Week 2-3

Light Emitters 3

TADF

Rolloff and Annihilation

WOLEDs

Ch. 6.3.4 - 6.3.5, 6.5.1-6.5.4

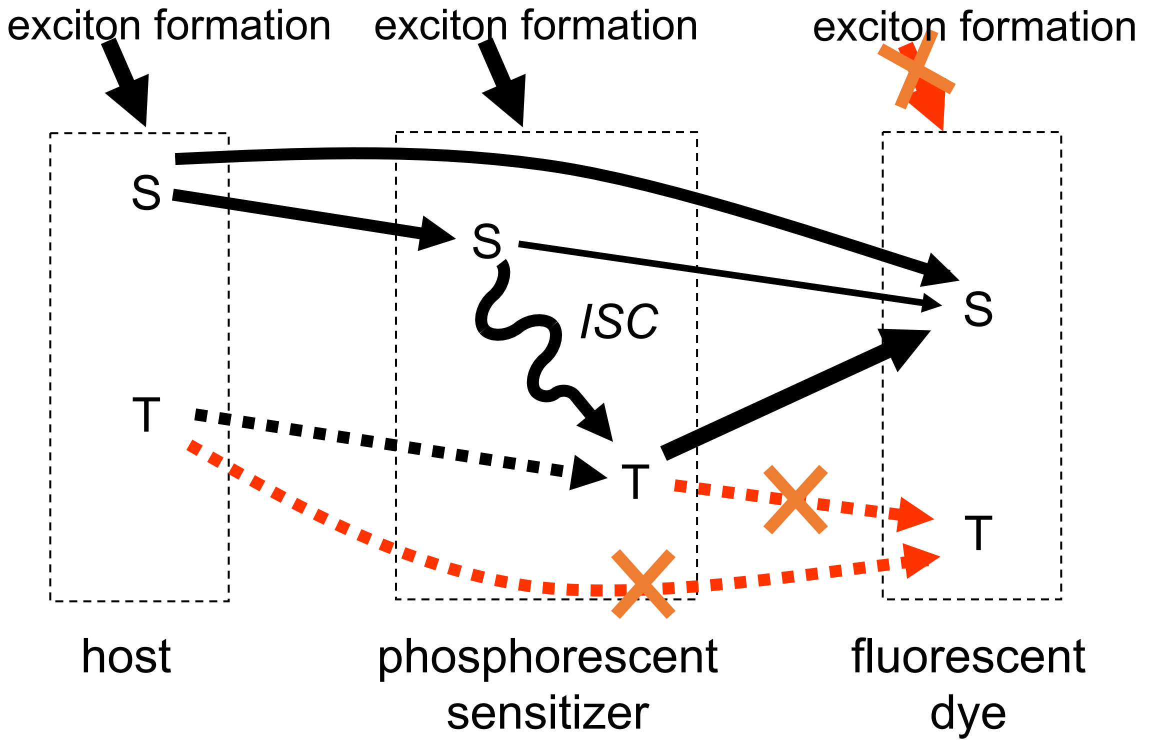
Organic Electronics
Stephen R. Forrest

Phosphor Sensitized Fluorescence

Transferring excitations from phosphor to increase fluorescent OLED efficiency
Opens door to 100% fluorescence efficiency

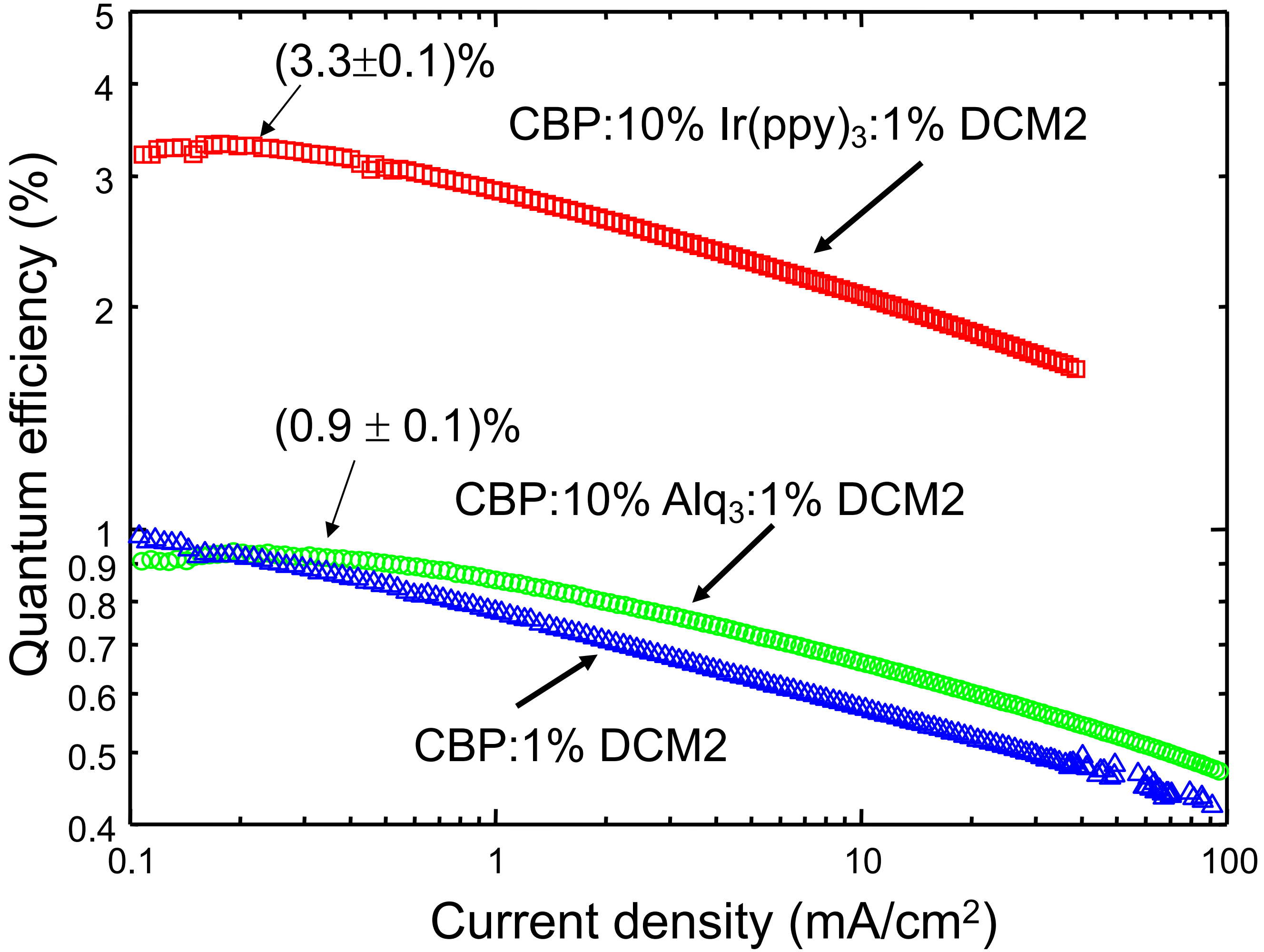
- Phosphorescent donor and fluorescent acceptor must be separated to prevent direct Dexter transfer to fluorescent triplet state
- Transfer possible for radiative triplet states

Process is exothermic from host to sensitizer to fluorophore



Baldo, et al. Nature 403, 750 (2000)

Sensitized Fluorescence from $Ir(ppy)_3$ to DCM2

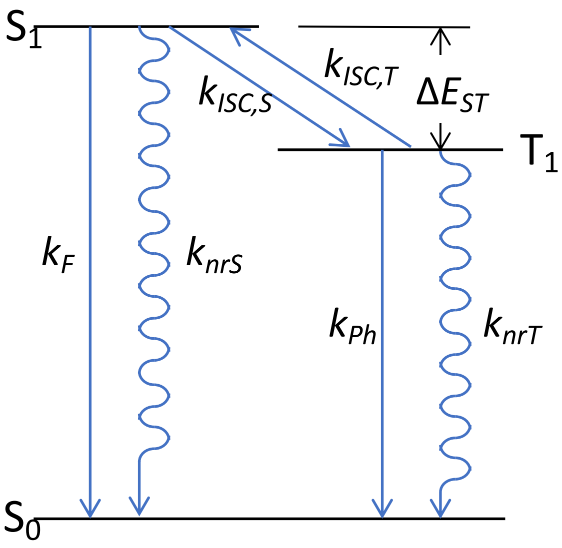


- Phosphorescent sensitizer improves efficiency by factor of **3.7**
- Fluorescent “sensitizer” makes no difference

Baldo, et al. Nature 403, 750 (2000)

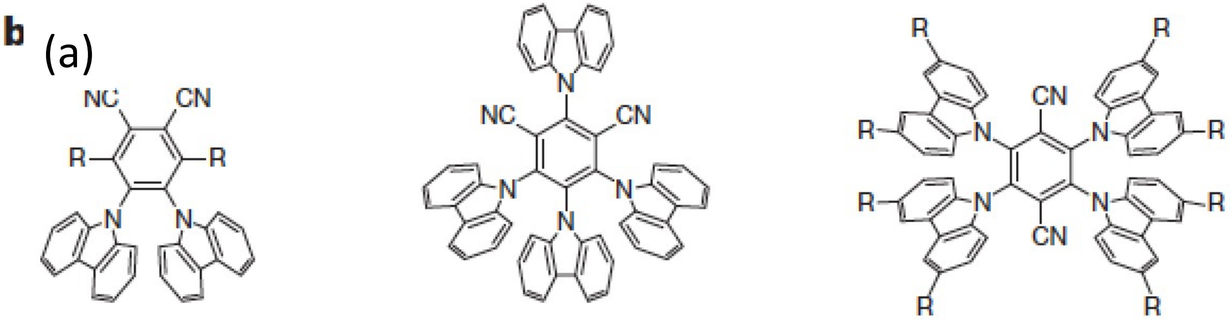
TADF: Another approach to high efficiency

η_{int} ~ 100%



k_F ~ $k_{ISC,T}$>> k_{Ph}

(a)

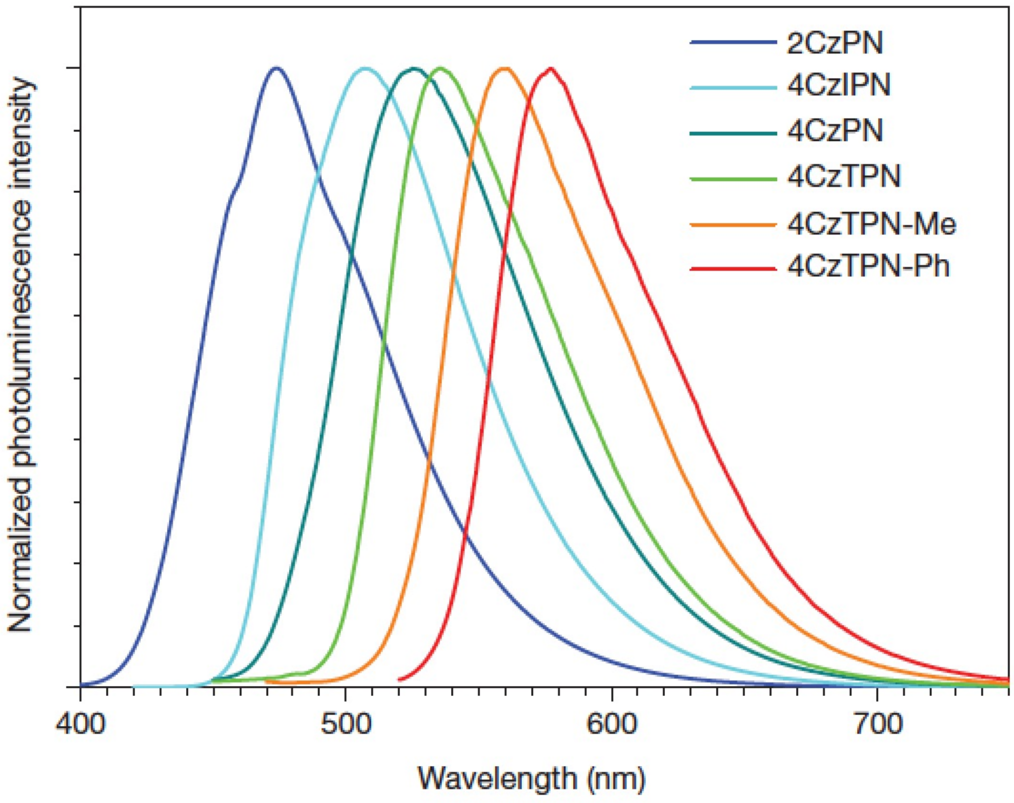


4CzPN: R = carbazolyl
2CzPN: R = H

4CzIPN

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

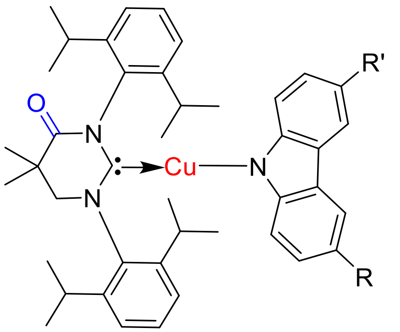
(b)



Uoyama et al., Nature, 492, 234 (2012).

