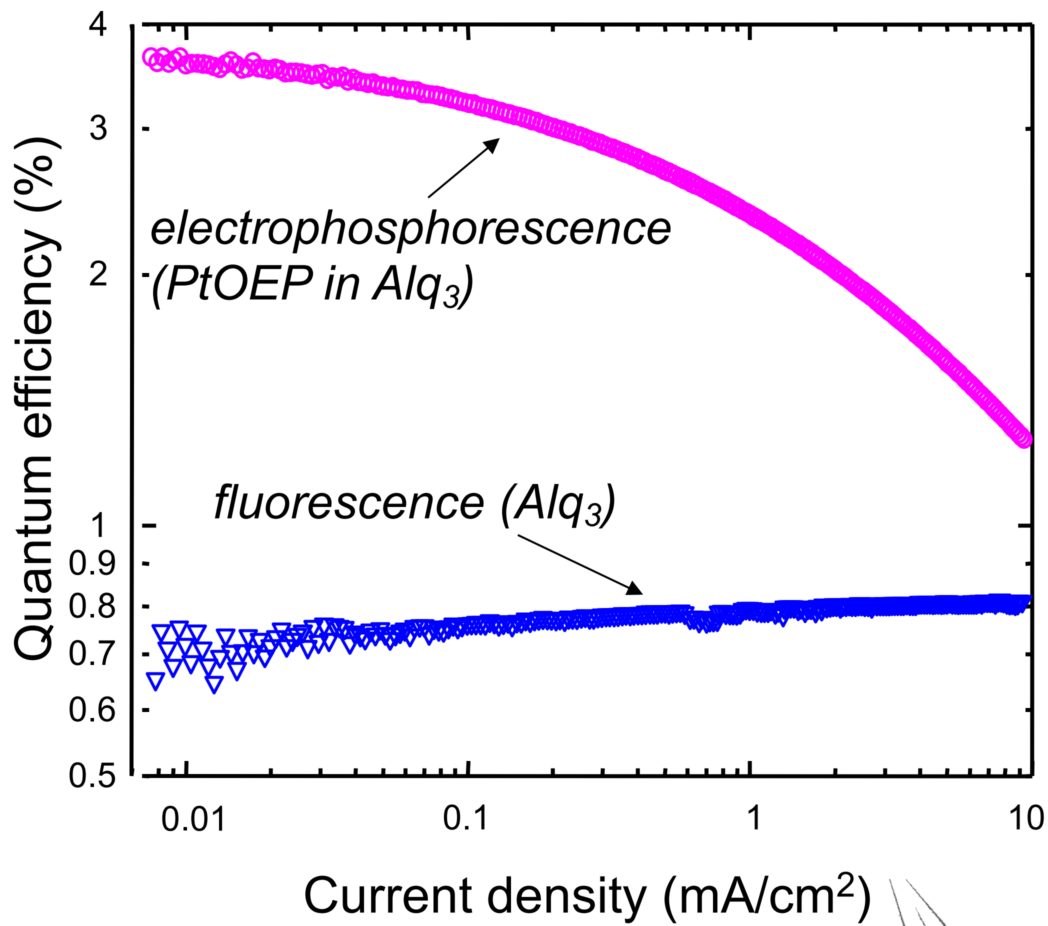
Efficiency Decreases with Increasing Current

Is it saturation of phosphorescent sites?

Current densities too low. Should be proportional to $1/J$ but actually closer to $1/\sqrt{J}$.

Or is it T-T annihilation?





How can the roll-off be minimized?

Roll-off due to TTA

T-T annihilation destroys two triplets and creates one singlet

$$^{3}M^{*} + {}^{3}M^{*} \rightarrow {}^{1}M^{*} + M$$

Transient model: $$\frac{d\left[{}^{3}M^{*}\right]}{dt} = -\frac{\left[{}^{3}M^{*}\right]}{\tau} - k_q\left[{}^{3}M^{*}\right]^2 + \frac{J}{qd}$$

τ : triplet lifetime	J : current density
k_q : T-T annihilation rate	d : thickness of active layer

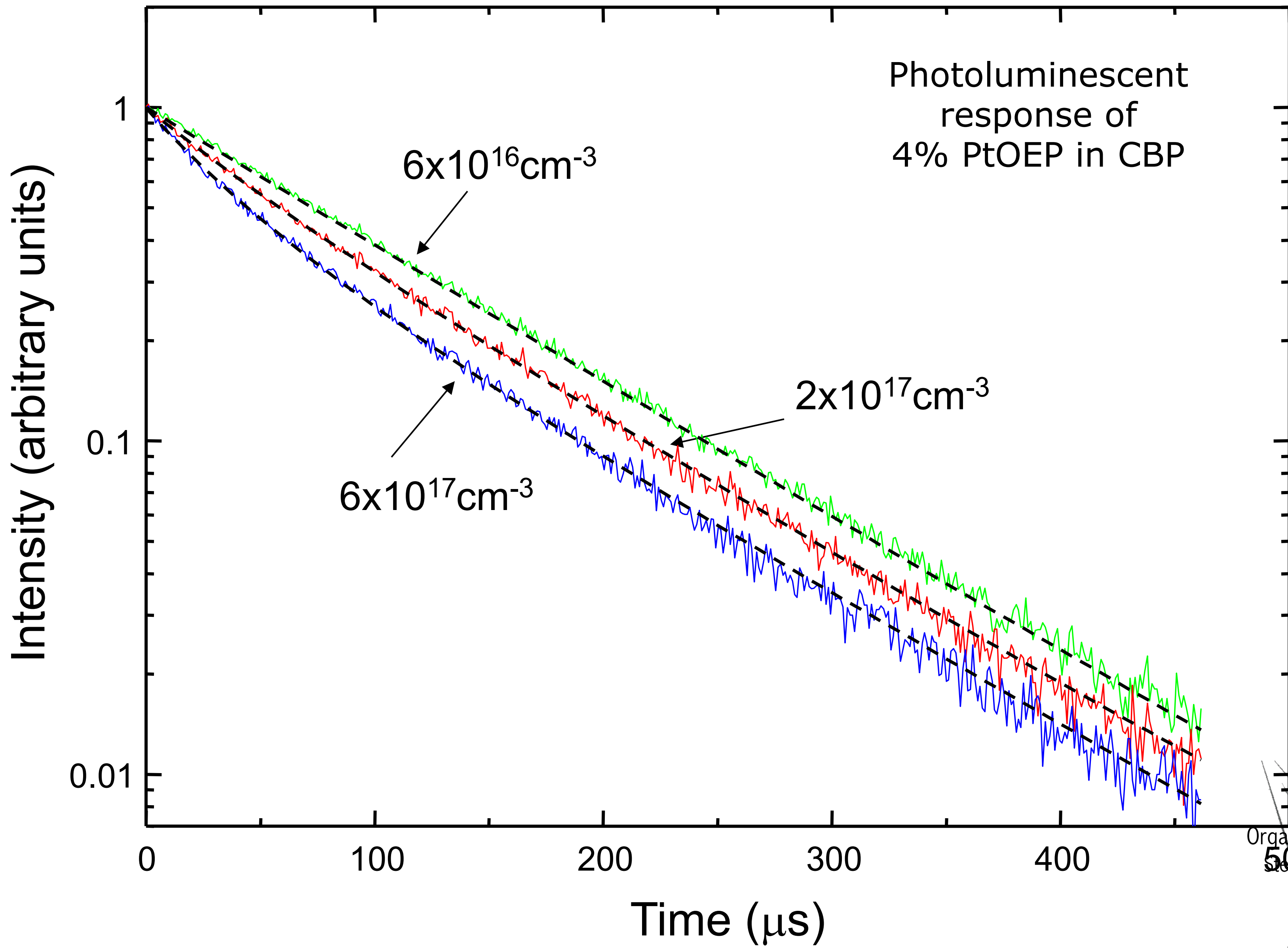
Transient solution: $$\left[{}^{3}M^{*}(t)\right] = \frac{\left[{}^{3}M^{*}(0)\right]}{\left(1+\left[{}^{3}M^{*}(0)\right]\tau k_q\right)e^{t/\tau} - \left[{}^{3}M^{*}(0)\right]\tau k_q}$$

Steady state solution: $$\frac{\eta}{\eta_0} = \frac{J_T}{4J}\left(\sqrt{1+8\frac{J}{J_T}} - 1\right)$$

