Week 2-5

Light emitters 5

OLED Reliability
Lasers

Chapter 6.7-6.8

Reliability Testing Methodologies

- Need to set clear metrics for failure
  - ➢Example: Operating time for initial luminance (L_0) to decrease 10% from its initial value (called T90, or LT90)
  - ➢Employ a population of equivalent devices and monitor their performance parameter (e.g. luminance) under normal operating conditions
  - ➢If degradation slow, then an empirical degradation relationship is determined to extrapolate time to failure
    - Example: **Stretched exponential function**:

$$L(t) = L_0 exp(-t/\tau)^\beta$$

τ, β = empirical constants

  - If degradation too slow, need to accelerate via increased T or L_0.
    - Accelerated conditions must not introduce new failure modes
    - Need empirical relations to normalize lifetime to standard operating conditions (called **acceleration factors**)

$$LTx\left(L_0\right) = LTx\left(L_{0tst}\right) \bullet \left[\frac{L_{0tst}}{L_0}\right]^n$$

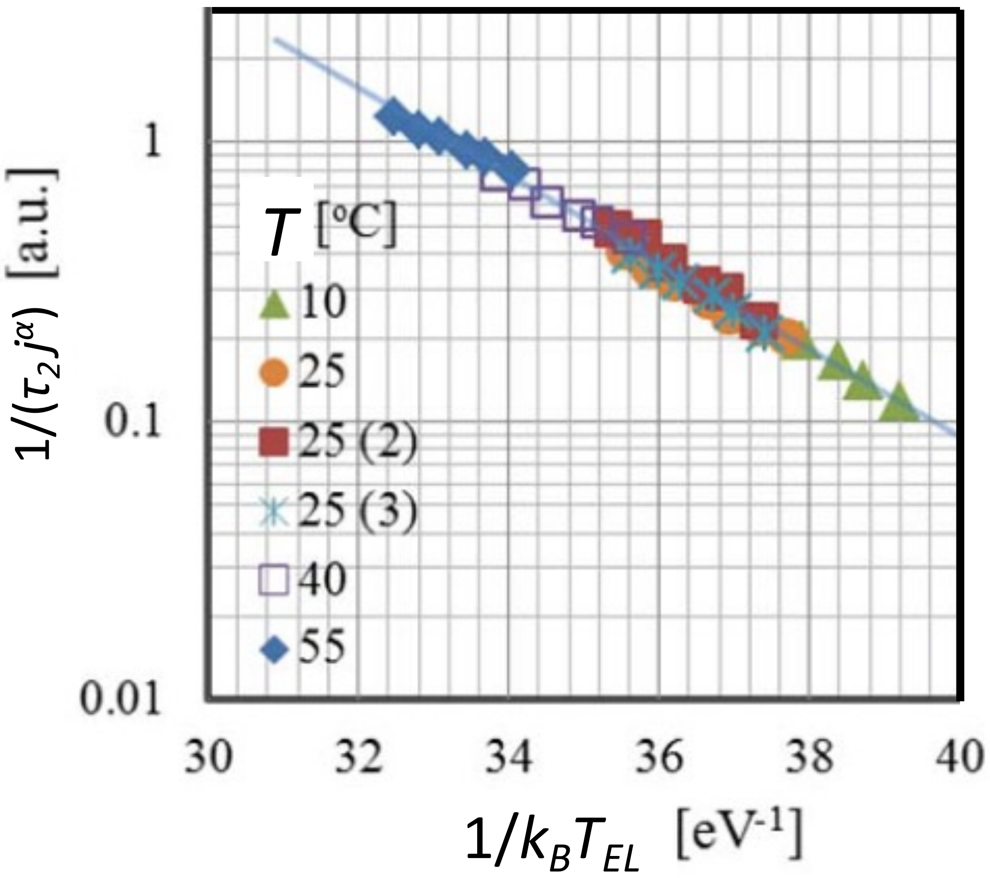
n = empirical acceleration factor

Accelerated Degradation Methodologies

Sum of lifetimes alternative empirical relation):

$$L(t)/L_0 = \overbrace{\lambda \exp(-t/\tau_1)}^{\text{Burn-in}} + \overbrace{(1-\lambda)\exp(-t/\tau_2)}^{\text{Long term decay}}$$