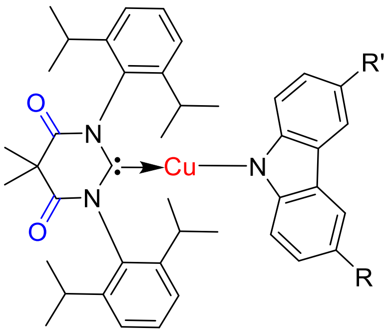
TADF Cu-complexes and the Energy Gap Law

(see Ch. 3)



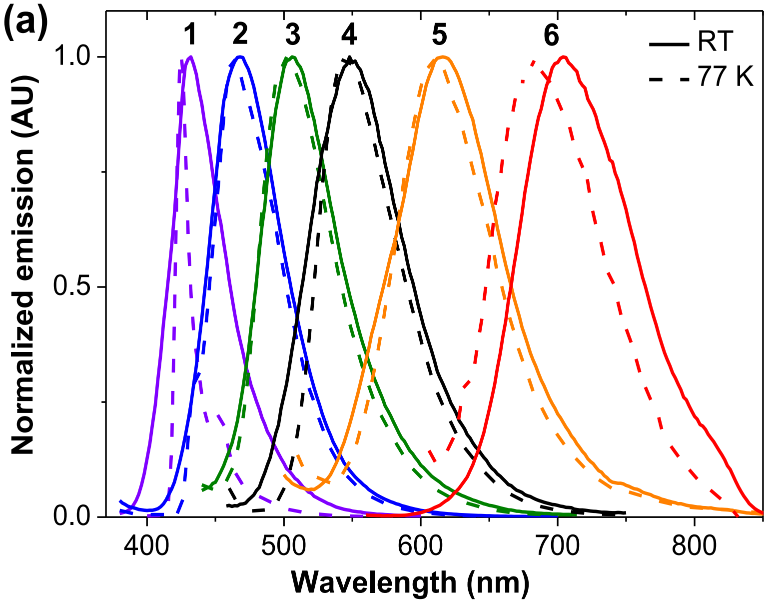
Carbene = MAC*

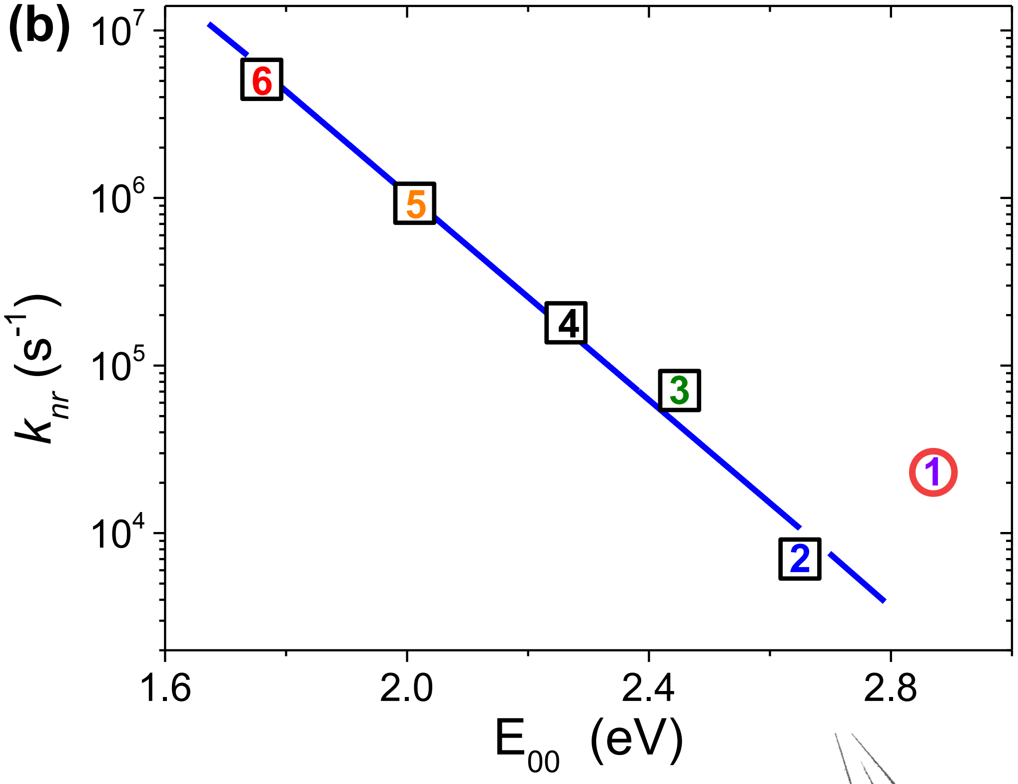
R, R' = CN (**1**)
R = CN, R' = H (**2**)
R, R' = H (**3**)



Carbene = DAC*

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





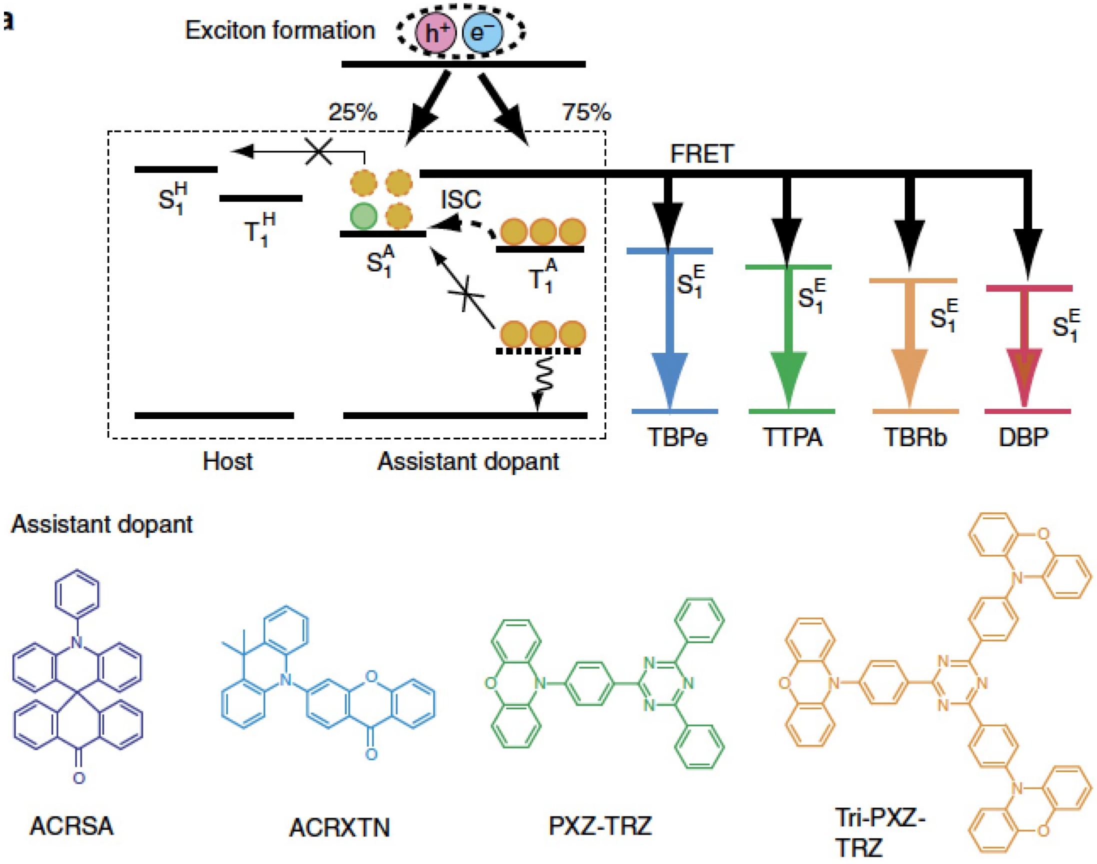
Au and Ag Complexes also show η_{int} ~ 100%

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

TADF Sensitized Fluorescence

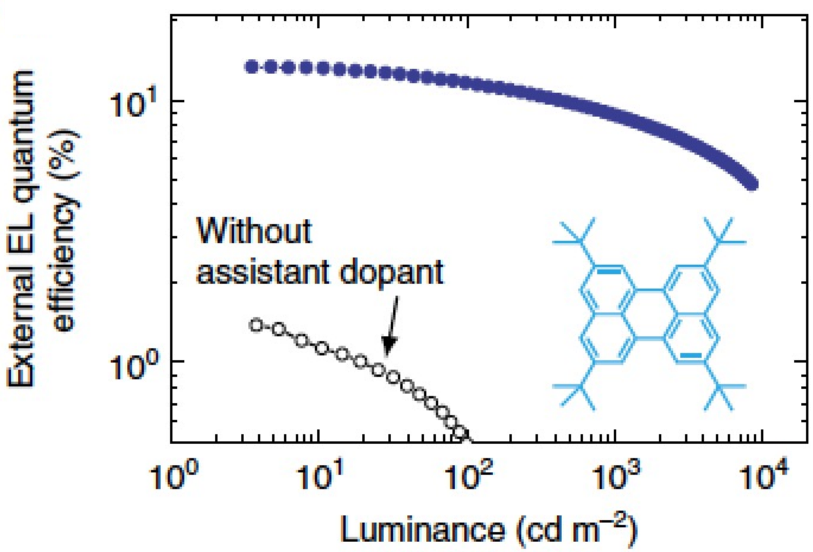
“Hyperfluorescence”

- Like phosphor sensitized fluorescence, transfer excitation from TADF molecule to fluorophore at lower energy
- Allows for the use of wide palette of fluorophores with improved spectral properties compared to host TADF “assistant” molecule

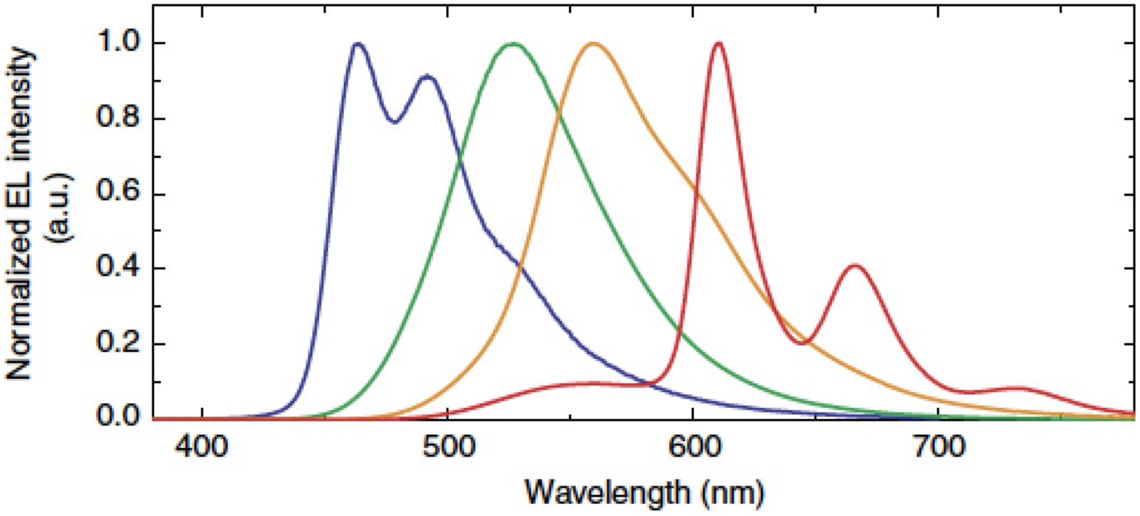


Nakanotani et al., Nat. Comm. 5, 4016 (2014)

TADF Sensitized Fluorescence: Results



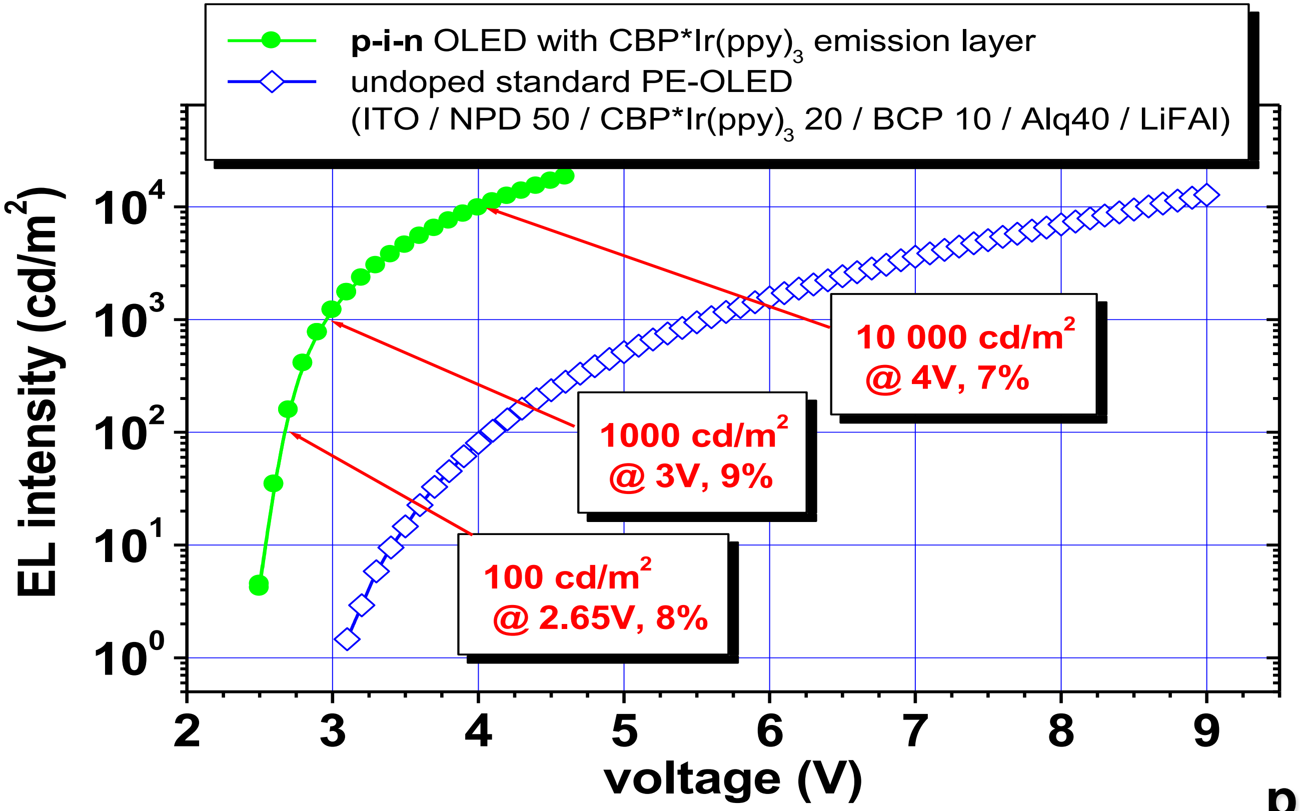
- Many colors possible
- Blue least accessible due to exothermic transfer from host to assistant to fluorophore