η : quantum efficiency
η_0: max efficiency

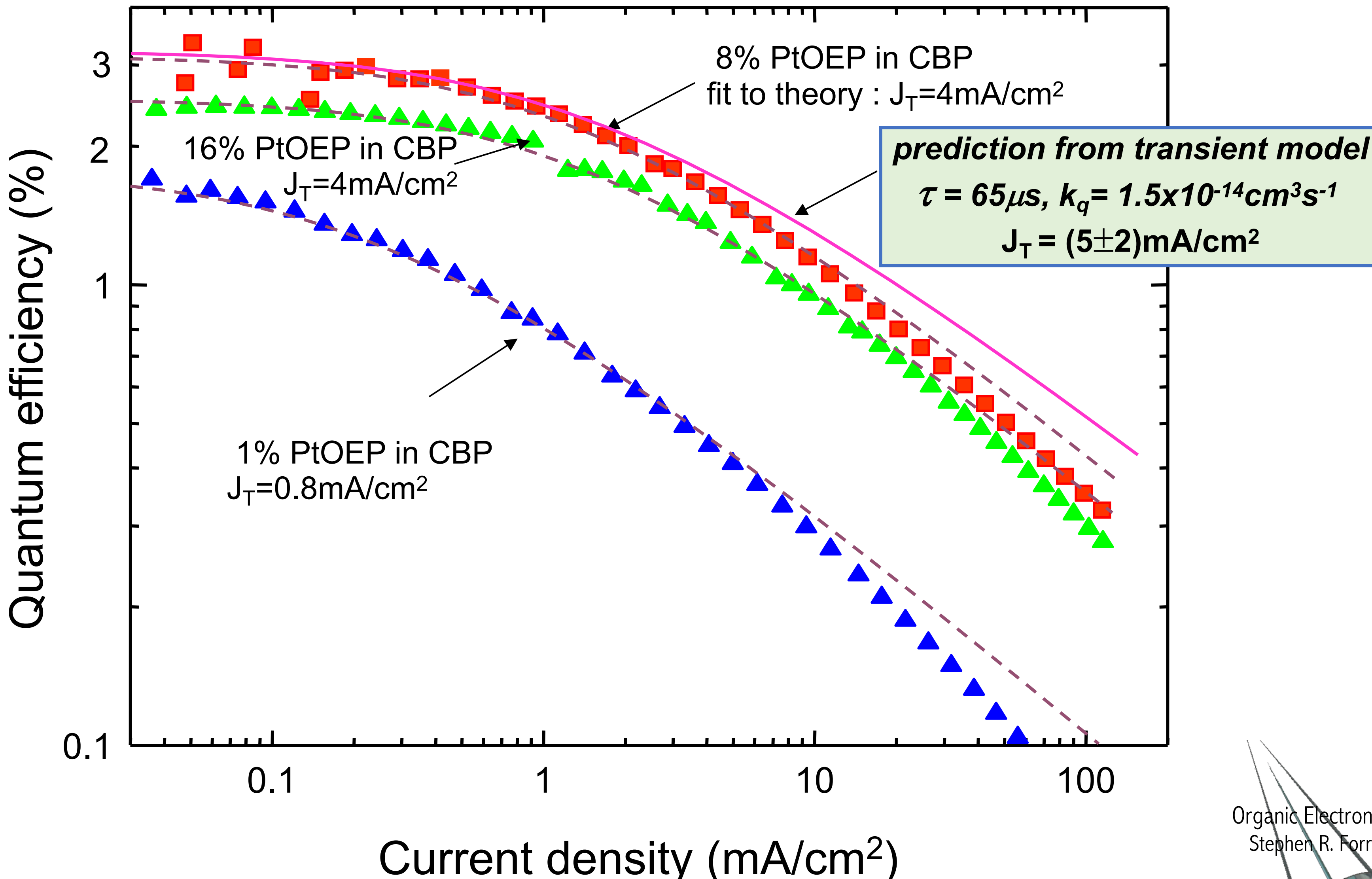
Threshold current density:
(for $\eta=\eta_0/2$) $$J_T = \frac{2qd}{k_q\tau^2}$$

Transient Fits to TTA Theory



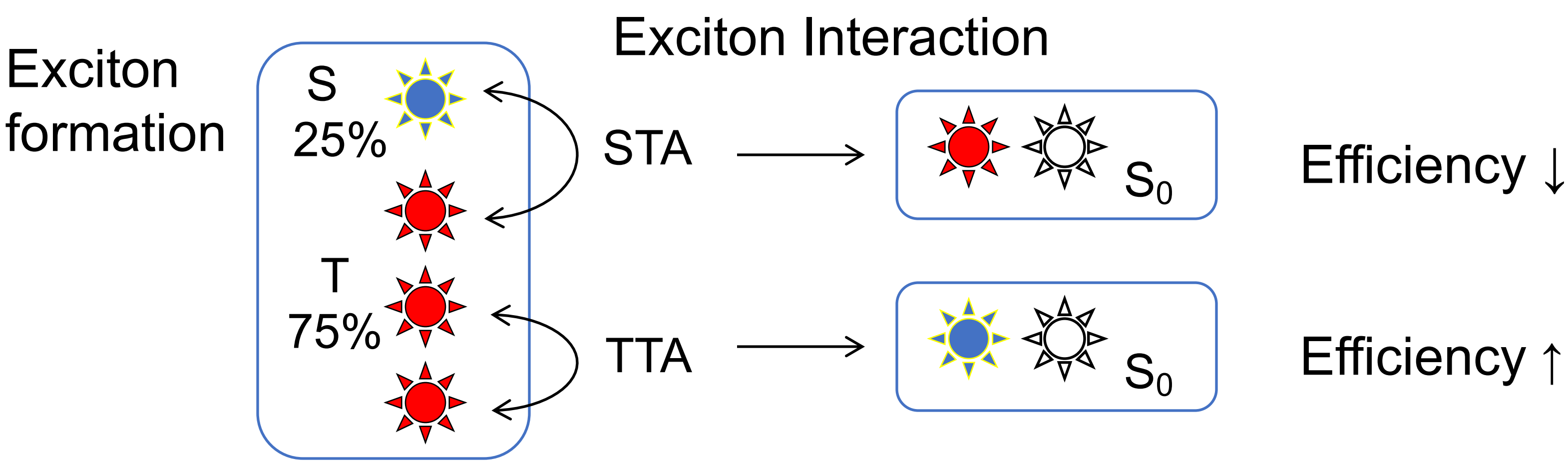
Baldo & Forrest, Phys. Rev. B 62, 10958 (2000)

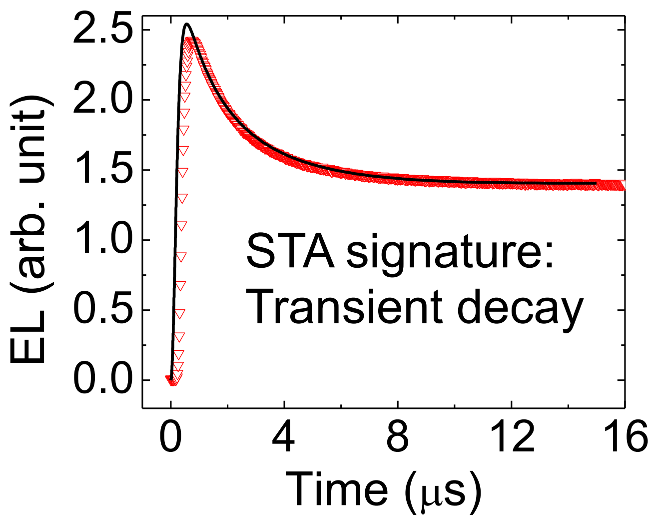
Steady State Roll off Matches Same TTA Theory



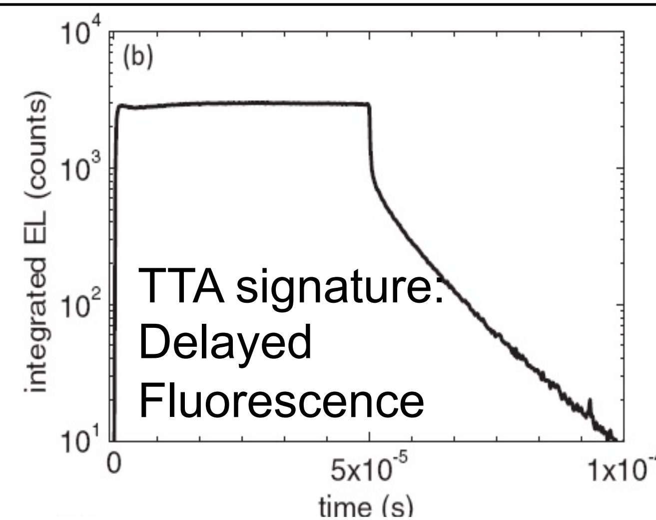
Baldo & Forrest, Phys. Rev. B 62, 10958 (2000)

Making 1 from 2: TT vs. ST annihilation





Zhang *et al*, CPL (2010)
Kasemann *et al*, PRB (2011)

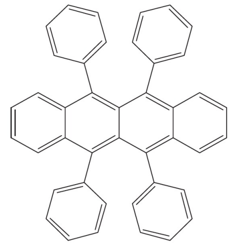


Kondakov *et al*, JAP (2007, 09)
Wallikewitz *et al*, PRB (2012)

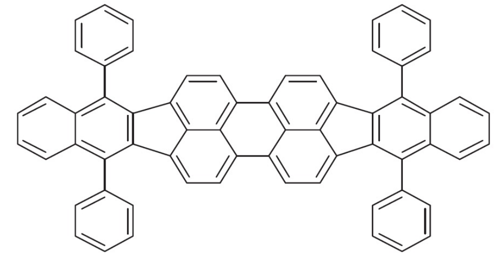
Organic Electronics
Stephen R. Forrest

Fluorescent OLED Efficiency Increase Due to TTA

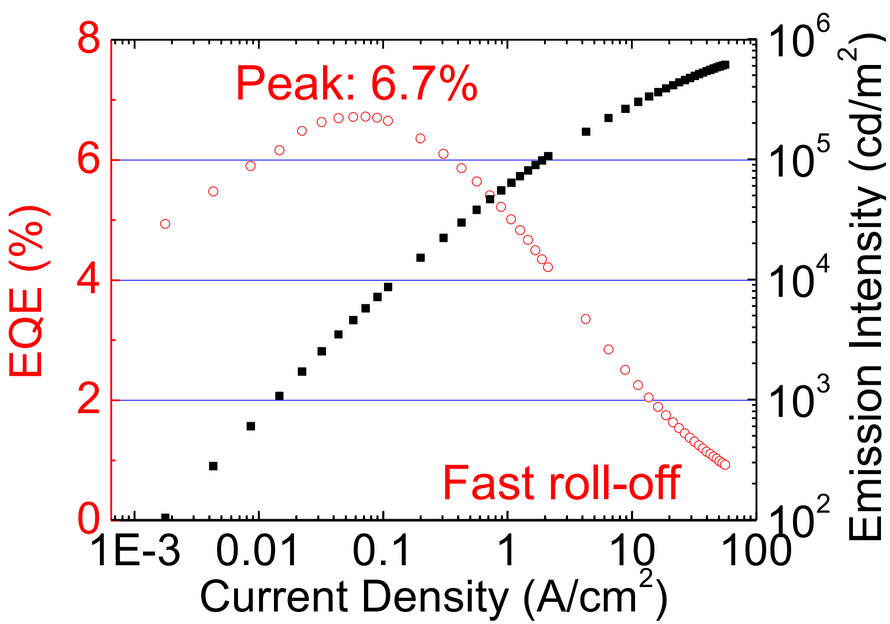
LiF/Al	
5 nm	BPhen
40nm	Rubrene
35 nm	DBP: Rubrene
40nm	NPD
ITO	