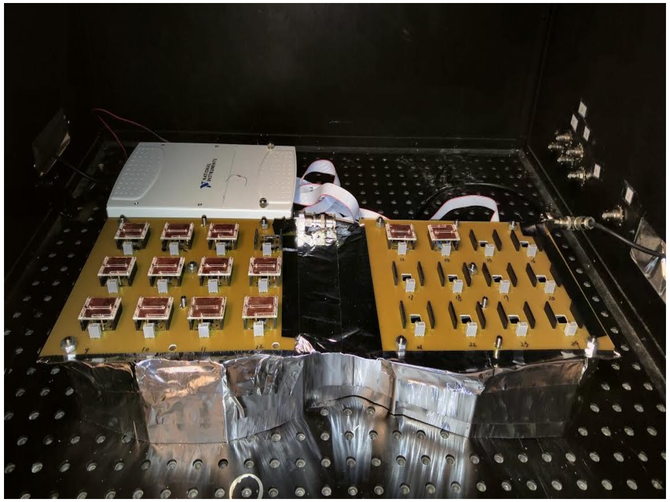
Example data: Green PHOLED



$$\frac{1}{\tau_2} = K'' j^\alpha \exp\left(-\Delta E_{A0}/k_B T\right)$$

ΔE_{A0}=thermal activation of degradation

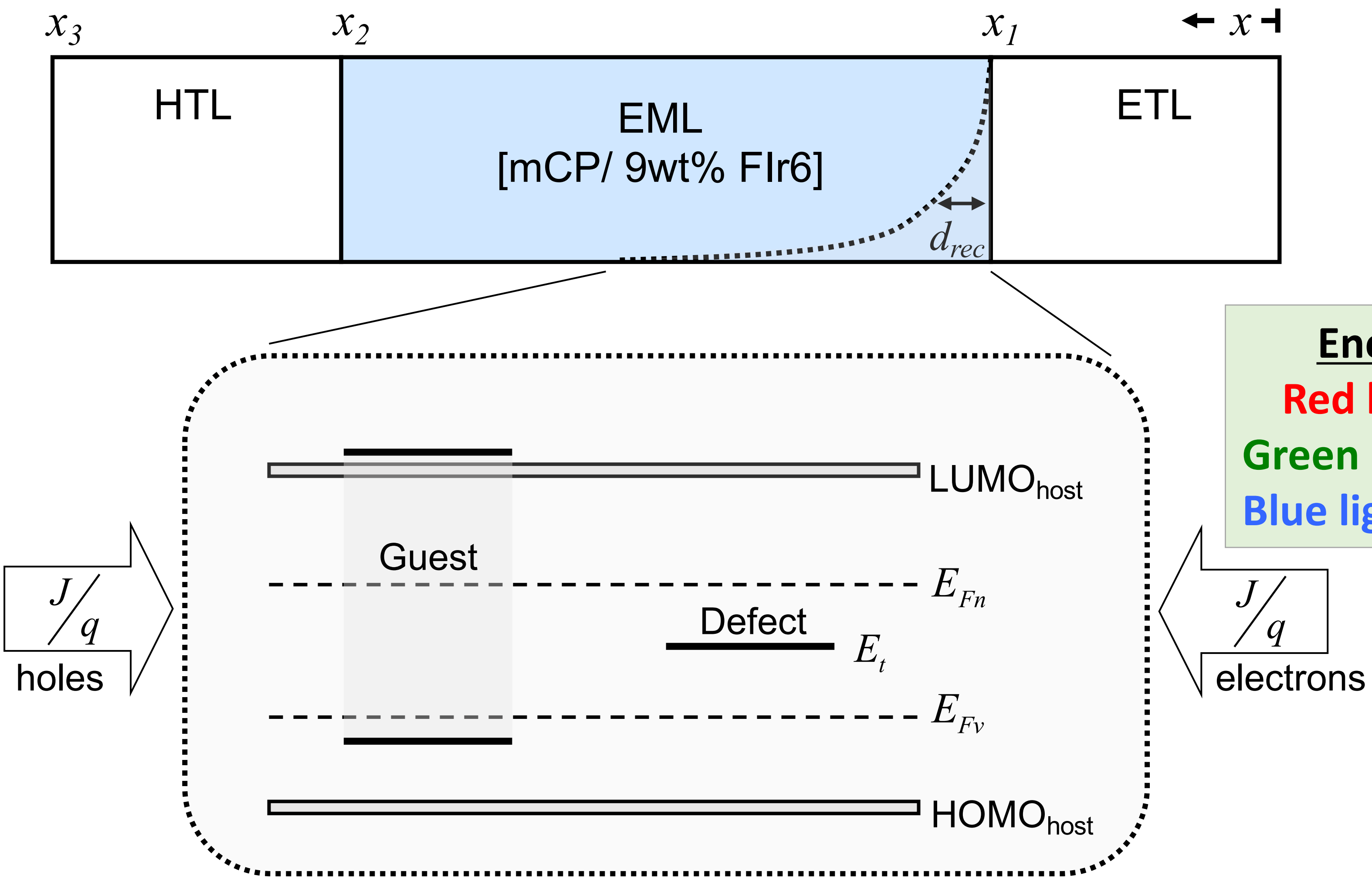
α = current acceleration factor



Measuring populations of identical devices

Yoshioka, et al.. 2014,*SID Digest Tech. Papers,* 45**,** 642.

Intrinsic Lifetime Limits of OLEDs