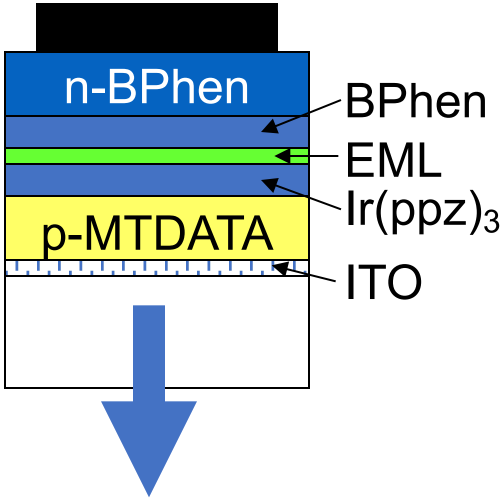


Nakanotani et al., Nat. Comm. 5, 4016 (2014)

Low voltage high efficiency p-i-n PHOLEDs

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



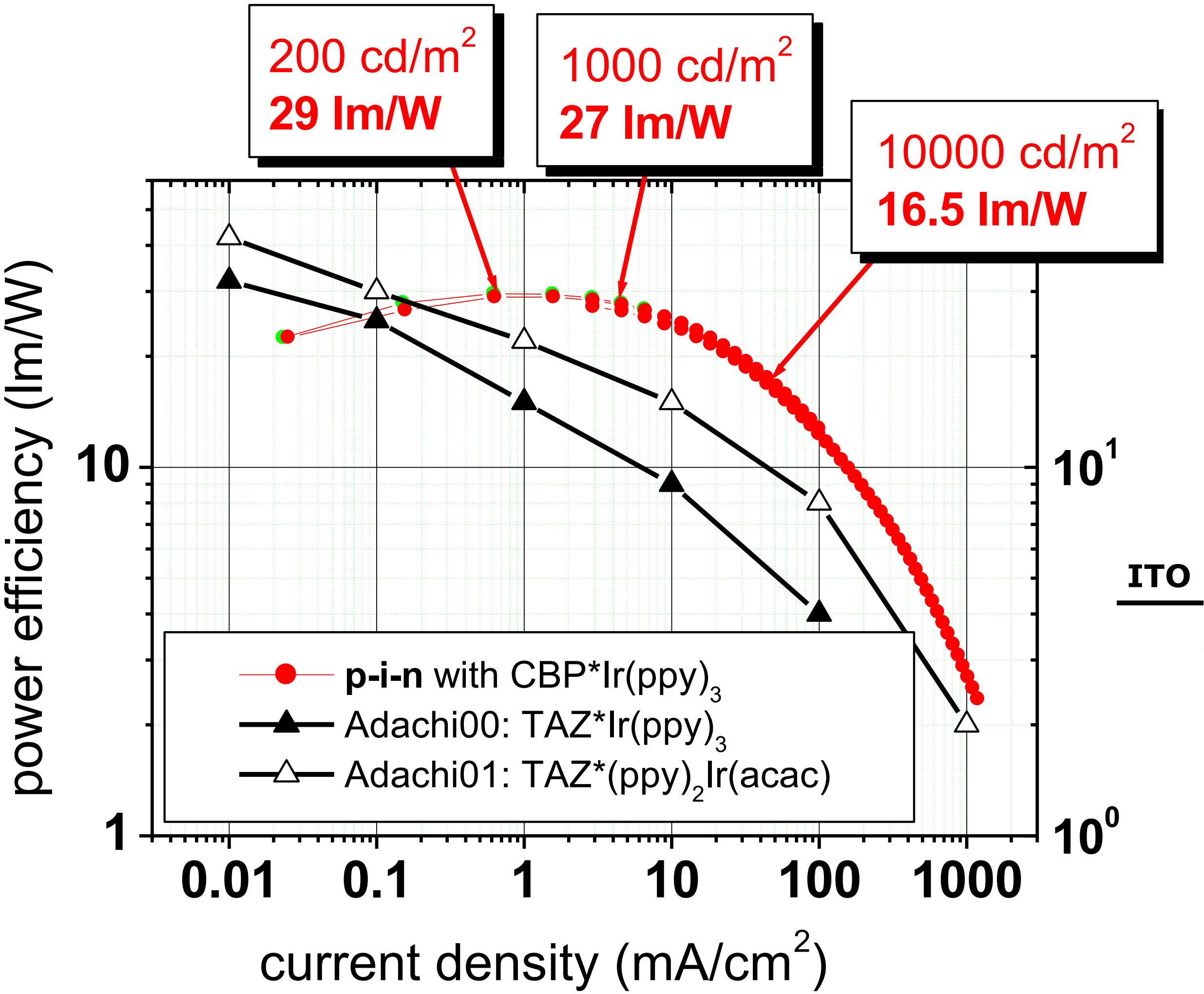


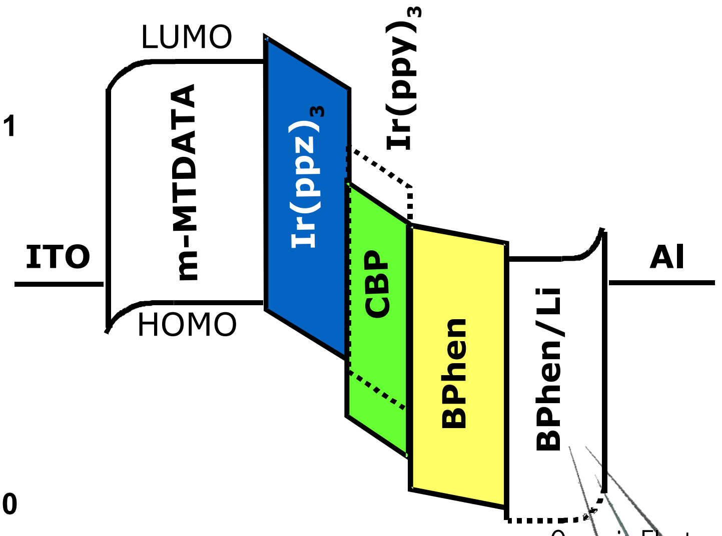
p-i-n PHOLED Structure

- 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





without bias

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

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

$$S+T \overset{k_{STA}}{\rightarrow} T^{n}+S_{0} \overset{k_{Tn}}{\rightarrow} T+S_{0} \qquad \text{(STA)}$$

$$S+P \overset{k_{SPA}}{\rightarrow} P^{n}+S_{0} \overset{k_{Pn}}{\rightarrow} P+S_{0} \qquad \text{(SPA)}$$

$$S+S \overset{k_{SSA}}{\rightarrow} S^{n}+S_{0} \overset{k_{Sn}}{\rightarrow} S+S_{0} \qquad \text{(SSA)}$$

Delayed fluorescence
Triplet fusion

$$T+T \overset{k_{TTA-S}}{\rightarrow} S^{n}+S_{0} \overset{k_{Sn}}{\rightarrow} S+S_{0} \qquad \text{(TTA-S)}$$

$$T+T \overset{k_{TTA-T}}{\rightarrow} T^{n}+S_{0} \overset{k_{Tn}}{\rightarrow} T+S_{0} \qquad \text{(TTA-T)}$$

$$T+P \overset{k_{TPA}}{\rightarrow} P^{n}+S_{0} \overset{k_{Pn}}{\rightarrow} P+S_{0} \qquad \text{(TPA)}$$

Singlet fission when
$E_S \geq 2E_T$

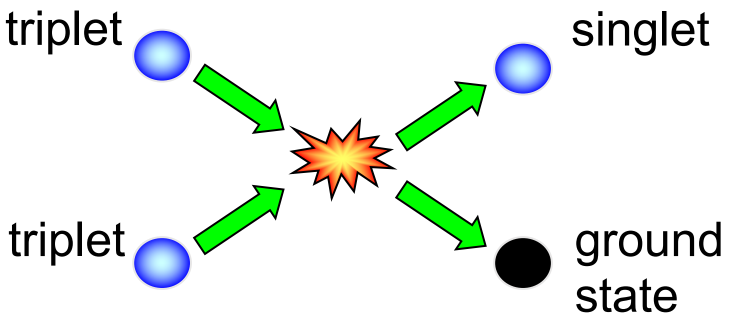
$$S \rightarrow 2T$$

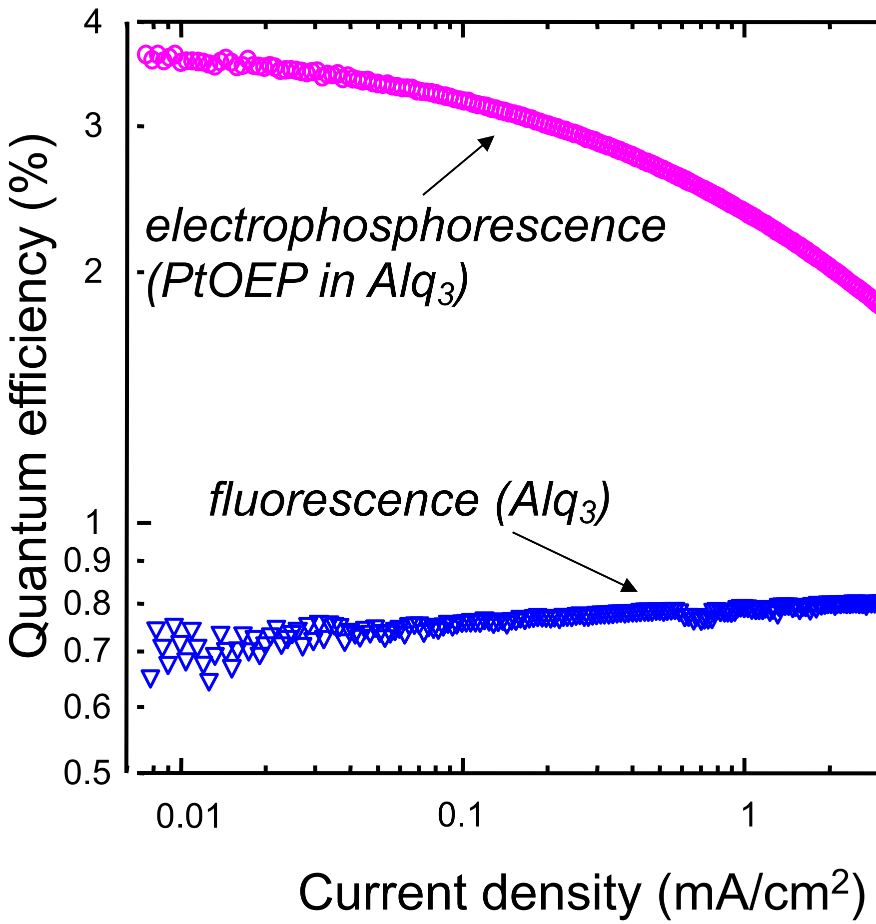
Efficiency Decreases with Increasing Current