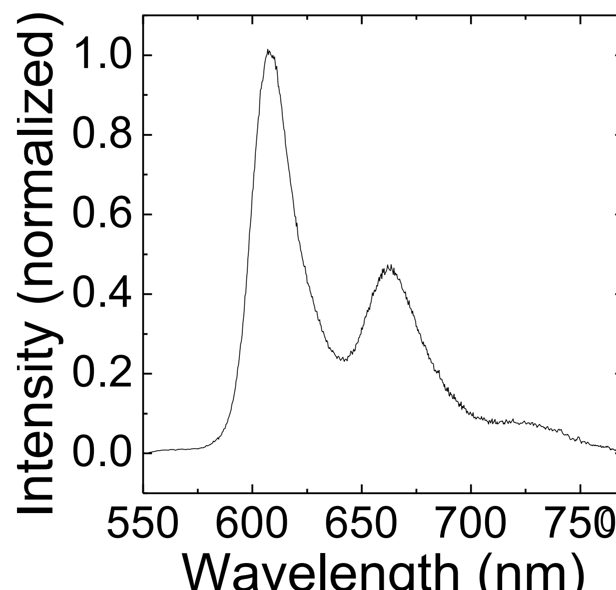


Rubrene
(E_T=1.1eV, E_S=2.2eV)



DBP
(E_T=1.4eV, E_S=2.0eV)





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 (α)