Energy Scale

Red light: ~ 2 eV

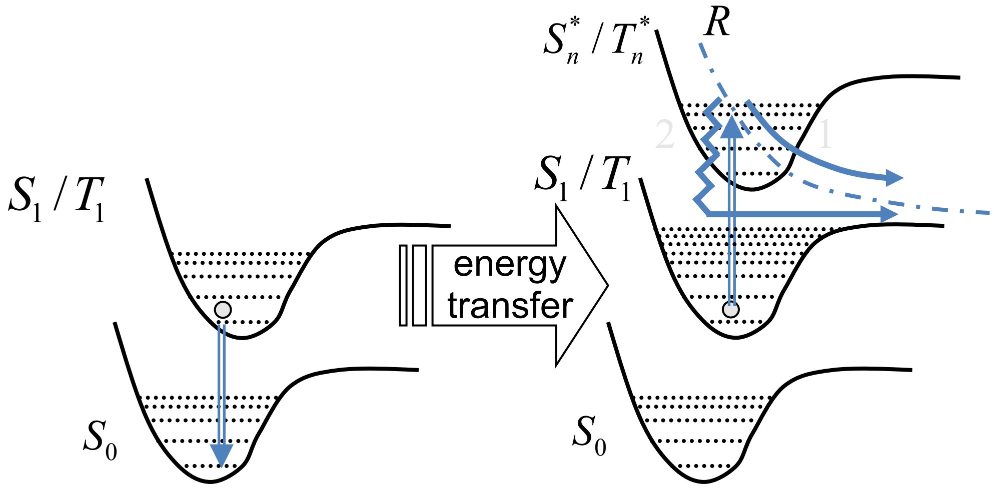
Green light: ~2.3 eV

Blue light: ~ 2.9 eV

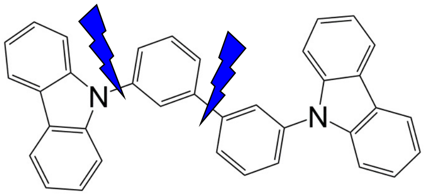
Giebink, et al., *J. Appl. Phys.*, **103**, 044509 (2008).

Degradation Routes

- Energetically Driven
  - Lifetime: R>G>B
- Two particle interactions lead to luminance loss
  - Exciton on phosphor, polaron on host
  - Exciton-exciton also possible