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

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

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

τ : triplet lifetime
k_q : T-T annihilation rate

J : current density
d : thickness of active layer

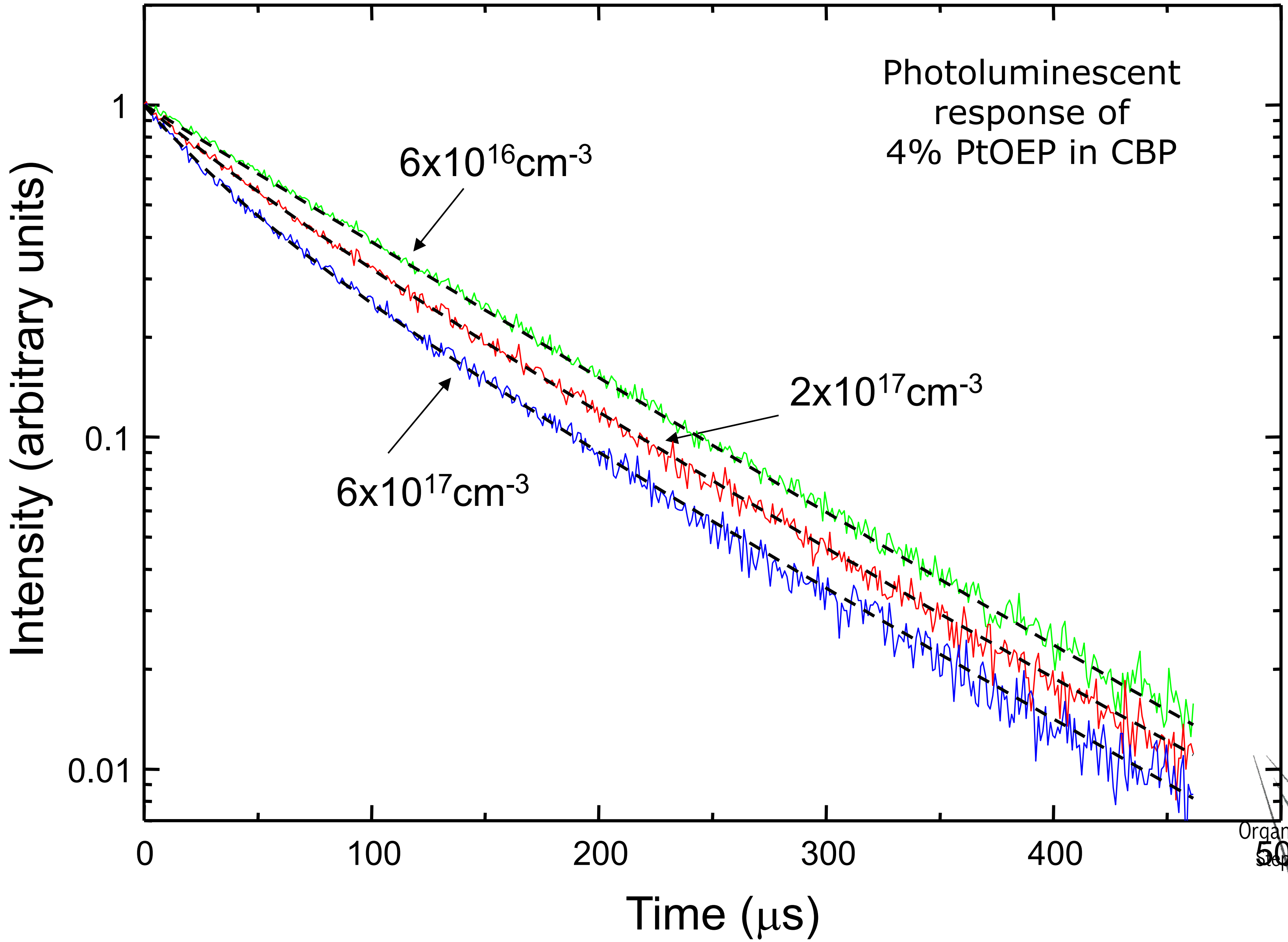
Transient solution:
$$\left[{}^3M^*(t)\right] = \frac{\left[{}^3M^*(0)\right]}{\left(1+\left[{}^3M^*(0)\right]\tau k_q\right)e^{t/\tau} - \left[{}^3M^*(0)\right]\tau k_q}$$

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

η : quantum efficiency
η_0: max efficiency

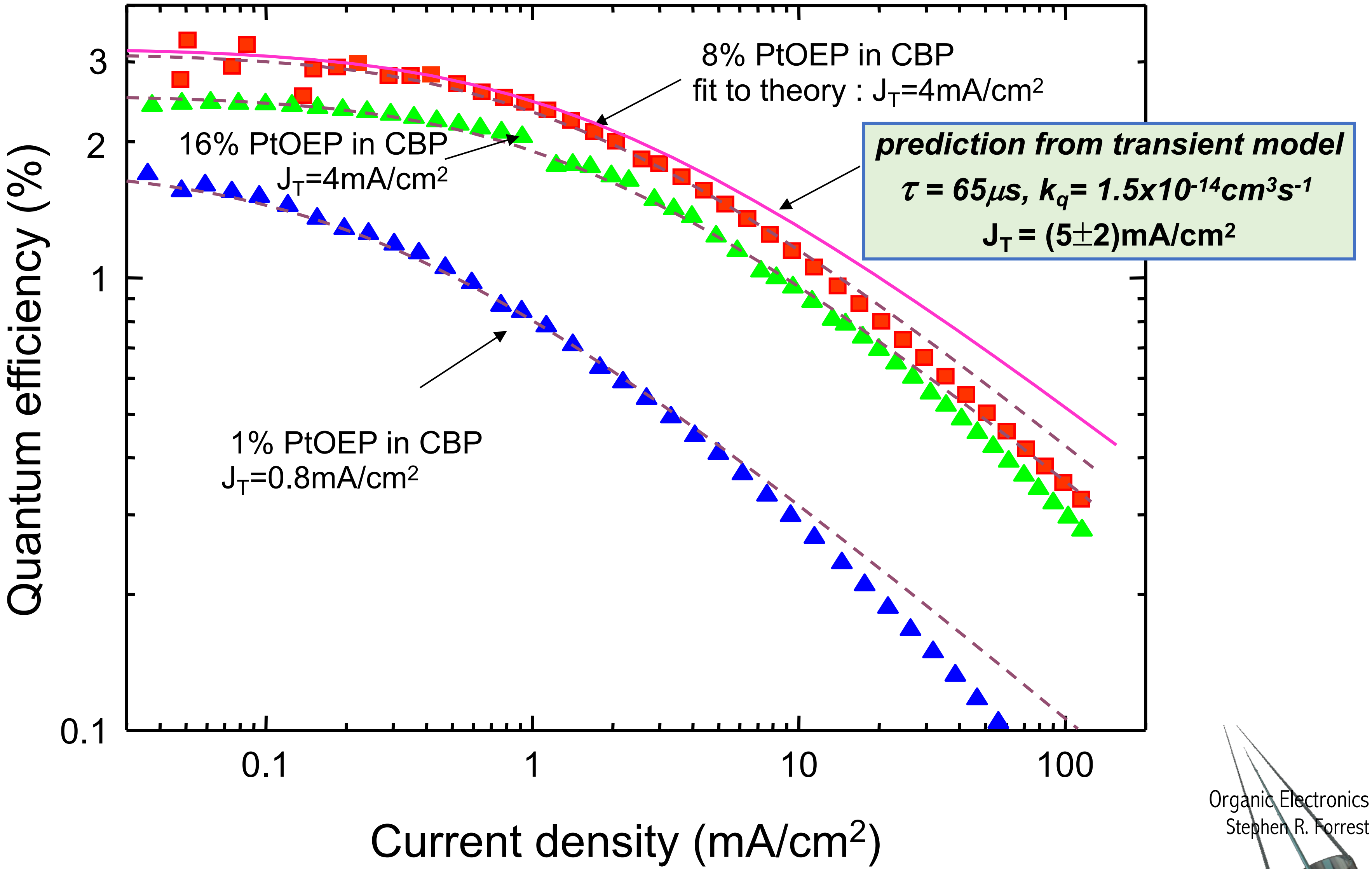
Threshold current density:
(for $\eta=\eta_0/2$)
$$J_T = \frac{2qd}{k_q\tau^2}$$

Transient Fits to TTA Theory



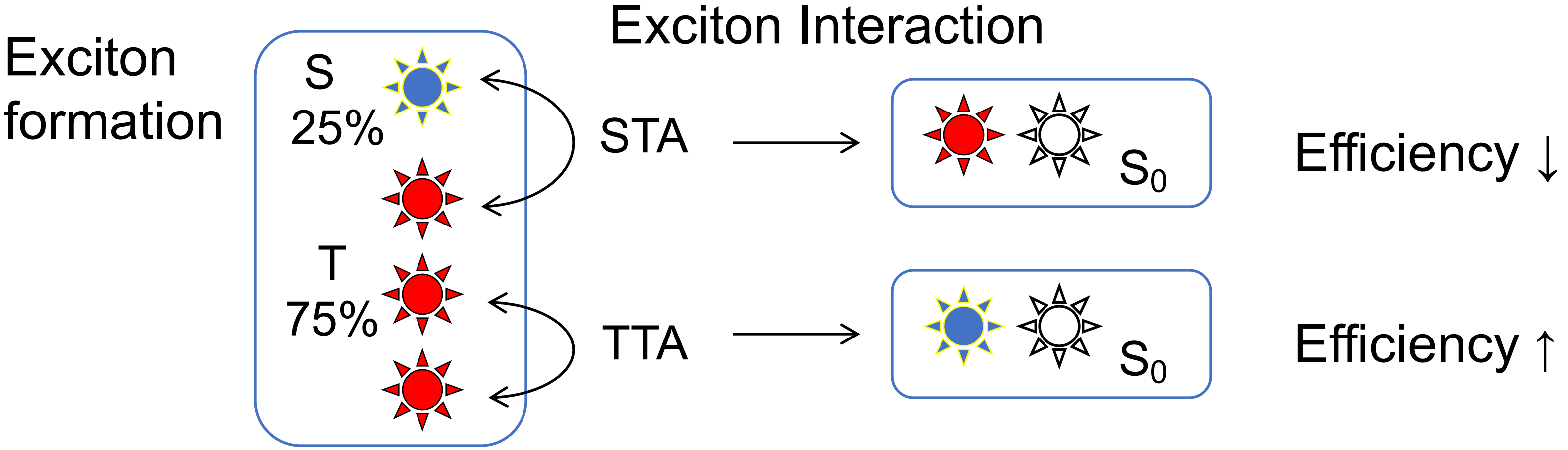
Baldo & Forrest, Phys. Rev. B 62, 10958 (2000)

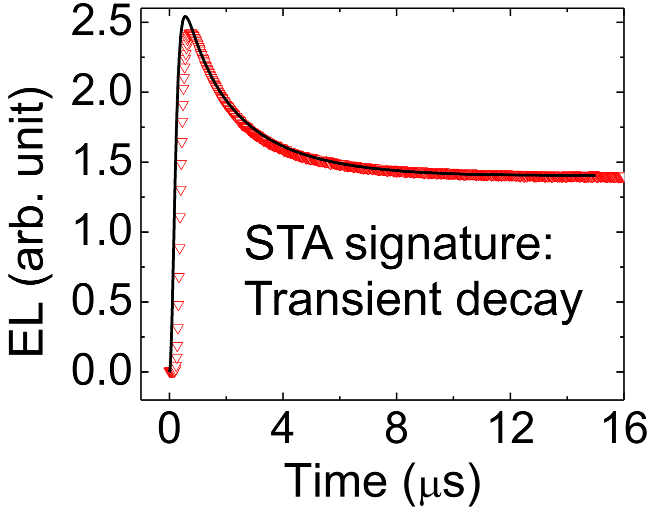
Steady State Roll off Matches Same TTA Theory



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

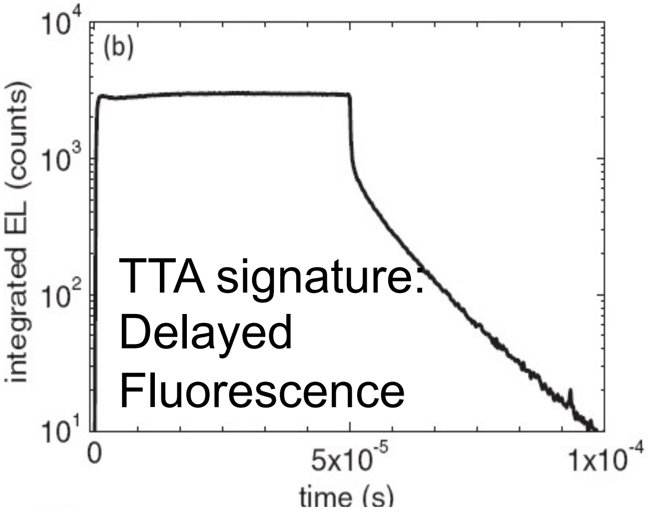
Making 1 from 2: TT vs. ST annihilation





STA signature:
Transient decay

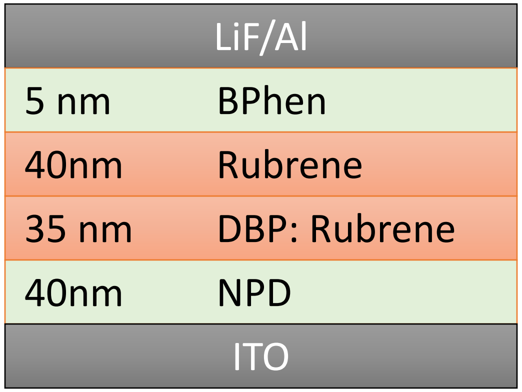
Zhang *et al*, CPL (2010)
Kasemann *et al*, PRB (2011)