Dynamics

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

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

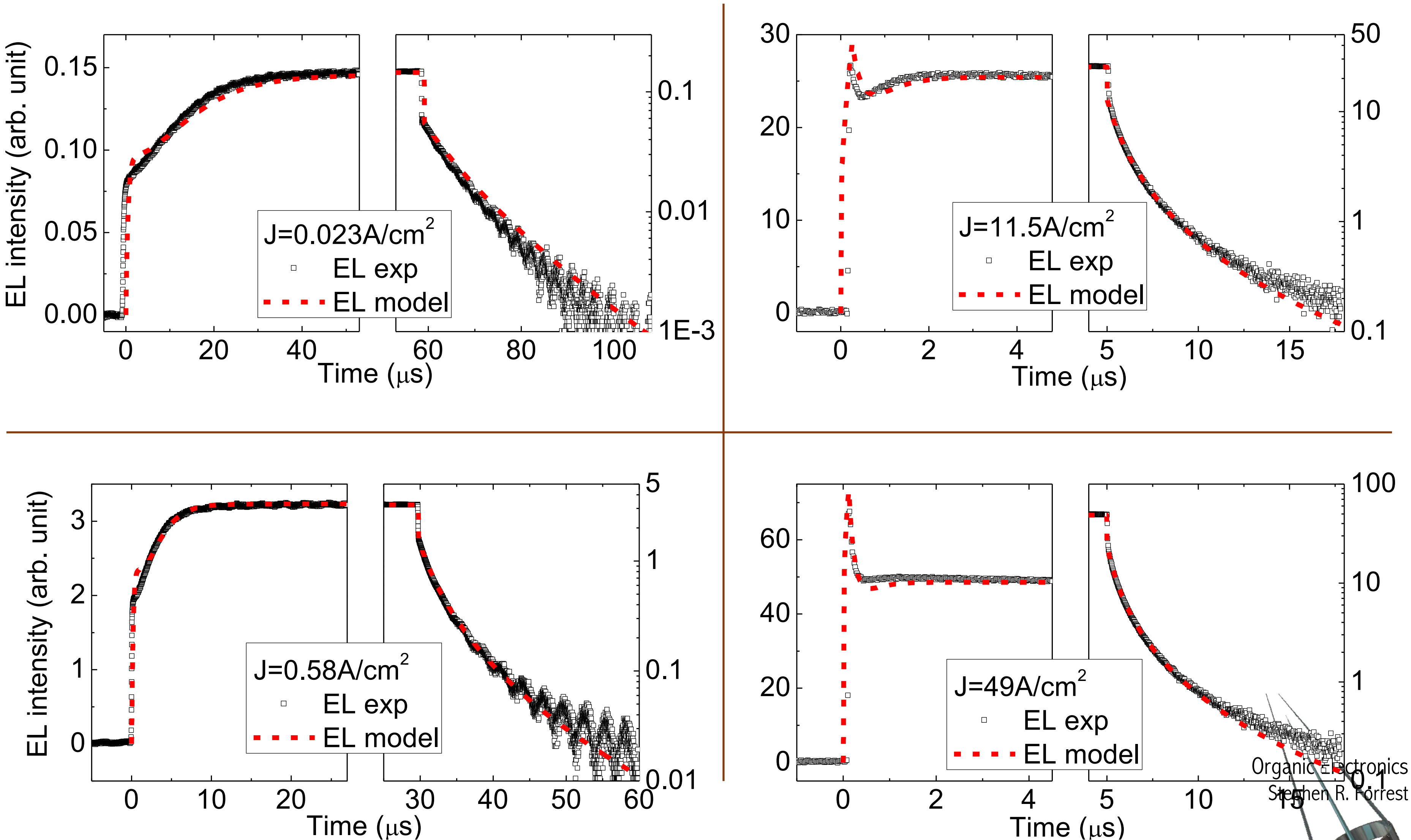
STA

TTA

Generation

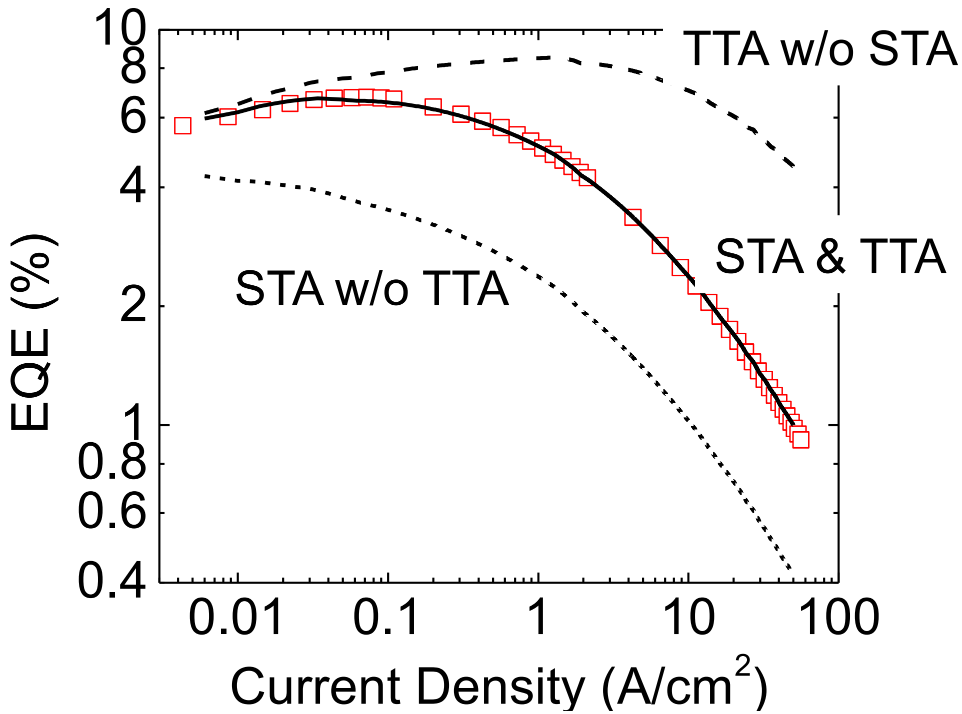
Natural decay

Model fits to experiment



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

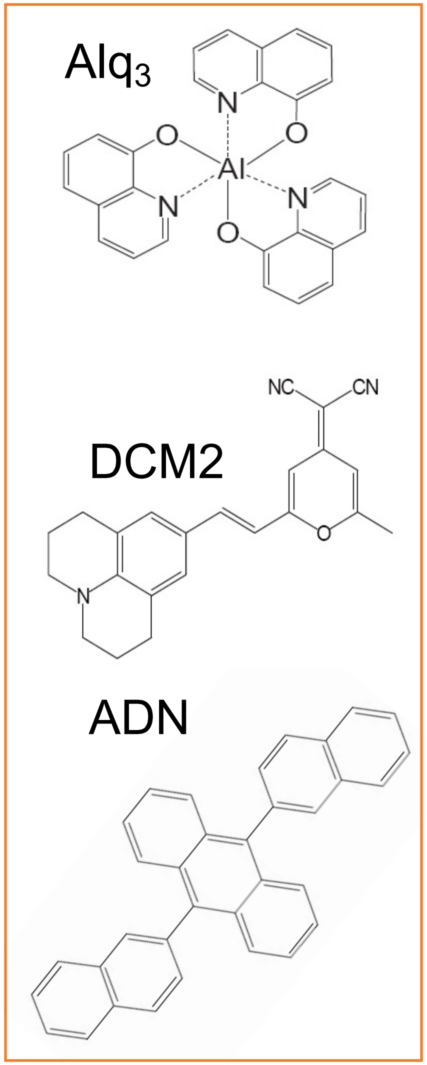
EQE of Rubrene OLEDs

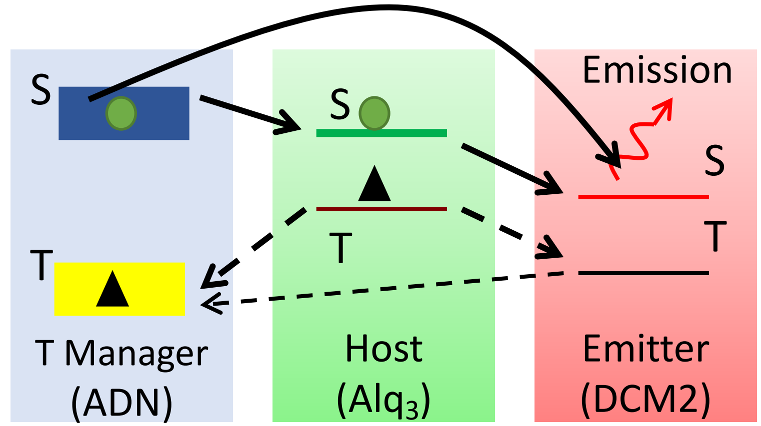


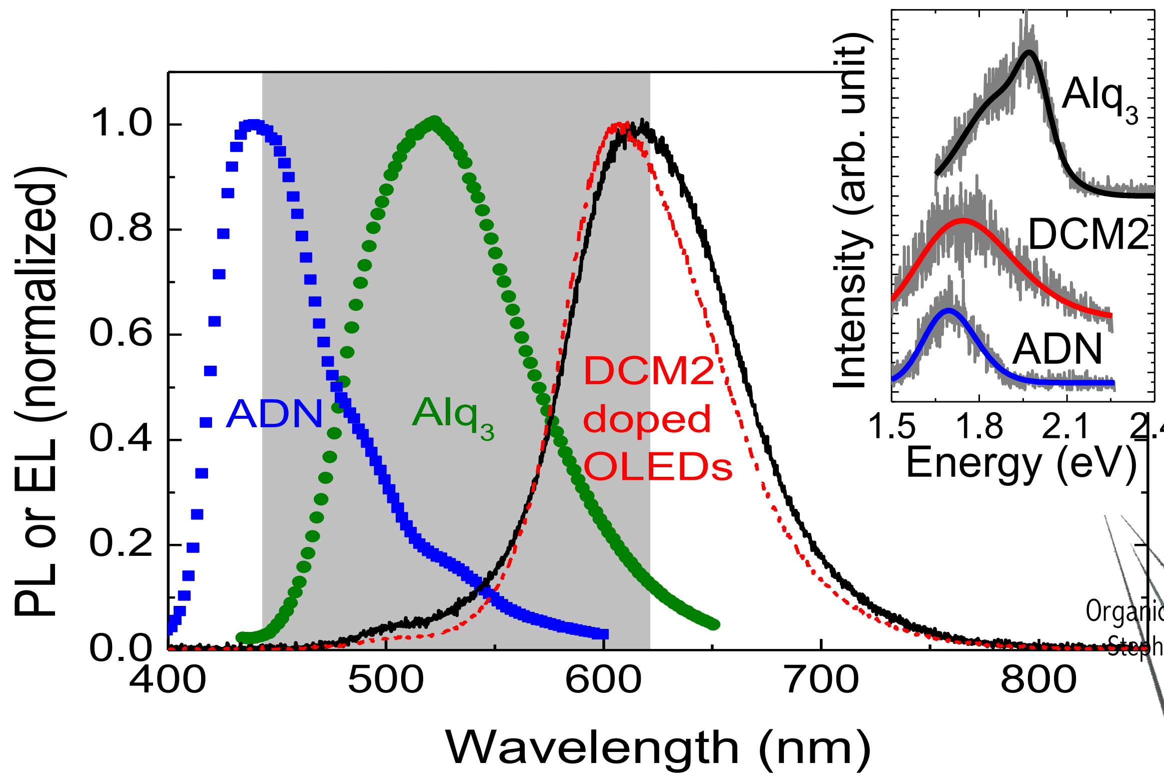
Route to high EQE & brightness fluorescent OLEDs:

- ➢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

Increasing Efficiency Through Triplet Management

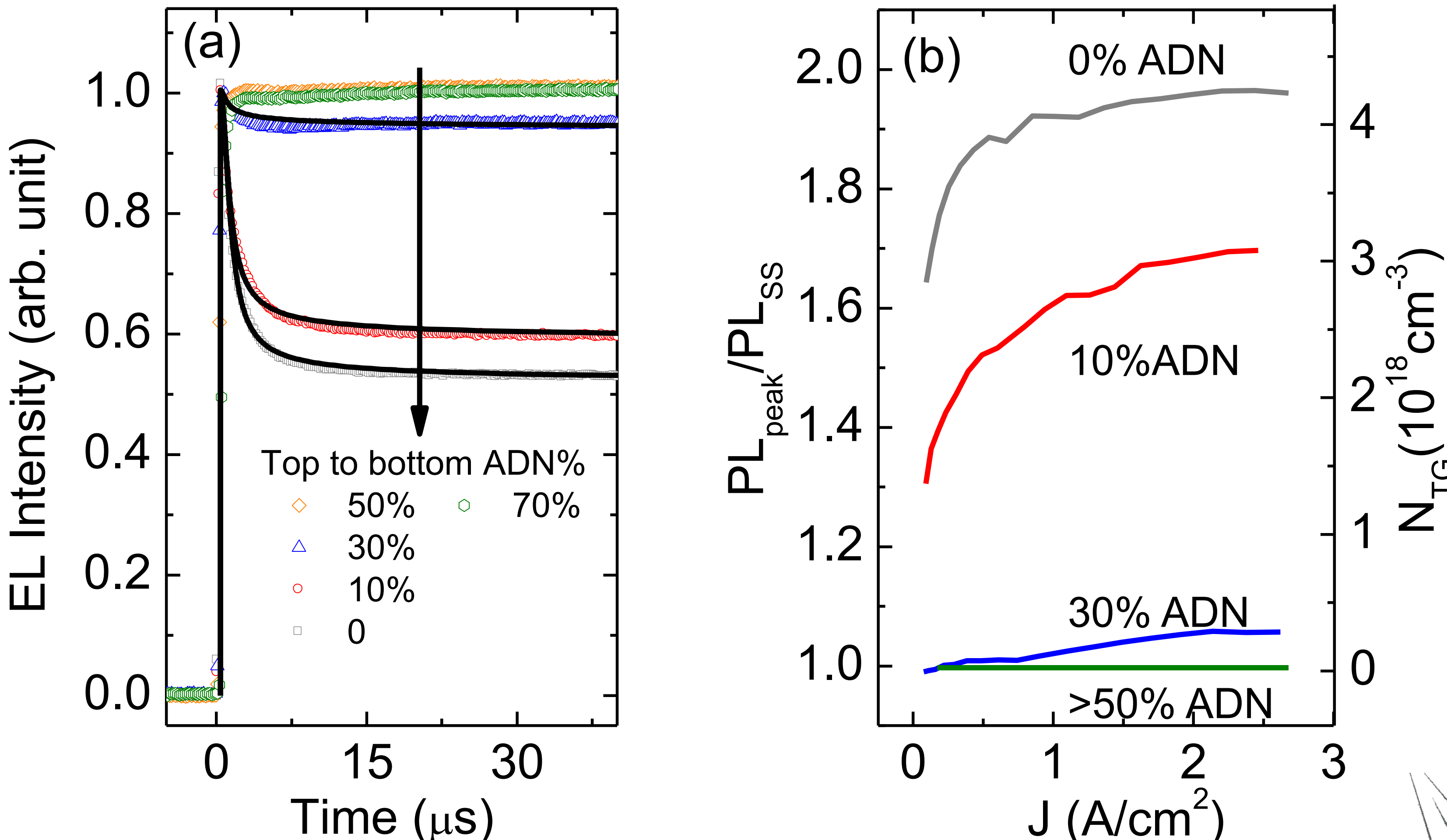






Y. Zhang, et al., APL, **99**, 223303 (2011)

Triplet-Managed ADN:Alq_3:DCM2 OLEDs

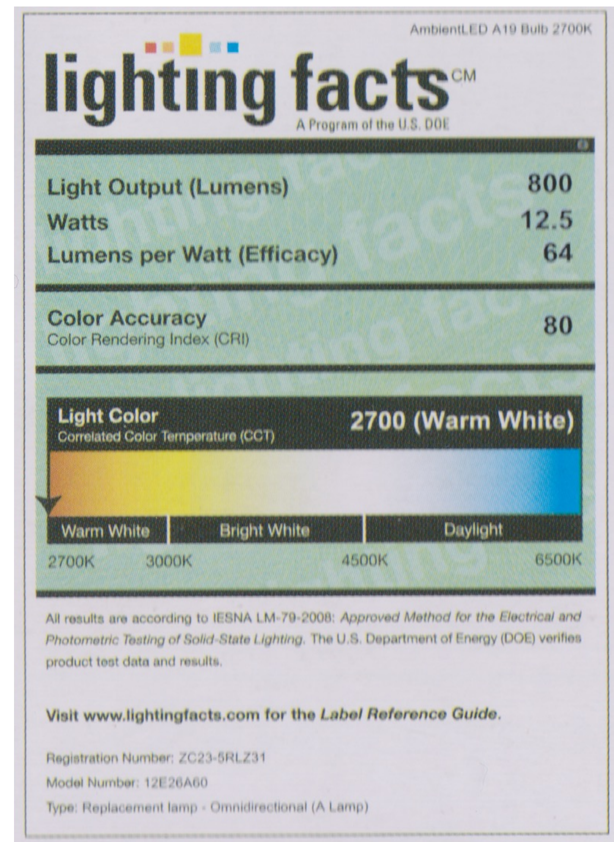


Quantifying White Light

- Color rendering index
  - Effect of an illuminant on the appearance of objects compared to that of a reference source (typically a black-body at a correlated color temperature, CCT)
  - CRI for white light sources should be >80 (i.e. <20% difference in integrated spectrum compared to black-body)

High CRI Low CRI

Note dull reds



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

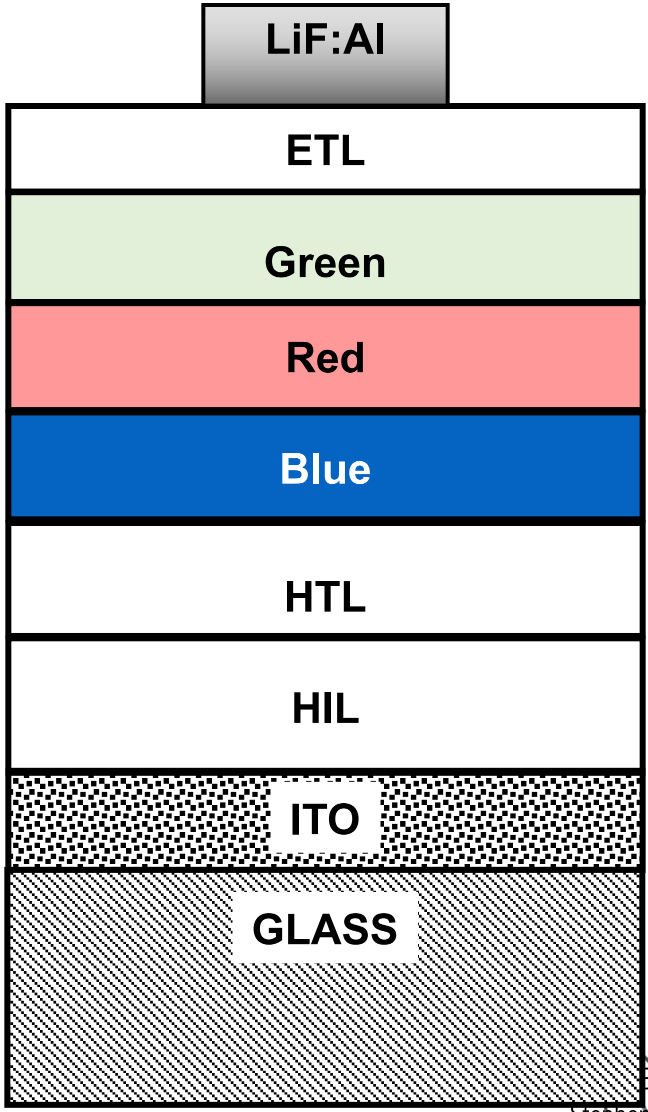
WOLED Challenges

- 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

OLEDs for White Light Generation

Separating dopants into bands

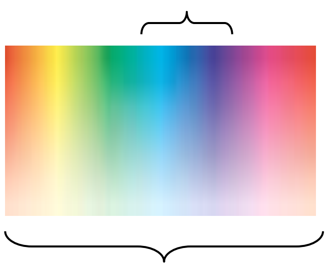
- Prevents energy transfer between dopants.
- Control relative emission intensity of dopants by:
  - ✓ Varying doping concentrations
  - ✓ Adjusting the thickness of bands
  - ✓ Inserting blocking layers
  - ✓ Adjusting the position of the dopants relative to the HTL