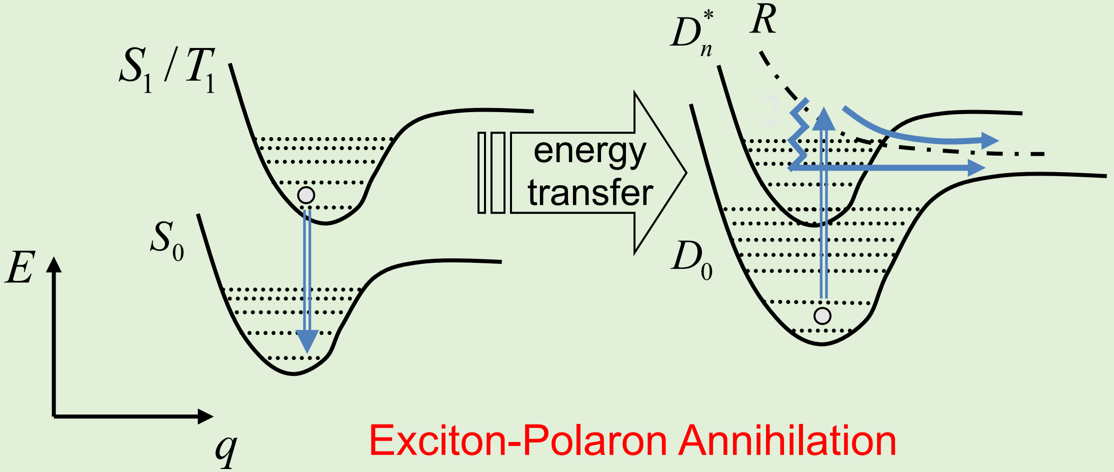


Exciton-Exciton Annihilation



Bond	BE(eV)	Bond	BE(eV)
C-C	3.64	N-N	1.69
C-H	4.28	N-O	2.08
C-O	3.71	N-H	4.05
C-N	3.04	O-O	1.51
C-F	5.03	H-H	4.52

Bond cleavage
Broken bonds? → Defects!

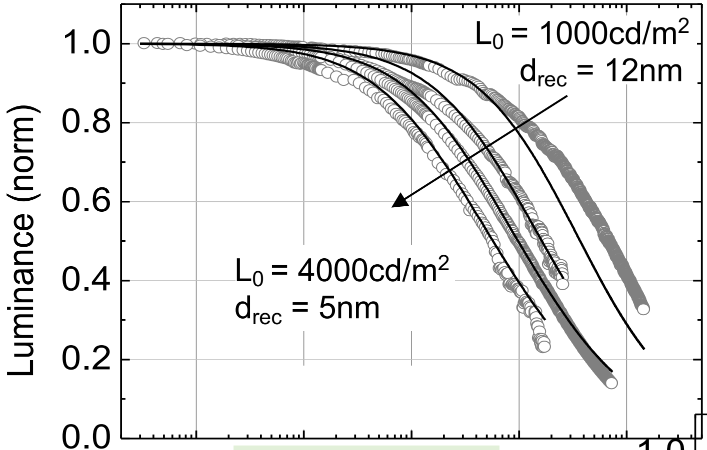


Exciton-Polaron Annihilation

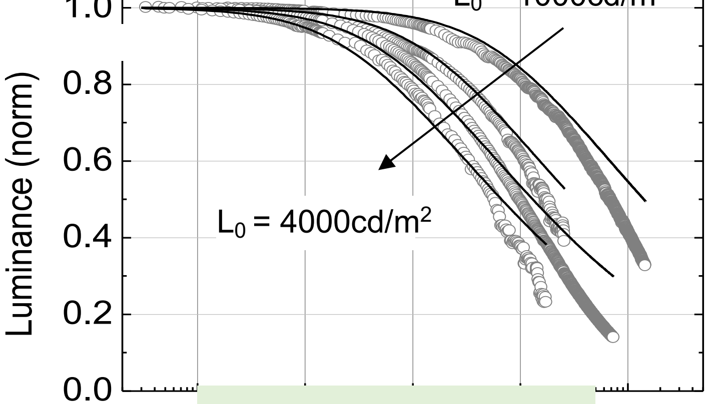
Triplet energy (~2.8 eV) + polaron (~3.3 eV) = hot polaron (≥ 6 eV)

Luminance Decay vs Time

- Blue PHOLED
- Prepared and packaged using industry std.