TTA signature:
Delayed
Fluorescence

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

Fluorescent OLED Efficiency Increase Due to TTA



LiF/Al

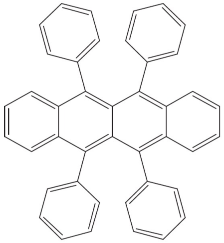
5 nm BPhen

40nm Rubrene

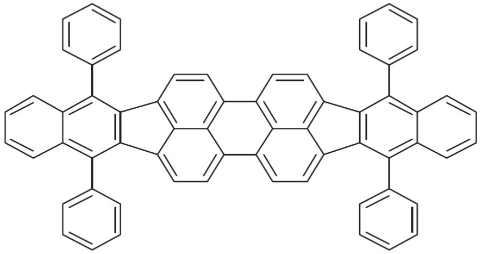
35 nm DBP: Rubrene

40nm NPD

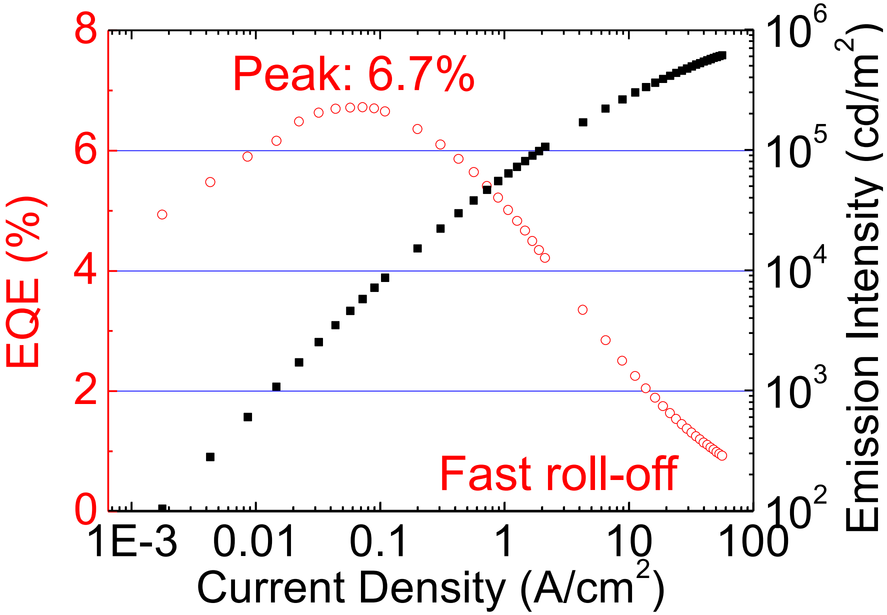
ITO

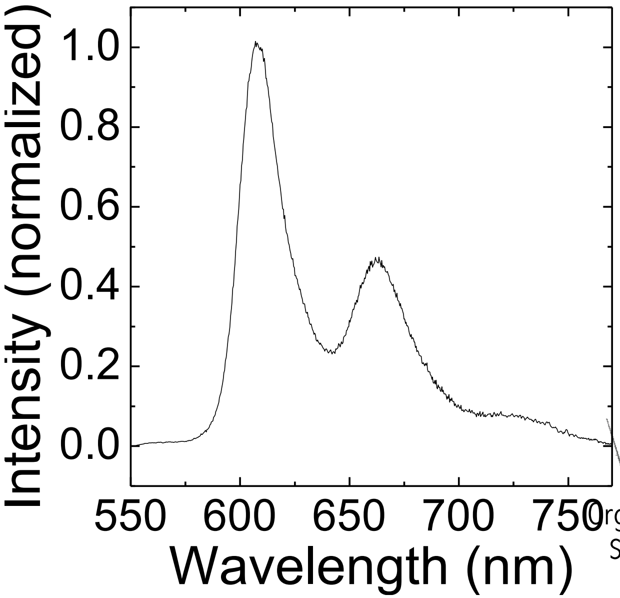


Rubrene
(E_T=1.1eV, E_S=2.2eV)



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





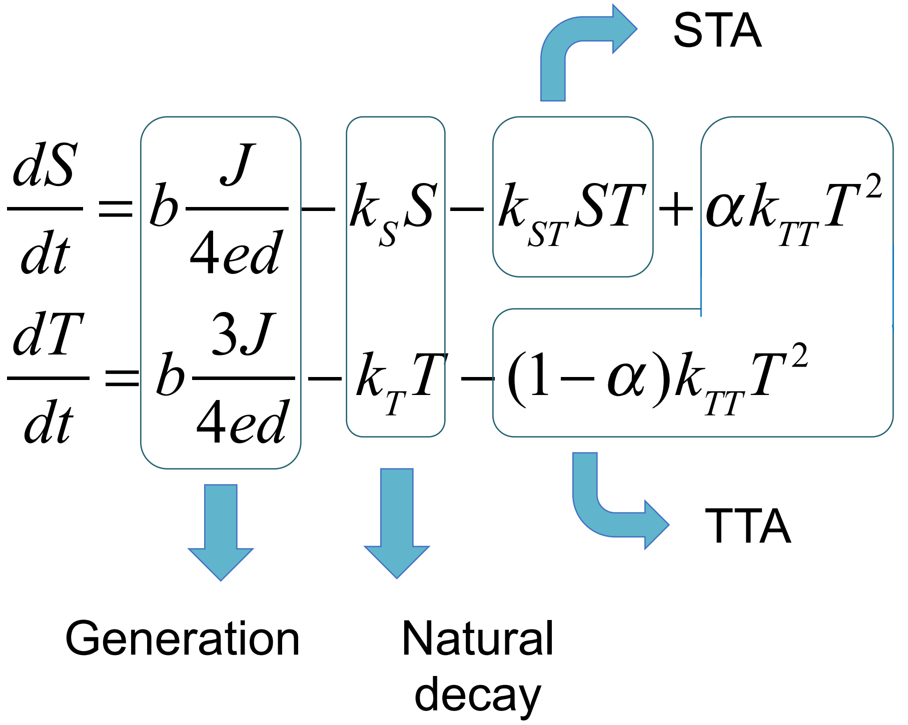
S and T Dynamics Describe TTA

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

Dynamics



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

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

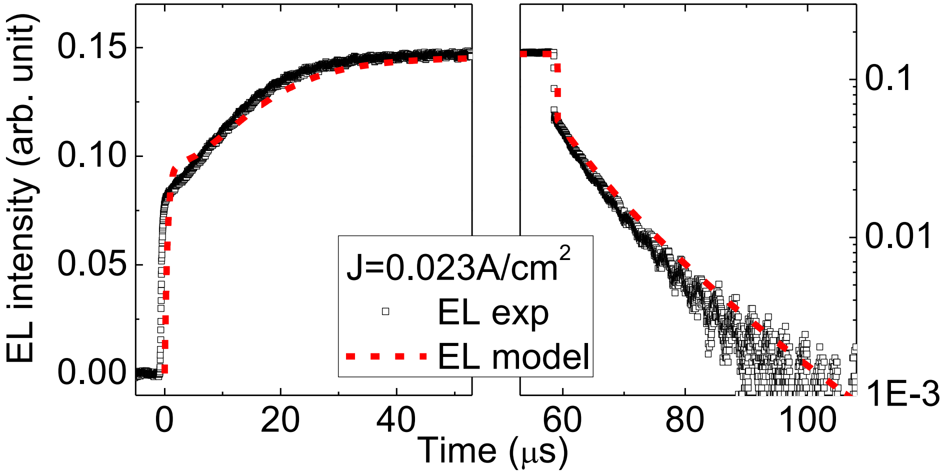
STA

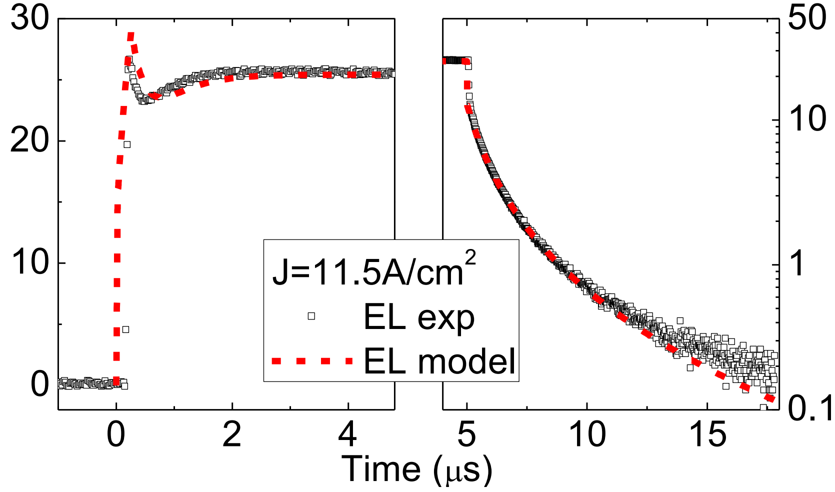
TTA

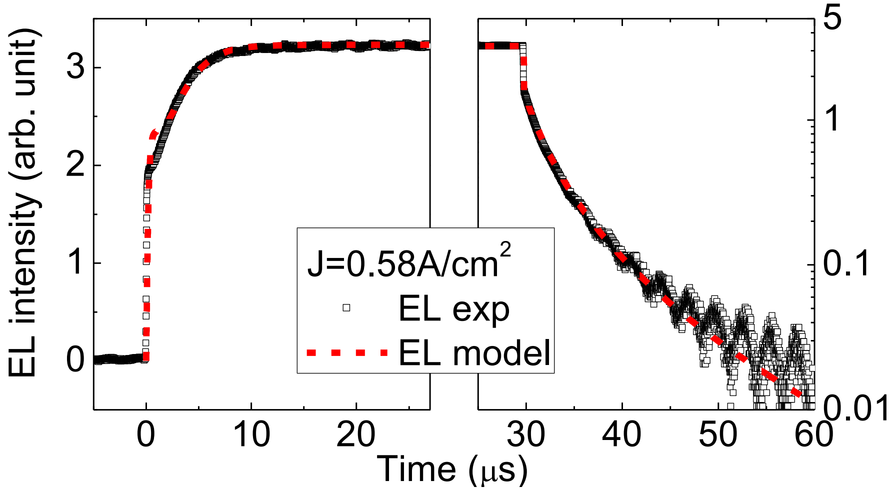
Generation

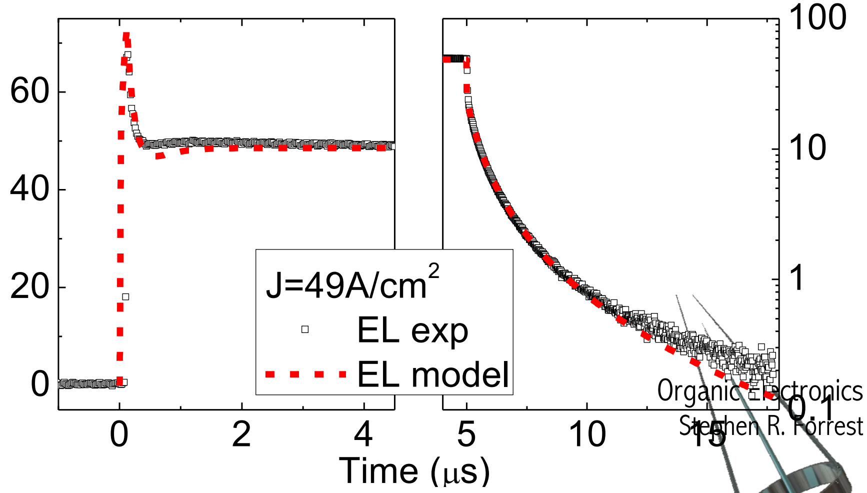
Natural decay

Model fits to experiment



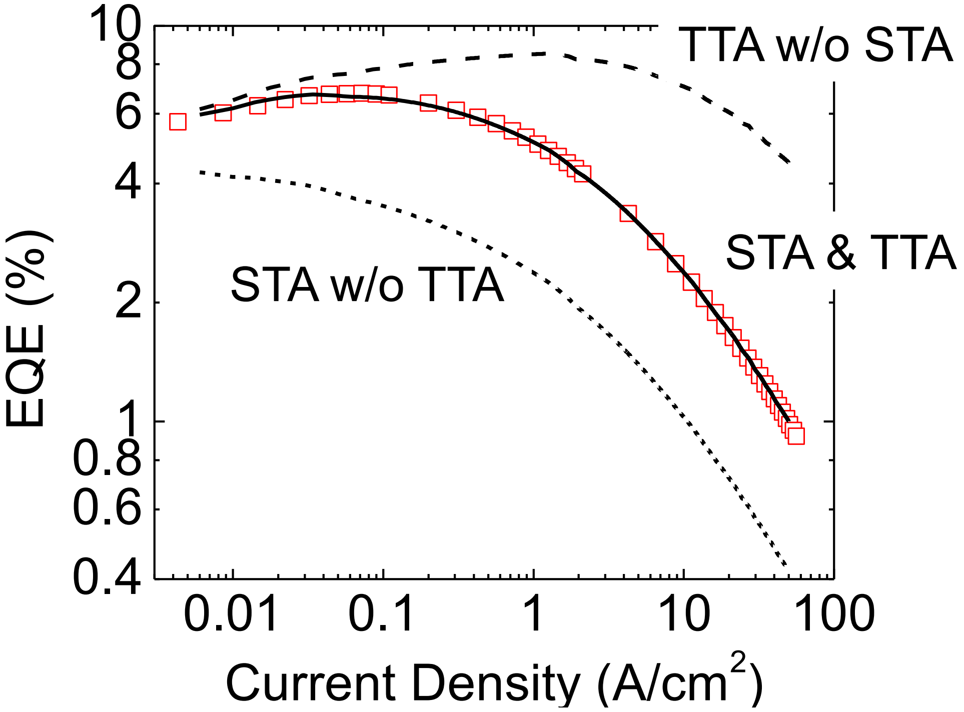






Y. Zhang, S. Forrest *Phys. Rev. Lett.*, **108**, 267474 (2012)

EQE of Rubrene OLEDs

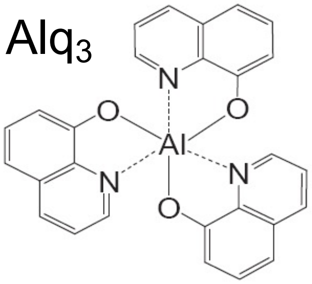


Route to high EQE & brightness fluorescent OLEDs:

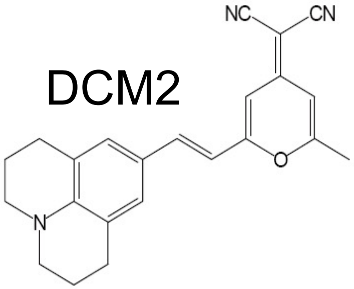
- ➢High S fraction in TTA: α
  - ✓$2\mathrm{x}E_T$ slightly larger than E_S
- ➢High TTA: k_{TT}
  - ✓Strong triplet diffusion
- ➢Low STA: k_{ST}
  - ✓Low S emis./T abs overlap

Increasing Efficiency Through Triplet Management

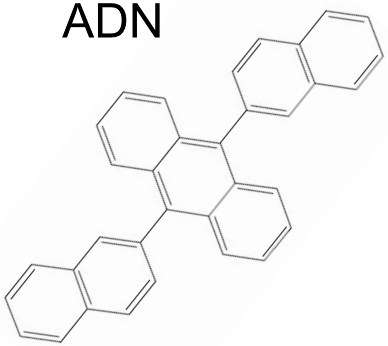
Alq$_3$

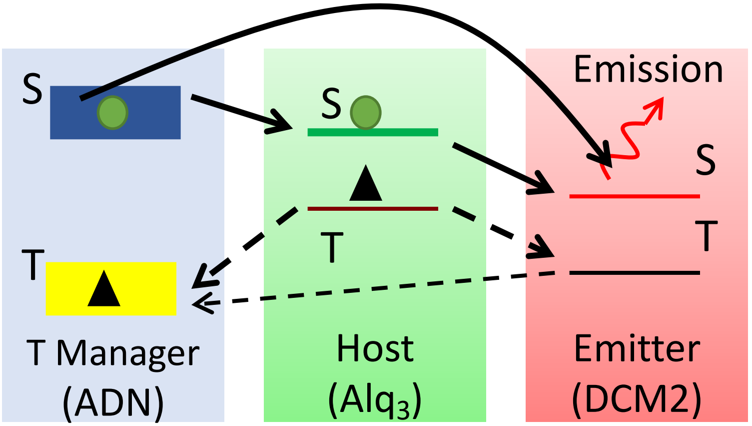


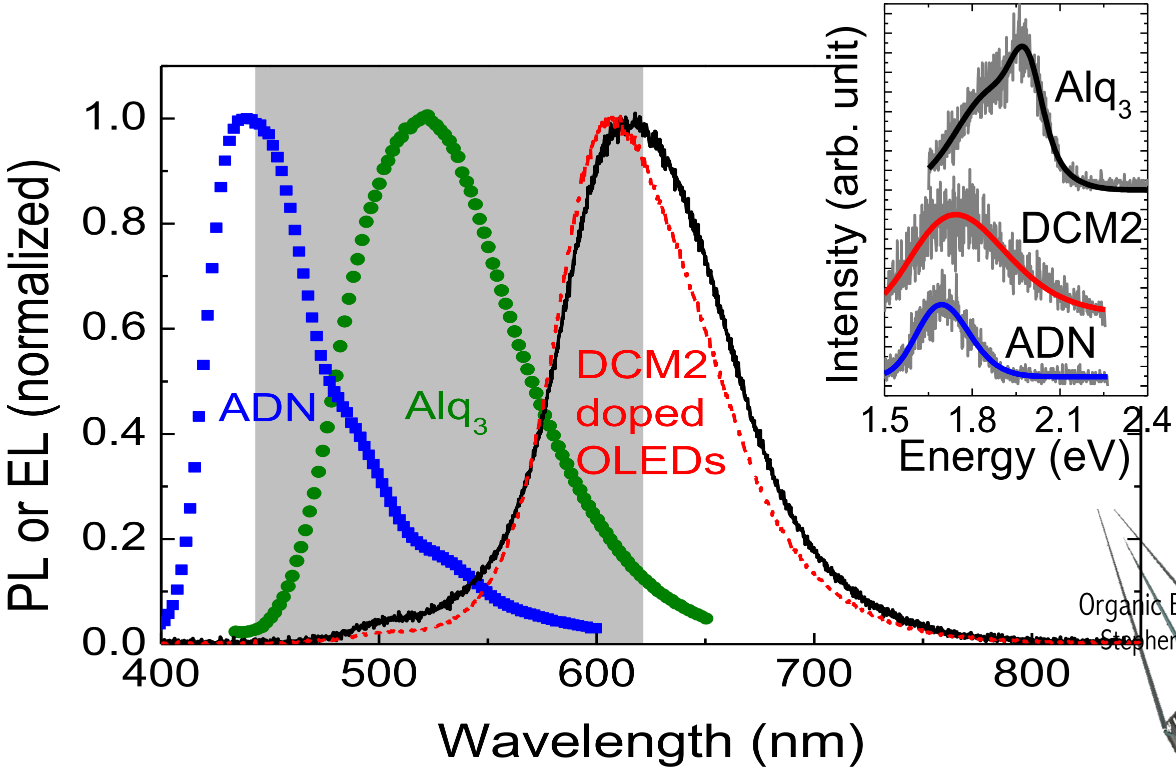
DCM2



ADN

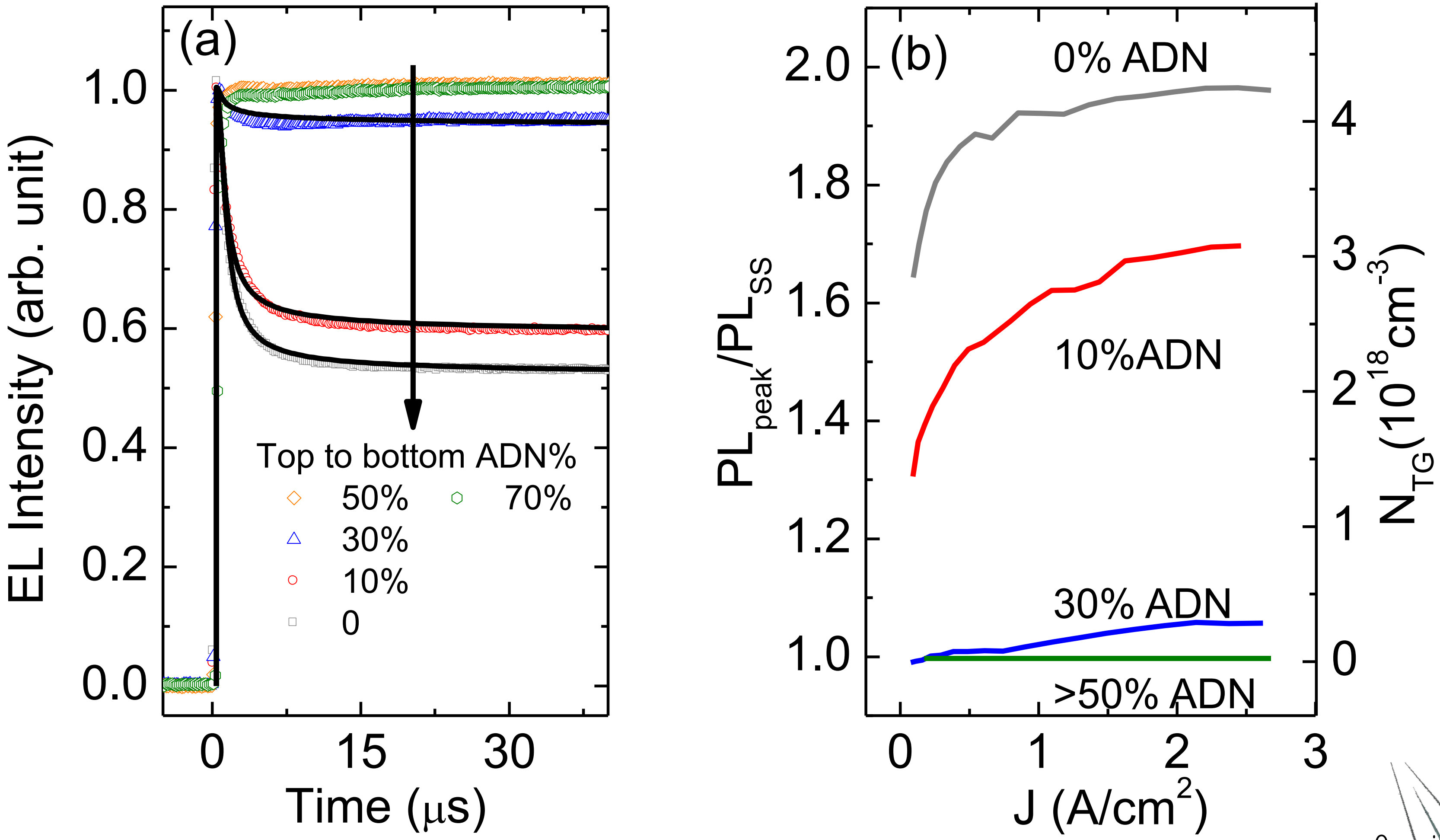






Y. Zhang, et al., APL, **99**, 223303 (2011)

Triplet-Managed ADN:Alq$_3$:DCM2 OLEDs



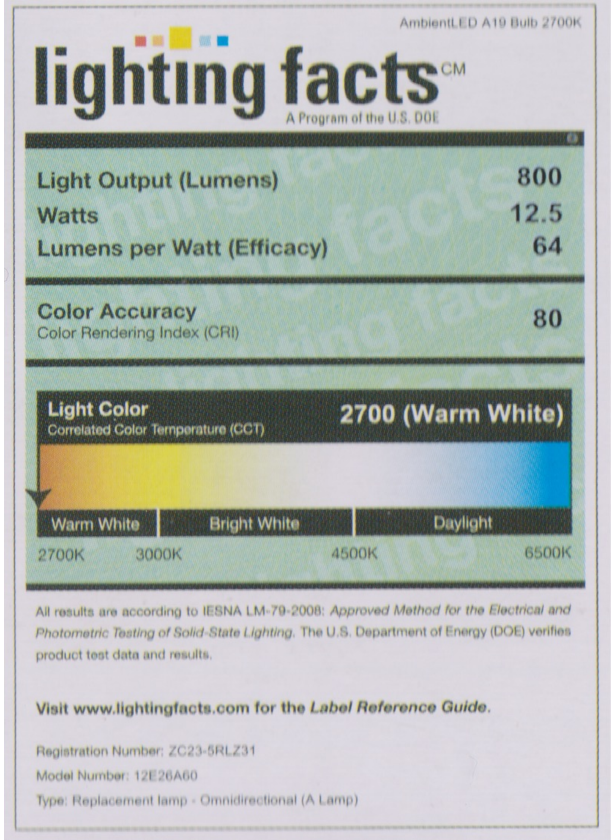
Quantifying White Light

- 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



AmbientLED A19 Bulb 2700K

lighting facts℠

A Program of the U.S. DOE

Light Output (Lumens)	**800**
Watts	**12.5**
Lumens per Watt (Efficacy)	**64**
Color Accuracy Color Rendering Index (CRI)	**80**
Light Color Correlated Color Temperature (CCT)	**2700 (Warm White)**

All results are according to IESNA LM-79-2008: *Approved Method for the Electrical and Photometric Testing of Solid-State Lighting*. The U.S. Department of Energy (DOE) verifies product test data and results.

Visit www.lightingfacts.com for the *Label Reference Guide*.

Registration Number: ZC23-5RLZ31

Model Number: 12E26A60

Type: Replacement lamp - Omnidirectional (A Lamp)

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

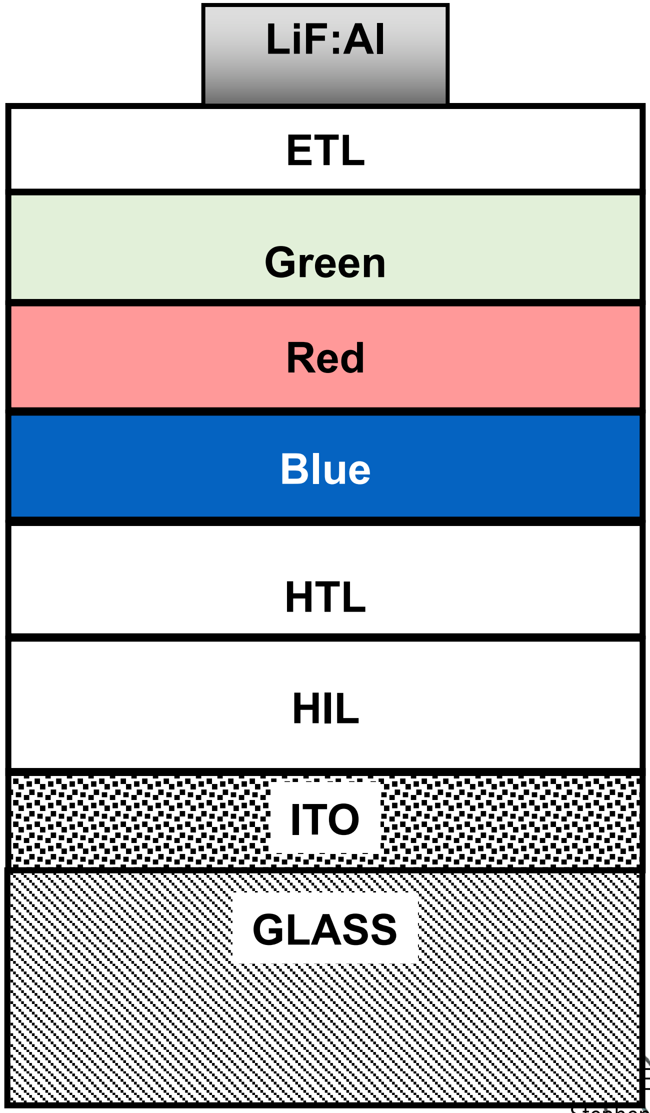
- Prevents energy transfer between dopants.