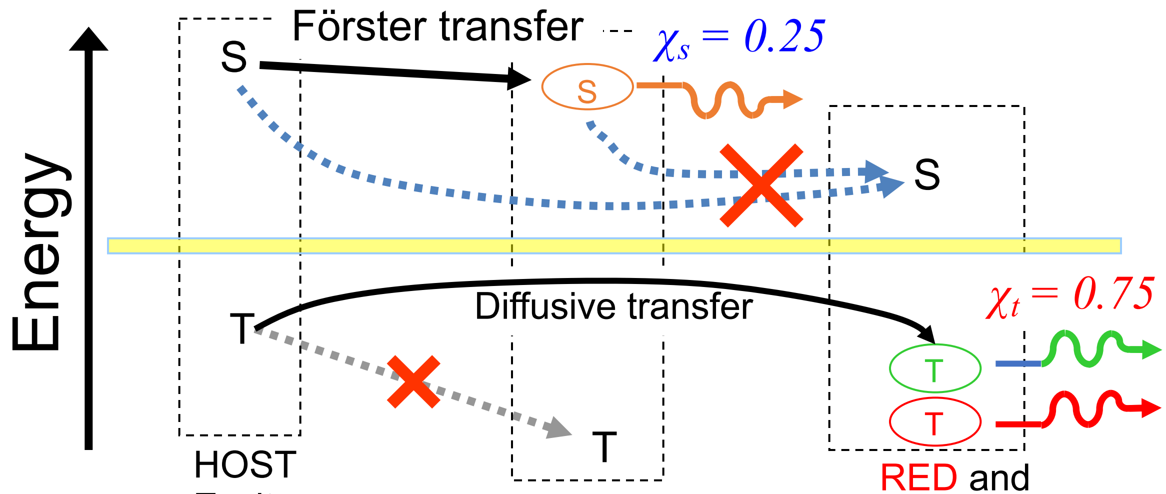


Why does it work?

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

Fluorescent/Phosphorescent WOLED



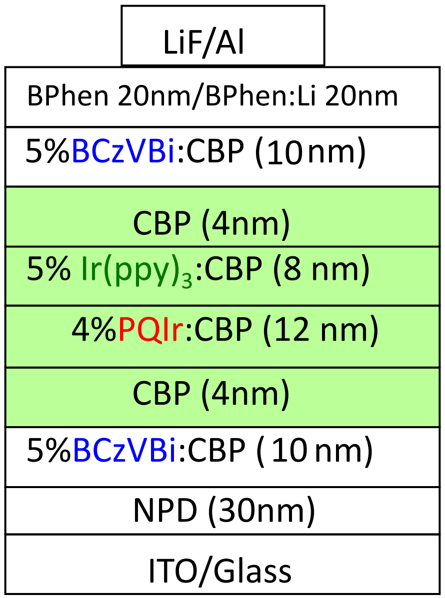


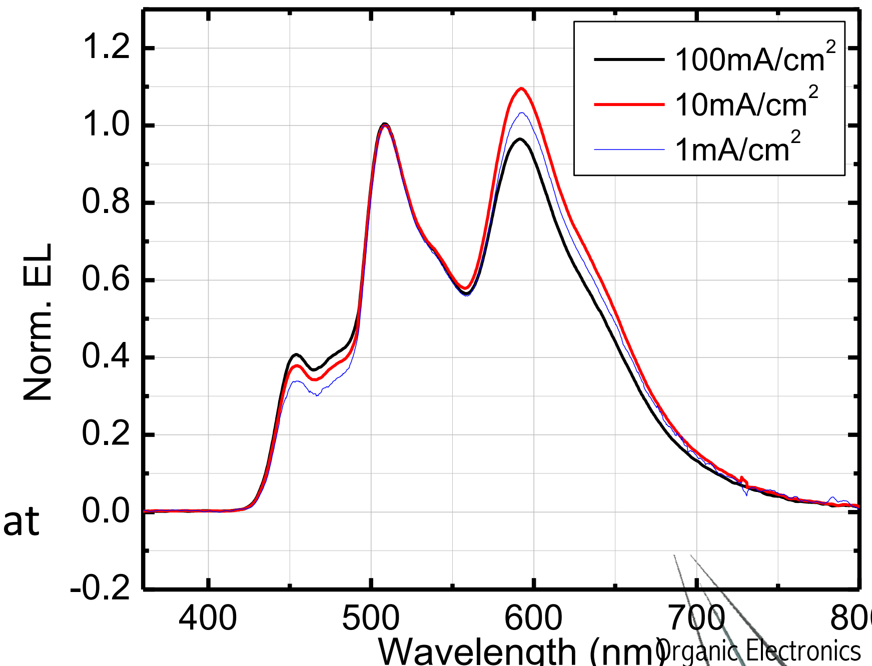
- Singlet and triplet excitons harvested along independent channels ➡ Resonant transfer of both excitonic species is independently optimized:
  - High energy singlet excitons for **blue** emission
  - Remainder of lower-energy triplet excitons for **green** and **red** emission

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

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

Performance of Hybrid WOLED





Total External Quantum Efficiency: (18.4 ±0.5)%

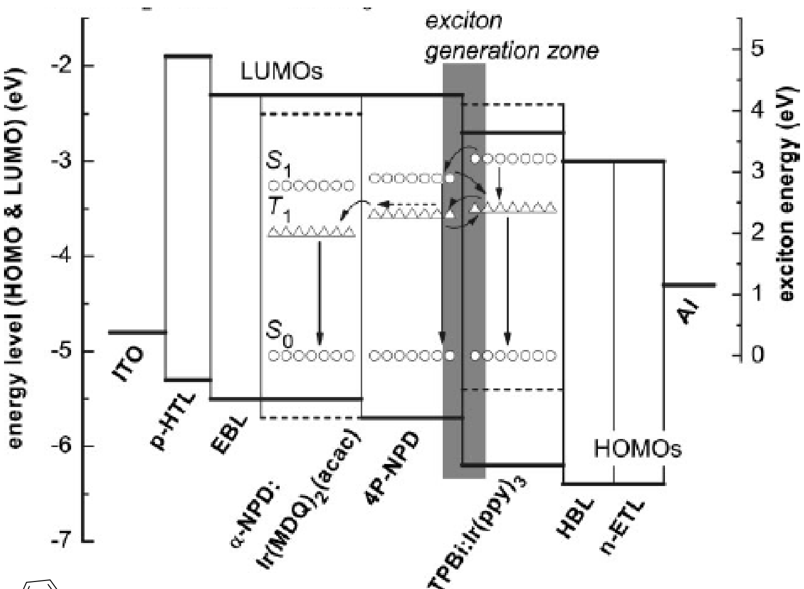
Total Power Efficiency:(23.8 ±0.5) lm/W

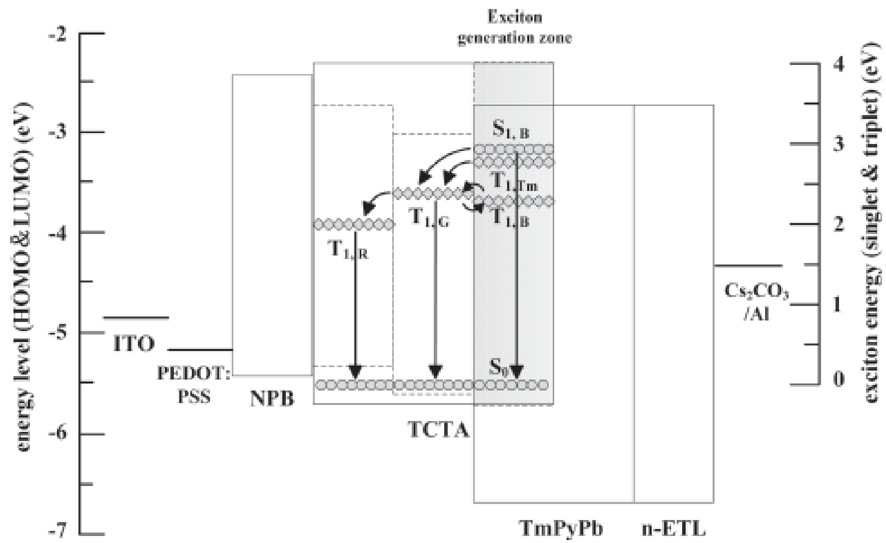
- Color Rendering Index (CRI): 84 at 1, 10 mA/cm², 83 at 100 mA/cm²
- CIE: (0.40, 0.44) → (0.39, 0.43)

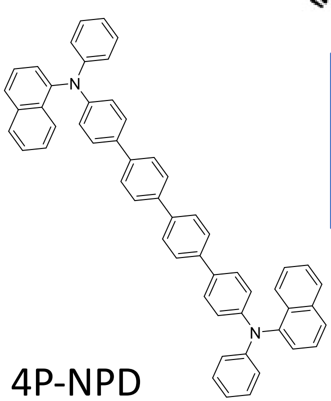
(Y. Sun, et al., *Nature*, 440, 908, 2006)