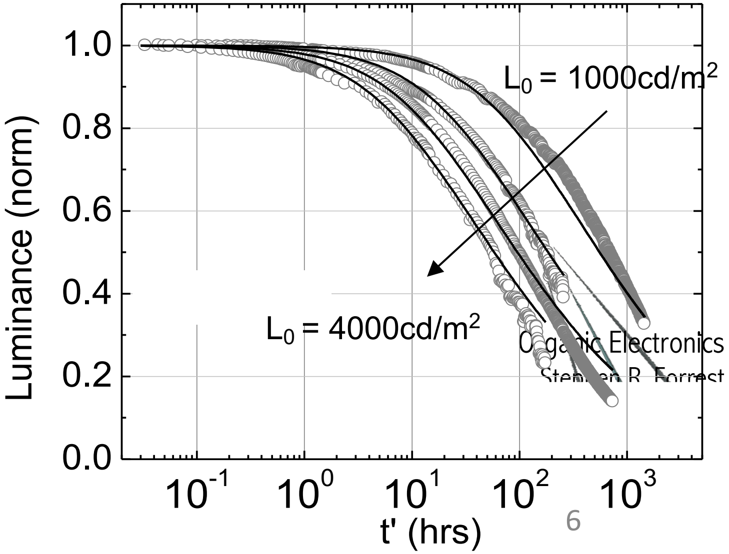


Exciton Localization



Exciton-Exciton Annihilation

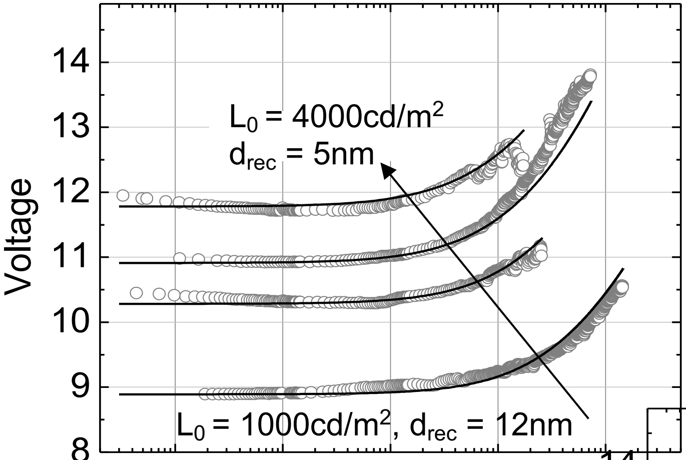
Exciton-Polaron Annihilation



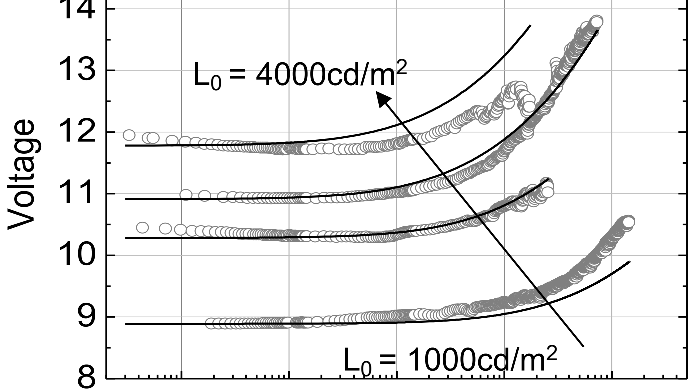
Defect Generation Rates

$$\frac{dQ(x,t')}{dt'} = \begin{cases} K_X n(x,t') \quad K_X p(x,t') & \text{P} \\ K_X N(x,t') & \text{E} \\ K_X N^2(x,t') & \text{E-E} \\ K_X N(x,t') n(x,t') \quad K_X N(x,t') p(x,t') & \text{E-P} \end{cases}$$