- 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

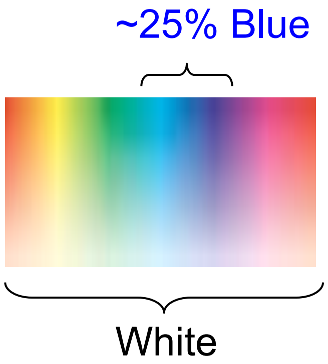
Why does it work?

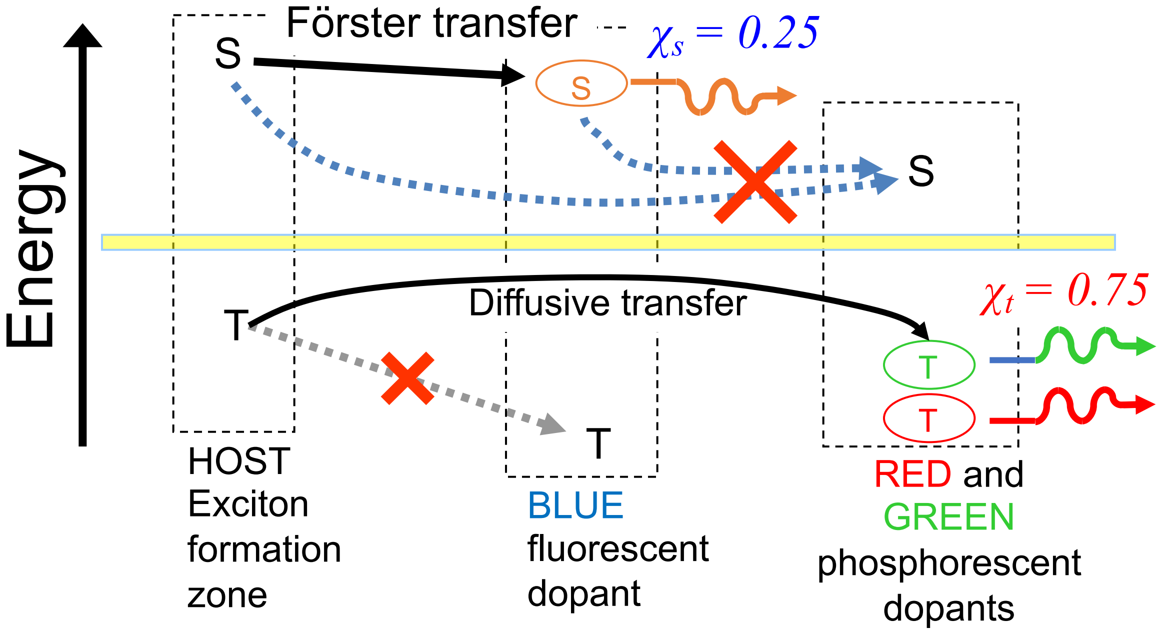
- Triplets can diffuse much further than singlets (measured ~1000Å)

- 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

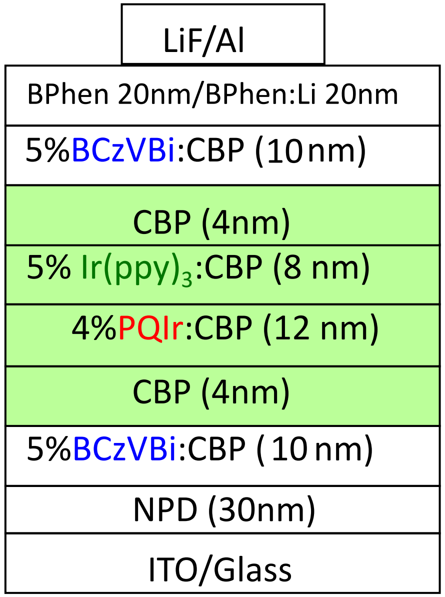
Potential for 100% IQE

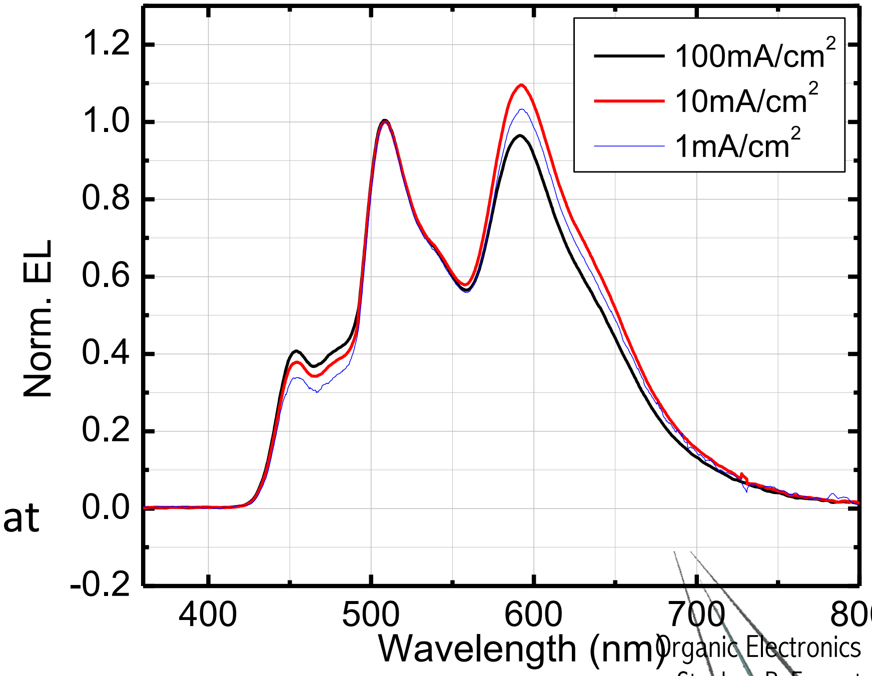
More stable color balance

Enhanced stability

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

Performance of Hybrid WOLED


LiF/Al
BPhen 20nm/BPhen:Li 20nm
5%BCzVBi:CBP (10nm)
CBP (4nm)
5% $Ir(ppy)_3$:CBP (8 nm)
4%PQIr:CBP (12 nm)
CBP (4nm)
5%BCzVBi:CBP (10 nm)
NPD (30nm)
ITO/Glass



Total External Quantum Efficiency: (18.4 ±0.5)%

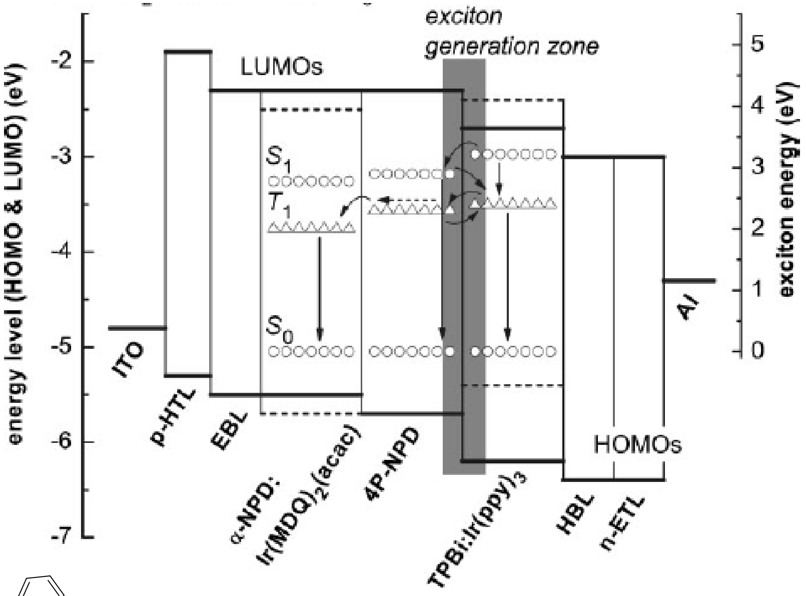
Total Power Efficiency:(23.8 ±0.5) lm/W

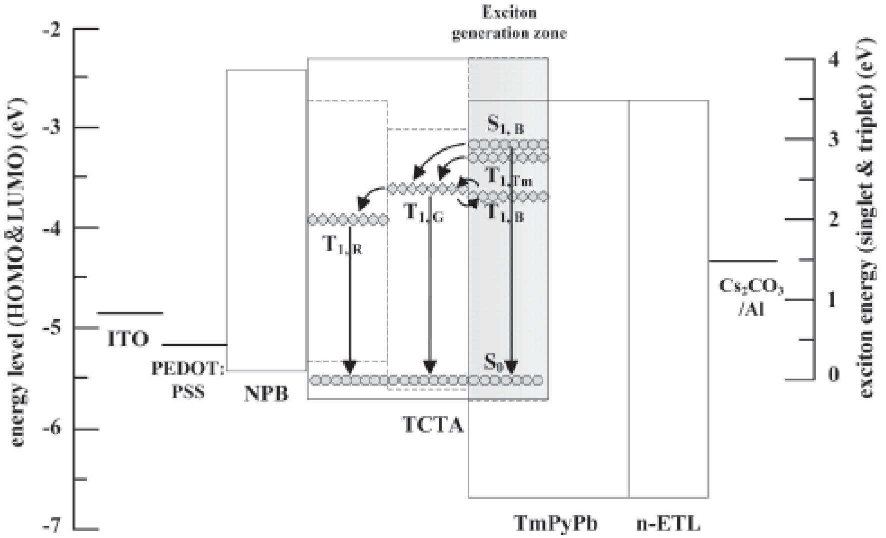
- Color Rendering Index (CRI): 84 at 1, 10 mA/cm^2, 83 at 100 mA/cm^2
- CIE: (0.40, 0.44) → (0.39, 0.43)

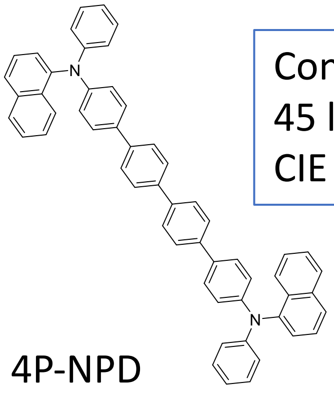
(Y. Sun, et al., *Nature*, 440, 908, 2006)