Other Approaches to Hybrid WOLEDs

K. Leo, 2007, 2009: introduced neat 4P-NPD layer as blue emitter, recombination at a single interface







4P-NPD

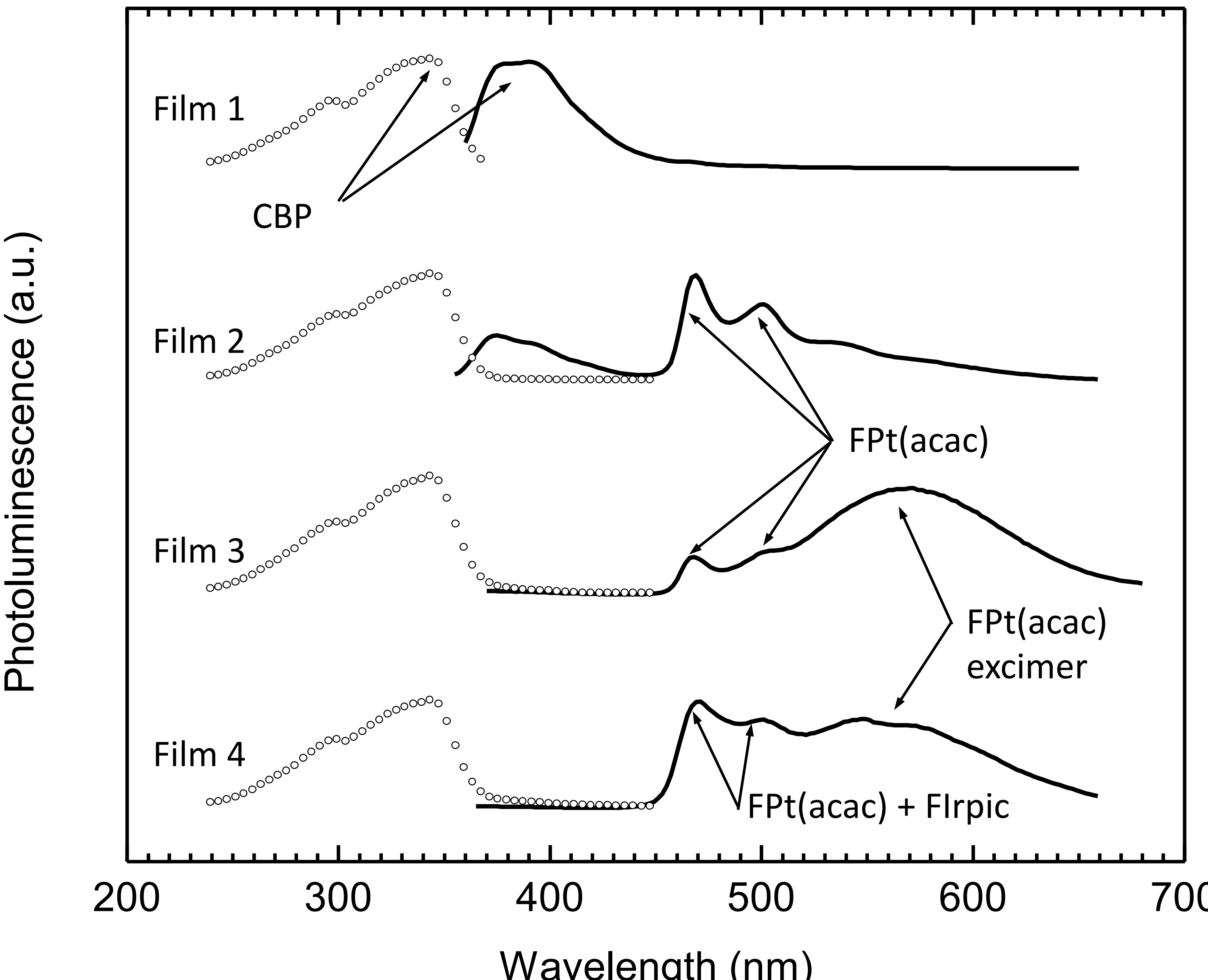
Φ_{PL}(film) = 92%

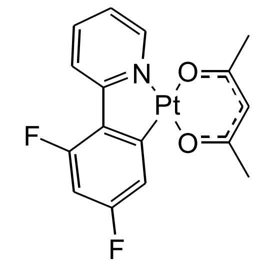
Conductivity doped layers
45 lm/W at 1000 cd/m^2
CIE = (0.45, 0.43)

4P-NPD blue fl dye (doped)
TCTA host for 4P-NPD, Ir(ppy)$_2$(acac), Ir(MDQ)$_2$(acac)
27 lm/W at 1000 cd/m^2, CIE = (0.43, 0.43), CRI = 87

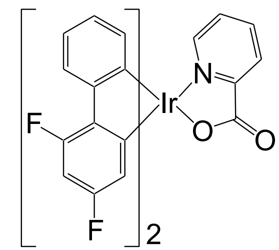
N. Sun, *et. al.*, *Adv. Mater.* **2014** *26*, 1617.

Broad Excimer Emission Simplifies Device Structure





FPt(acac)

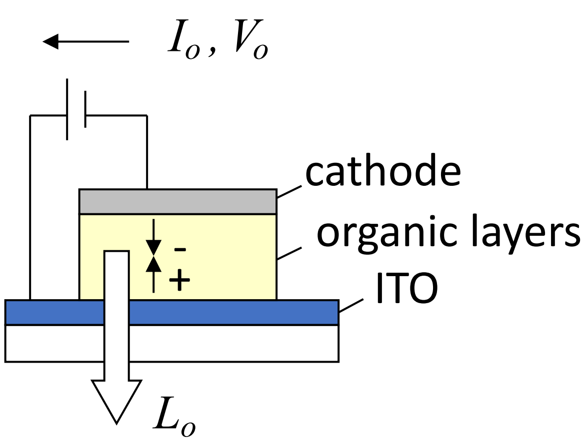


FIrpic

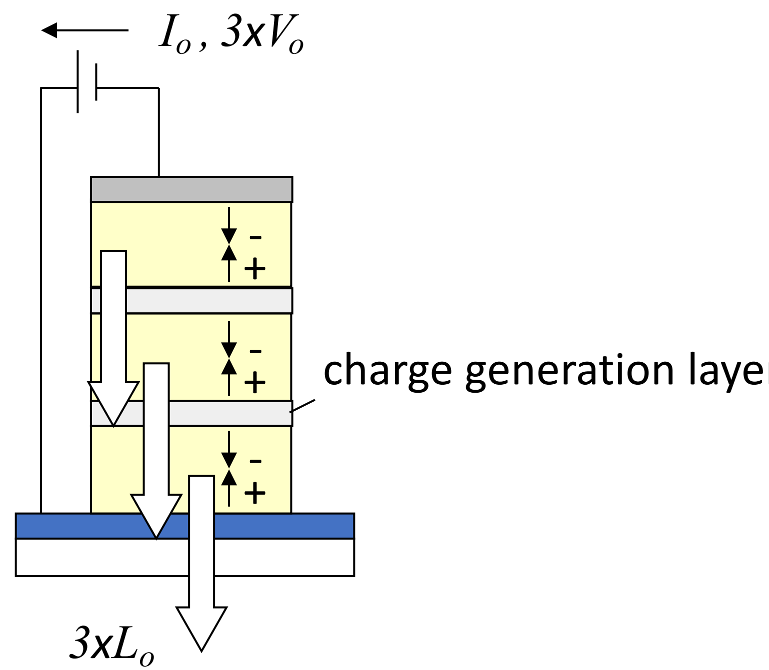
White Phosphorescent SOLEDs

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



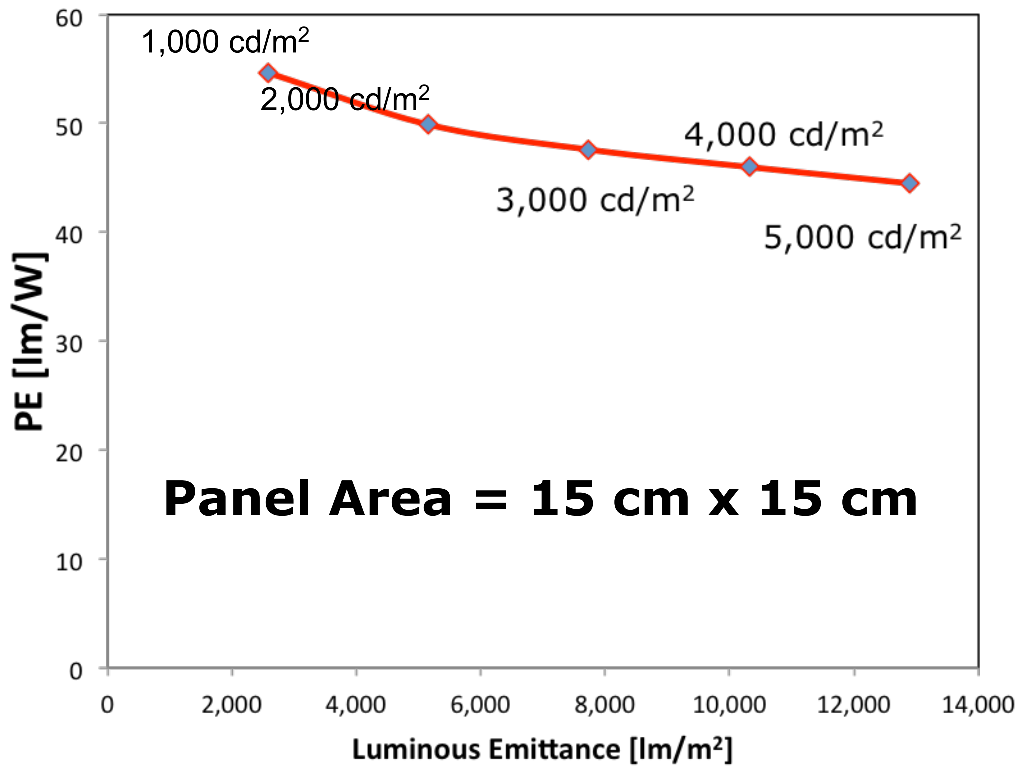
Conventional OLED

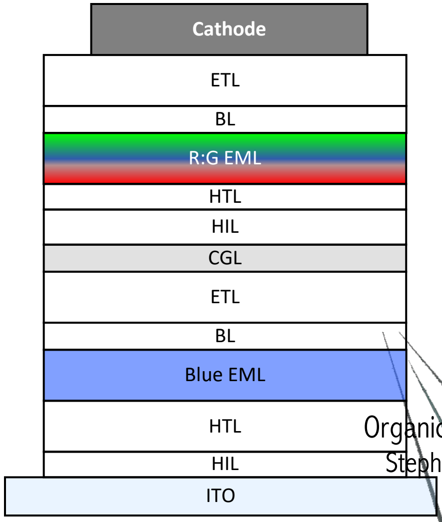


Stacked OLED (SOLED)

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

White SOLED Panel: Efficacy vs. Luminous Emittance

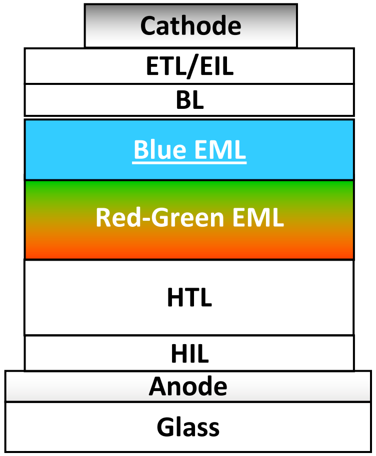




- Efficacy approaching 50 lm/W at 10,000 lm/m²
- CRI = 83
- LT70 = 4,000 hrs

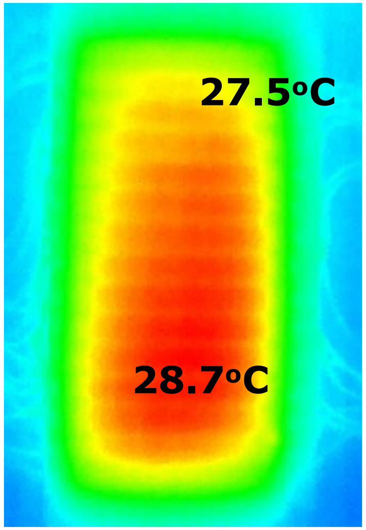
White PHOLED Panel

Panel 15 cm x 15 cm 15 mm thick	At 1,000 cd/m²	At 3,000 cd/m²
Efficacy [lm/W]	**58**	**49**
CRI	**82**	**83**
Luminous Emittance [lm/m²]	2,580	7,740
Voltage [V]	3.8	4.3
1931 CIE	(0.466, 0.413)	(0.471, 0.413)
Duv	0.001	0.000
CCT [K]	2,640	2,580
Efficacy Enhancement	1.75x	1.75x
Temperature Rise [°C]	**0.7**	**7.2**
LT70 [hrs]	**30,000**	**4,000**

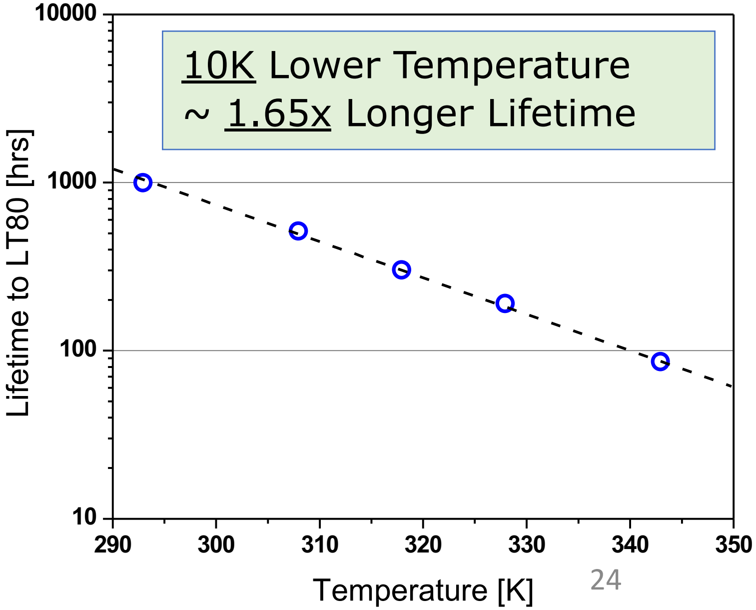


LT70 ~ 30K hrs at 1000 cd/m²
Warm White with CCT 2640K

Lower current at constant *L*
⇒lower temperature
⇒longer lifetime



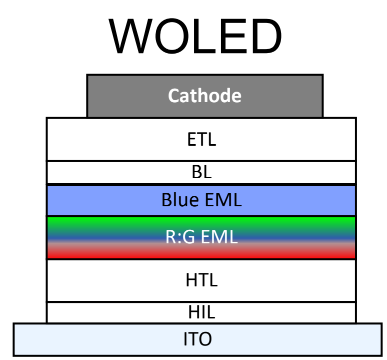
t = 60 min
3000 cd/m²

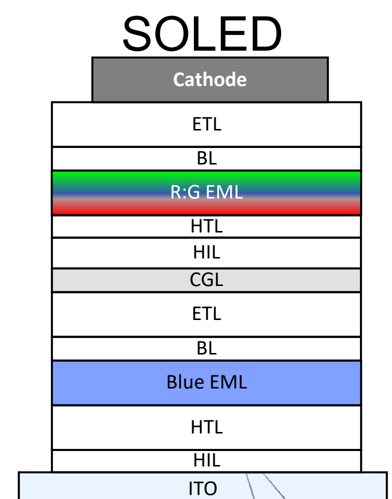


WOLED vs. SOLED Panel Comparison

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 [°C]	**27.2**	**26.2**
LT_{70} [hrs]	**4,000**	**13,000**

P.Levermore et al, **SID Digest,** 72.2, p.1060, 2011.

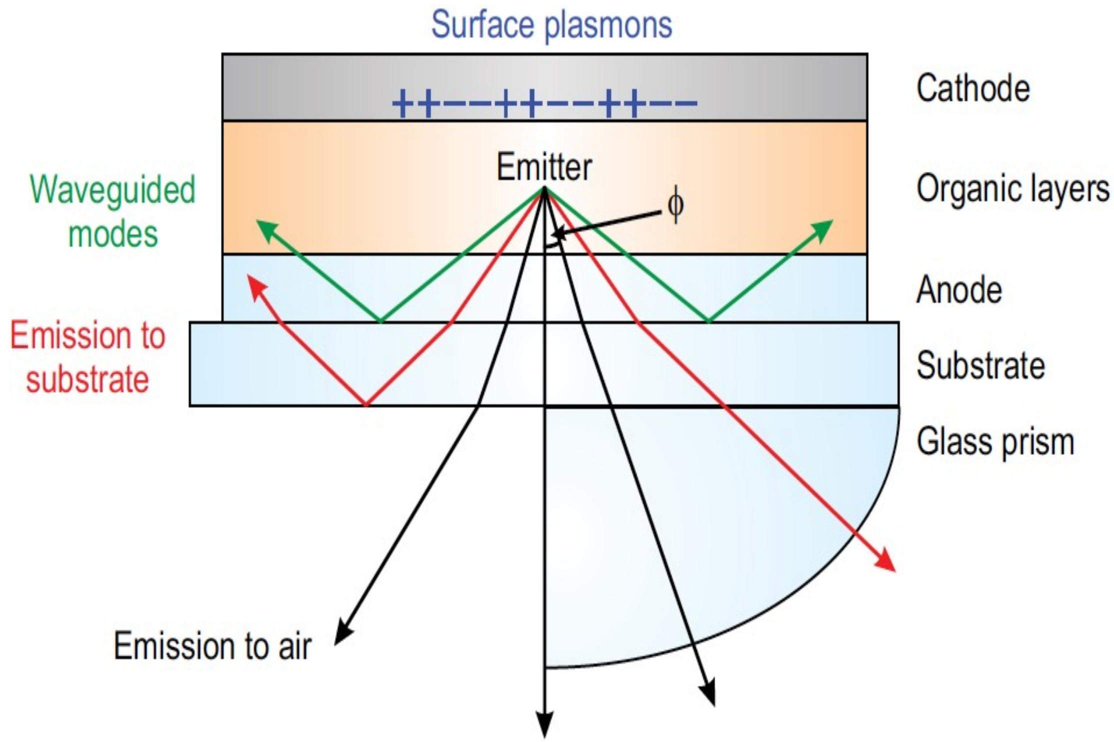




SOLED architecture: ~ 3x LT_{70} improvement vs. single unit WOLED with similar color and power efficacy

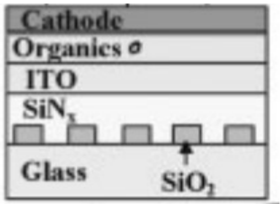
OLEDs: Not All Light Goes to the Viewer

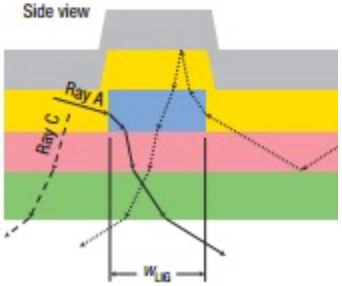
- Optical paths outcoupled with hemispherical lens

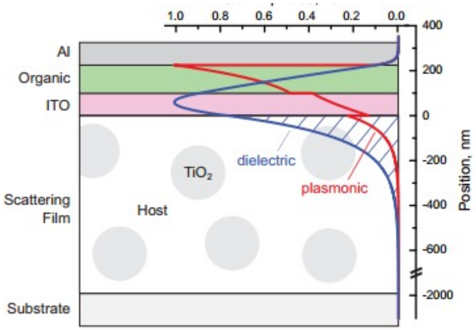


Getting all the photons out

- **Good solutions**
  - Inexpensive
  - Viewing angle independent
  - Independent of OLED structure
- **Among those things that have been tried**
  - Optical gratings or photonic crystals[1]
  - Corrugations or grids embedded in OLED[2]
  - Nano-scale scattering centers[3]
  - Dipole orientation management