Alternative Hybrid Designs

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







4P-NPD

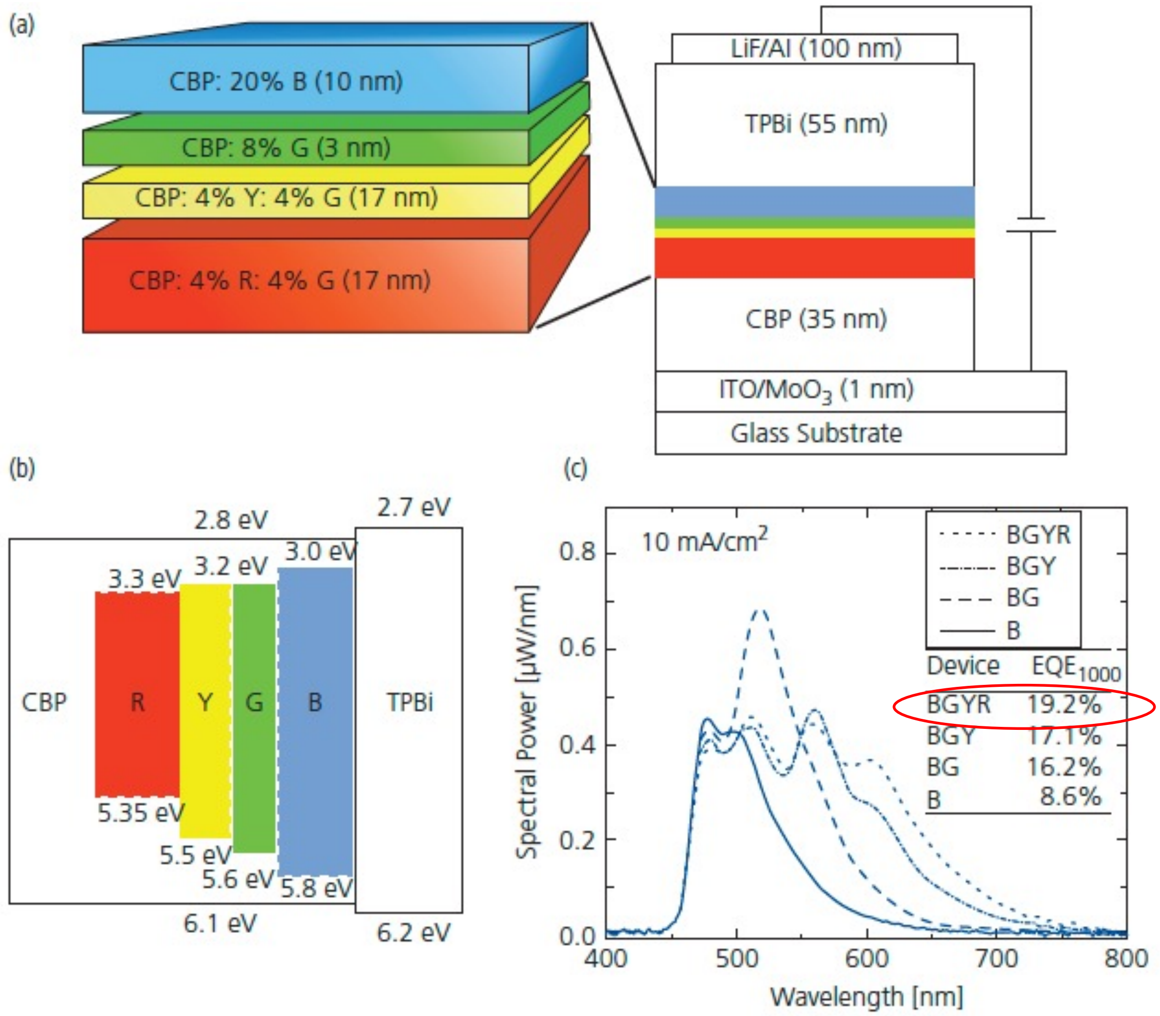
Φ_{PL}(film) = 92%

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

4 Color EML Results in High Efficiency and CRI



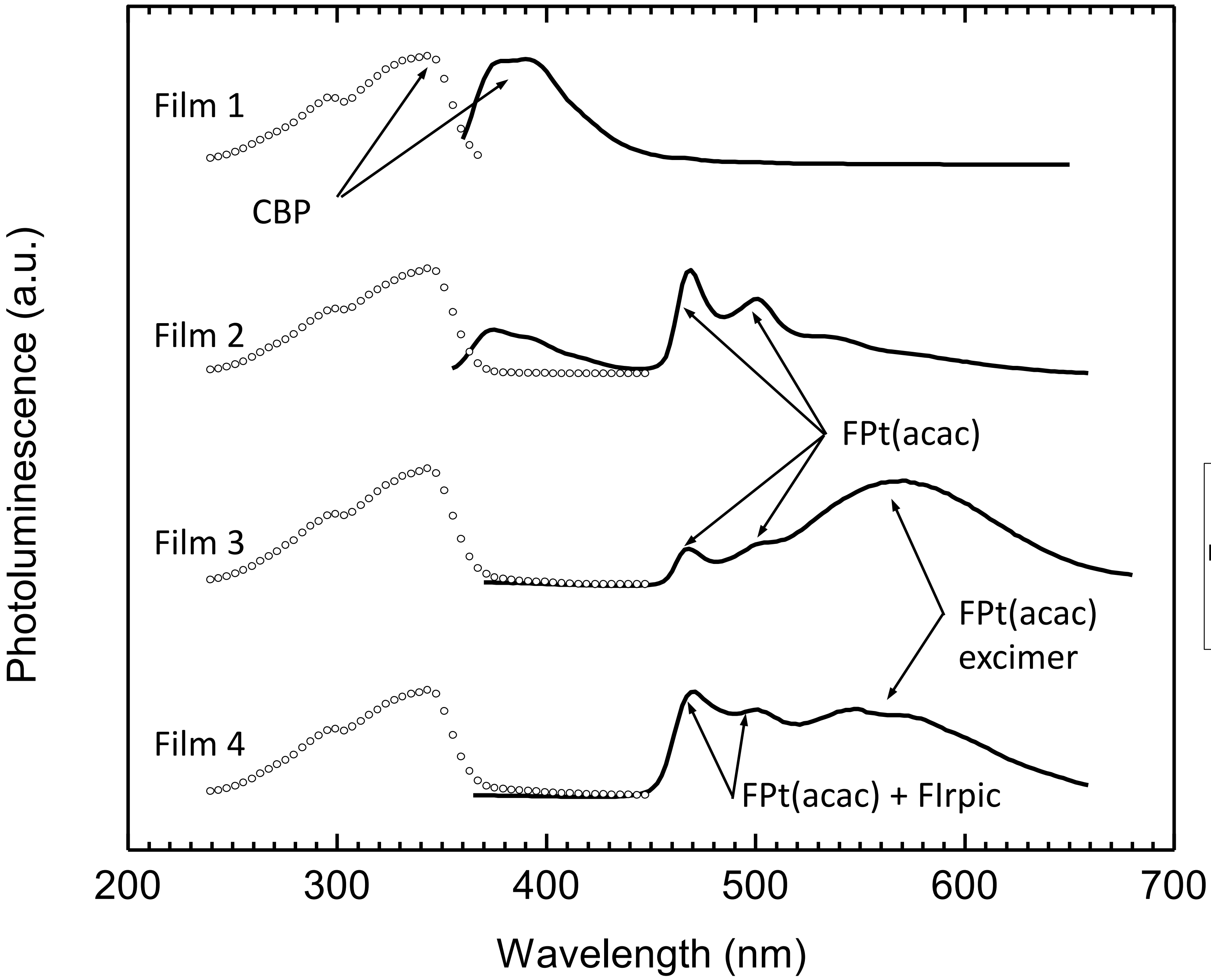
CRI = 83

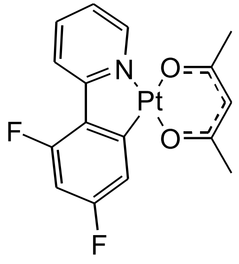
CCT = 3332K (warm white)

η_P = 61.7 lm/W

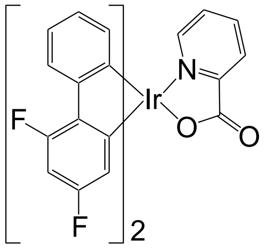
Chang, et al. Adv. Func. Mater., 23, 705 (2013)

Broad Excimer Emission Simplifies Device Structure





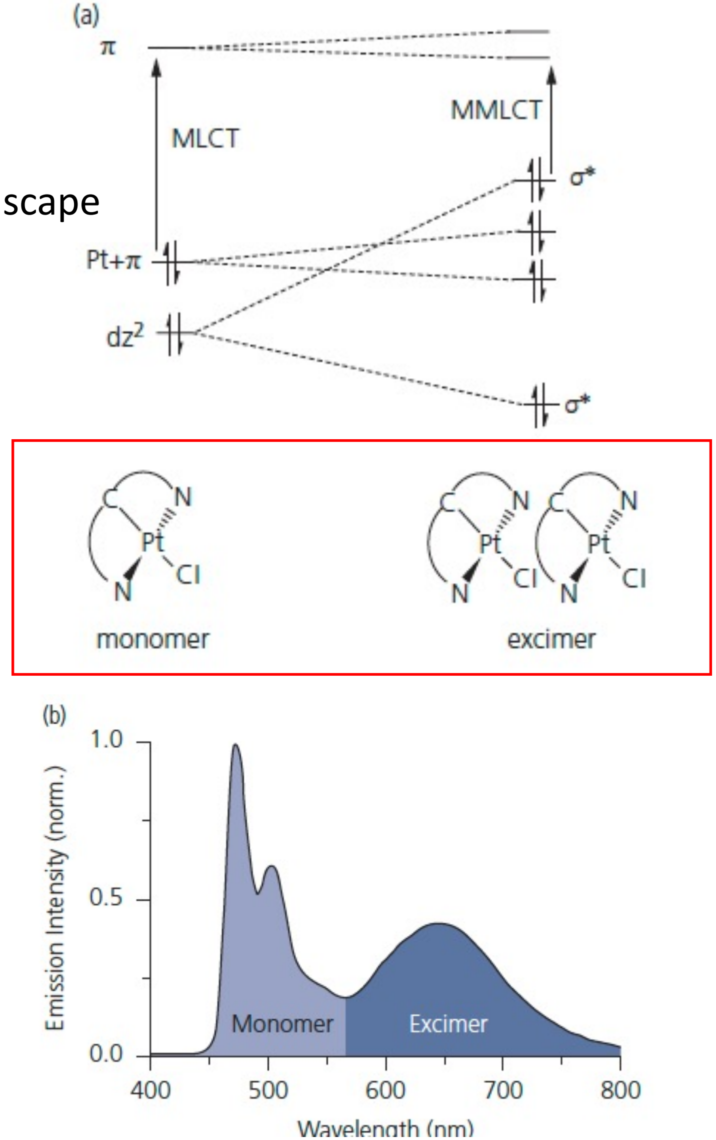
FPt(acac)



FIrpic

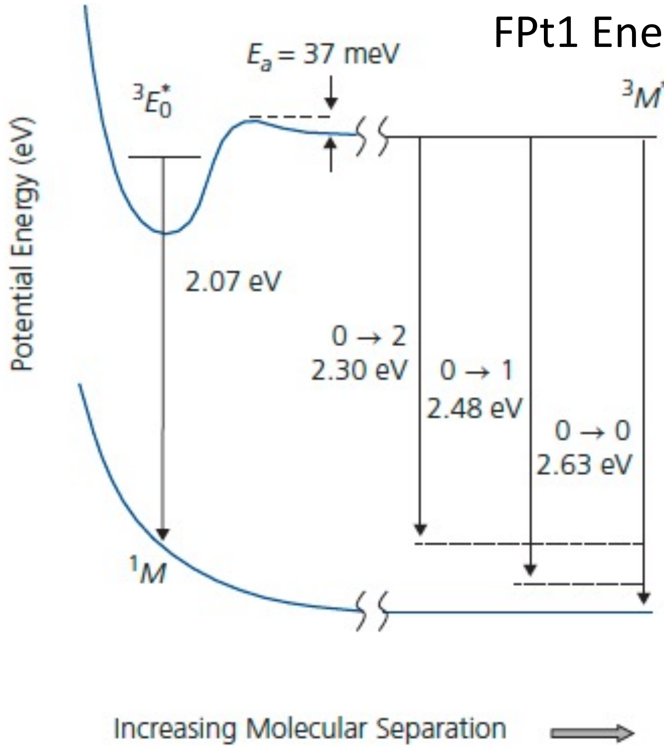
Simultaneous Blue Exciton & Broad Excimer Emission Can Generate White

Energetic landscape of dihedral Pt complexes



Fleetham & Lee, J. Photon. Energy 4, 040991 (2014)

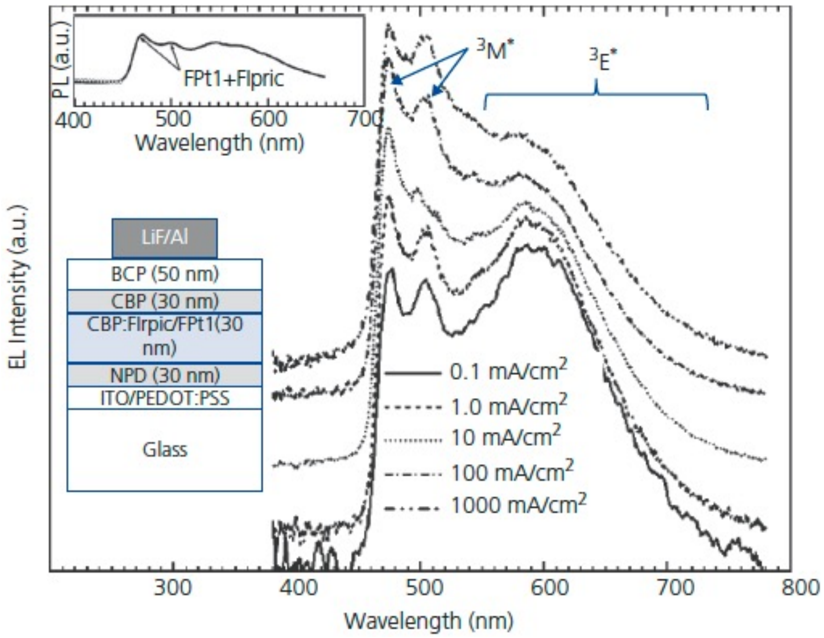
FPt1 Energetics



Thermal activation needed to access excimer state

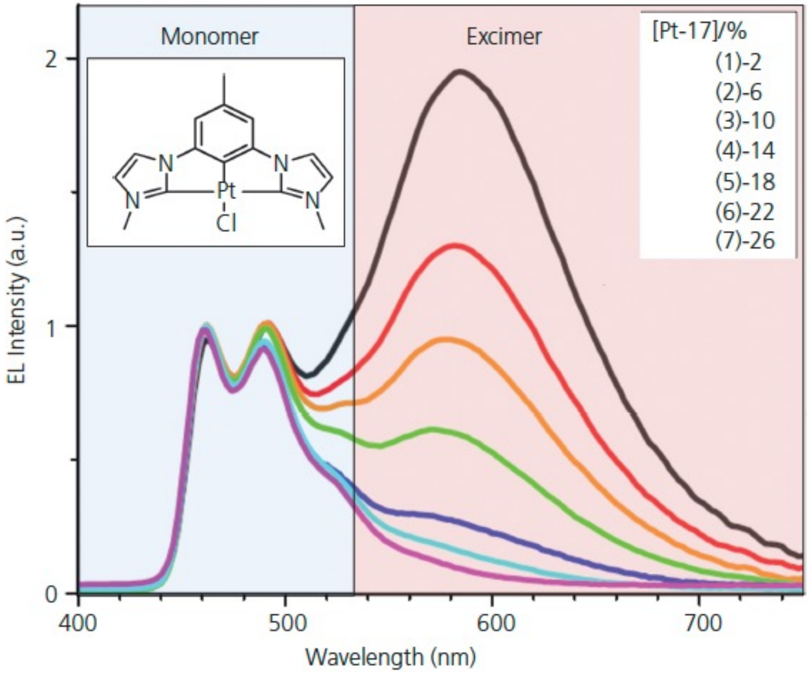
D'Andrade & Forrest, Chem. Phys. 286, 321 (2003)

Excimer WOLED Spectra



- Blend of monomer (FIrpic) and excimer (FPt1) emitters
- Excimer not as efficient as monomer emission

D'Andrade, et al. Adv. Mater. 14, 1032 (2002)



- Excimer emission increases with Pt-complex concentration

Bakken, et al. J. Photon. Energy, 2, 021203 (2012)