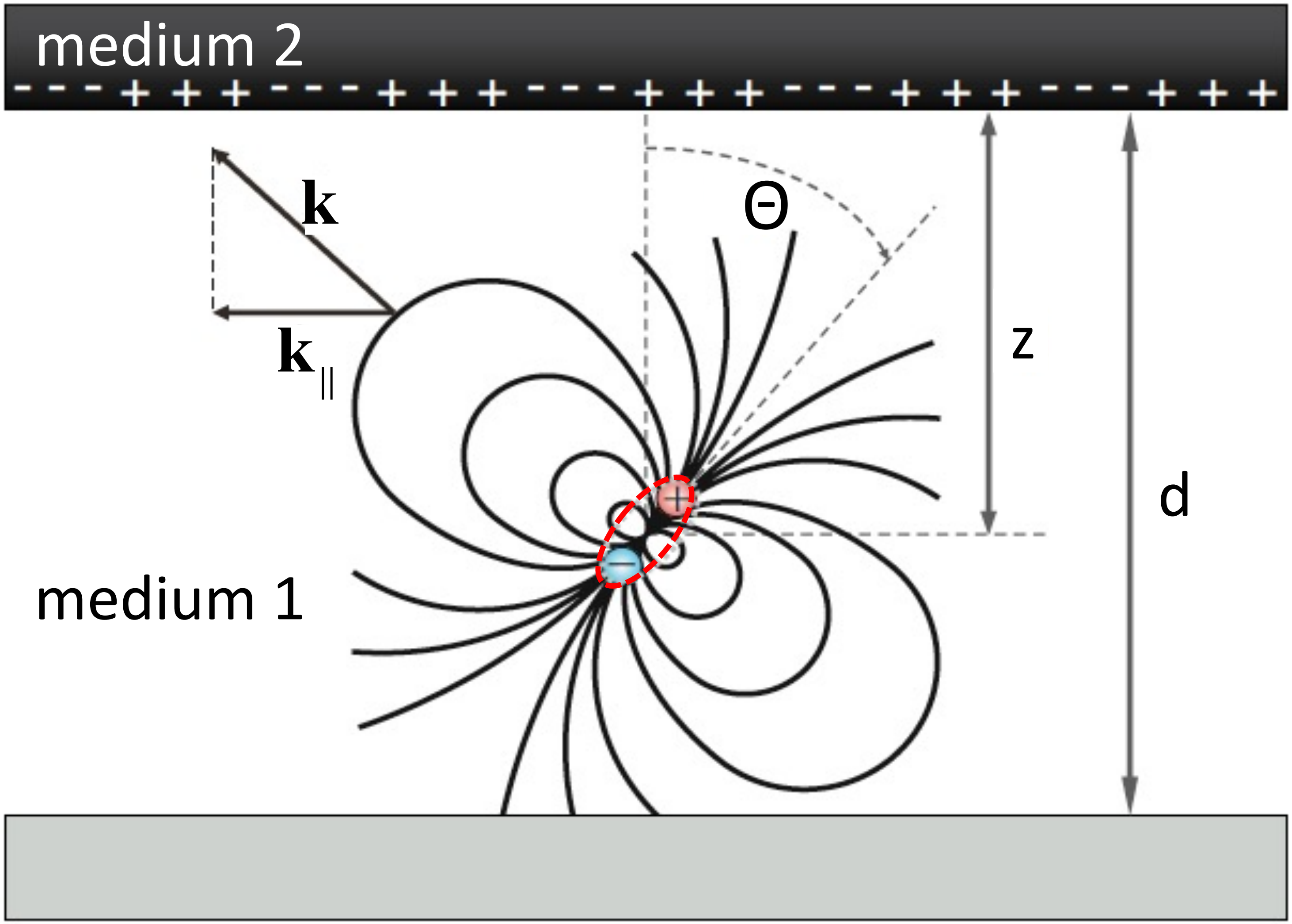




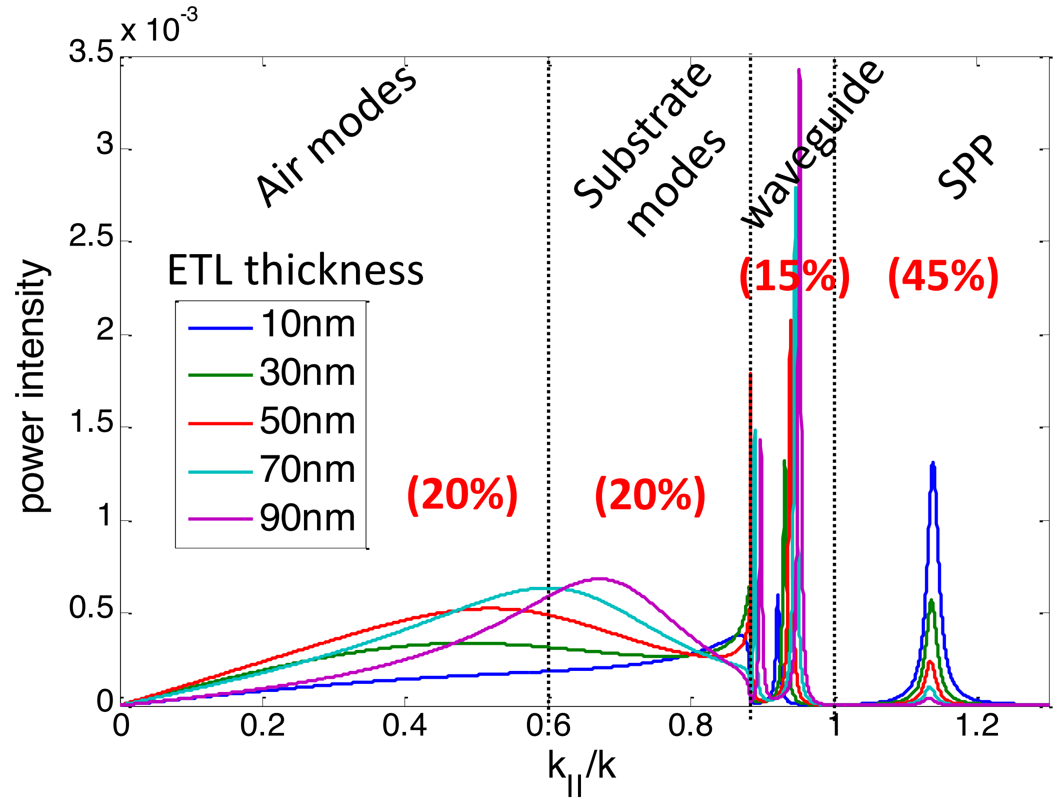


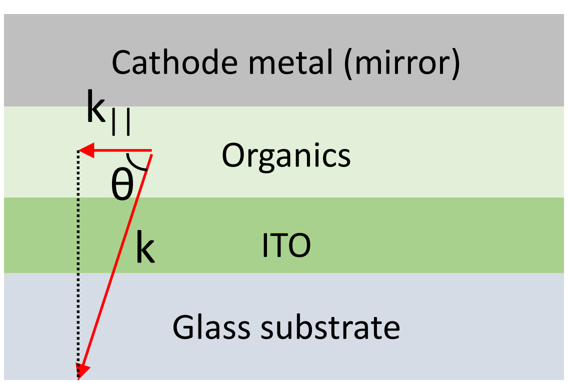
[1]Y .R. Do, et al, *Adv. Mater*. **15**, 1214 (2003).
[2]Y. Sun and S.R. Forrest, *Nat Phot*. **2**, 483 (2008).
[3]Chang, H.-W. *et al*. *J. Appl. Phys.* **113,** - (2013).

Molecules are radiating dipoles in inhomogeneous media



Where do all the photons go?

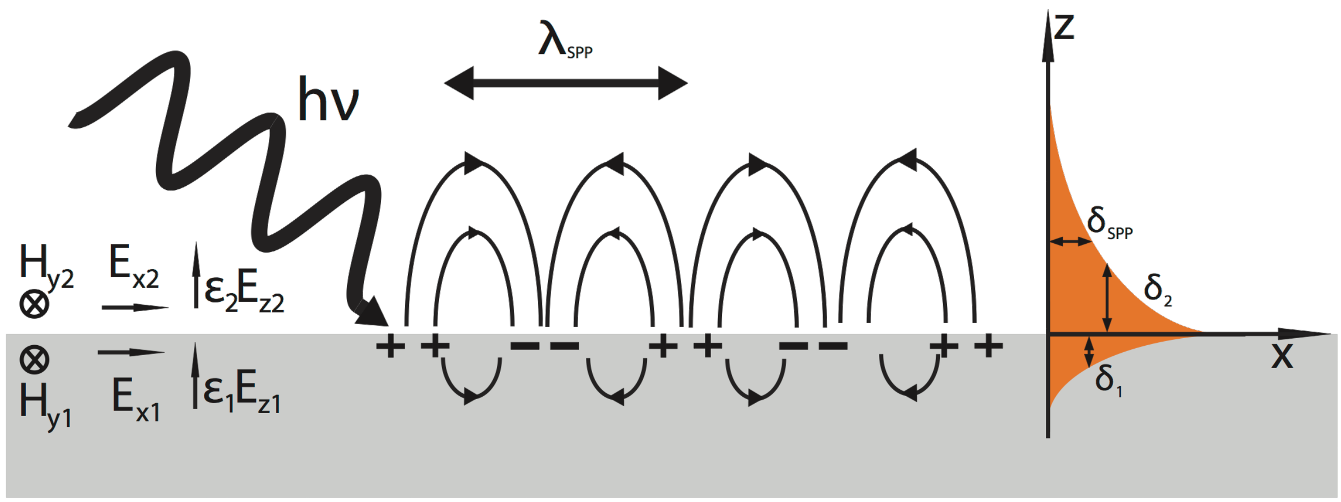




- **Air modes**: EQE first increases, then decreases with ETL thickness
- **Waveguide modes**: Only one waveguide mode TE_0 due to thin ETL (<30nm). TM_0 appears when >50nm.
- **Surface plasmon polariton modes:** Reduced with ETL thickness
- Both waveguide and SPP modes are quantized
- Total energy is the integral of Power Intensity x cos(θ), so SPP not as small as it looks

Surface Plasmon Polariton (SPP) Modes: Major Loss Channel

$\eta_{ext} > 80\%$ (incl. substrate + waveguide modes)



- Waveguided light excites lossy SPPs in metal cathode
- Major loss channel partially eliminated by rapid outcoupling of waveguide modes
- Most difficult to eliminate cost-effectively without impacting device structure