Drive Voltage Drift with Aging

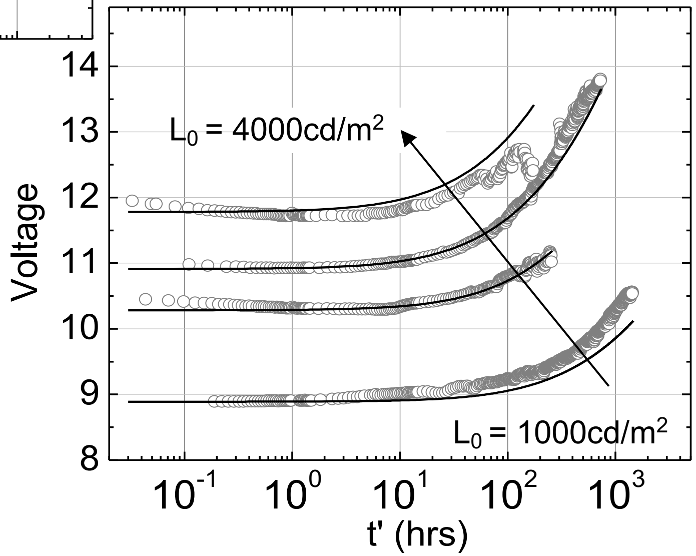


Exciton Localization



Exciton-Exciton Annihilation

Exciton-Polaron Annihilation

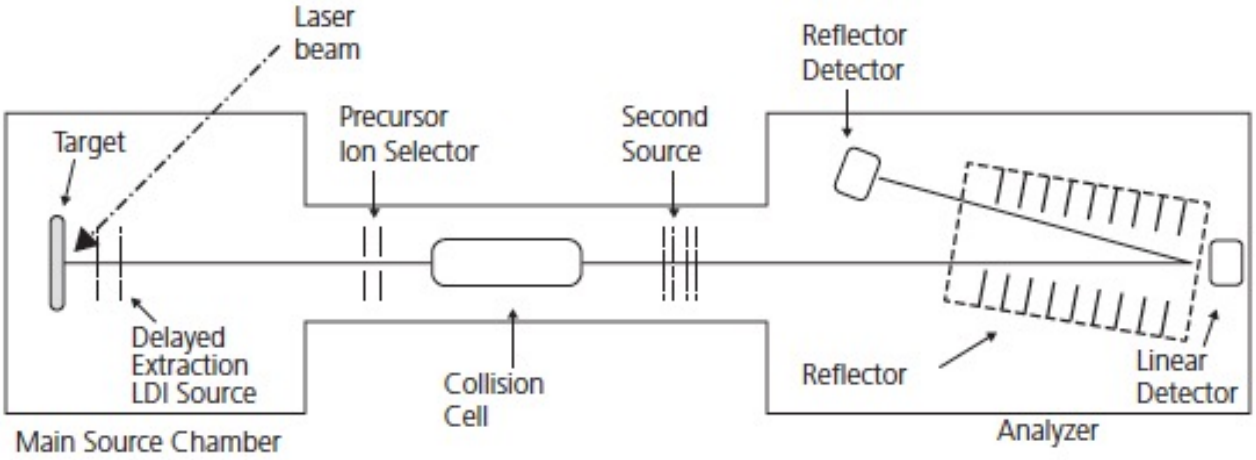


Conclusions

- Q~10^{18} cm^{-3} → 50% increase in quenching
- At 1000 cd/m^2, formation rate = 10^{12}cm^{-2}s^{-1}
  - 1 in 5 x10^8 E-P encounters leads to defect
  - Increasing recombination zone width extends lifetime
  - Guest triplets/host polarons most active

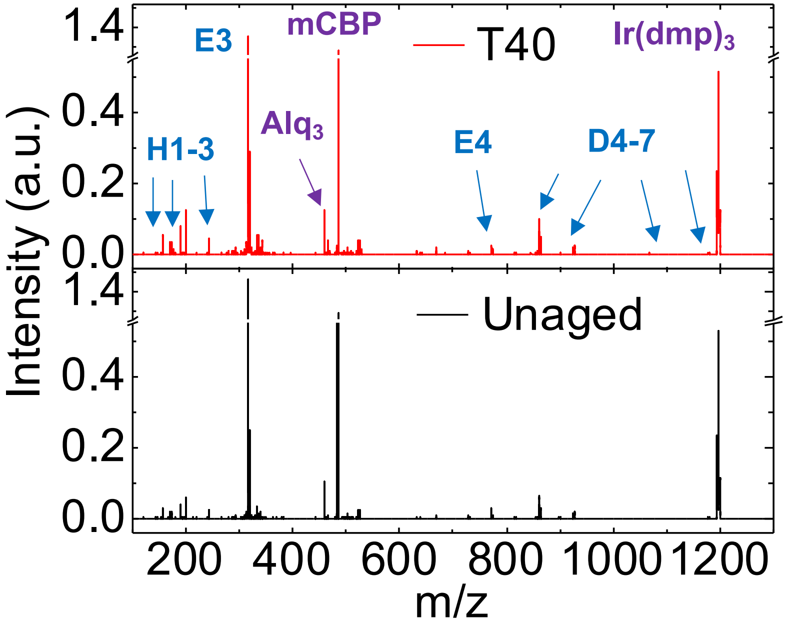
Giebink, et al., *J. Appl. Phys.*, **103**, 044509 (2008).

Evidence for Defect Formation: Molecular Fragmentation

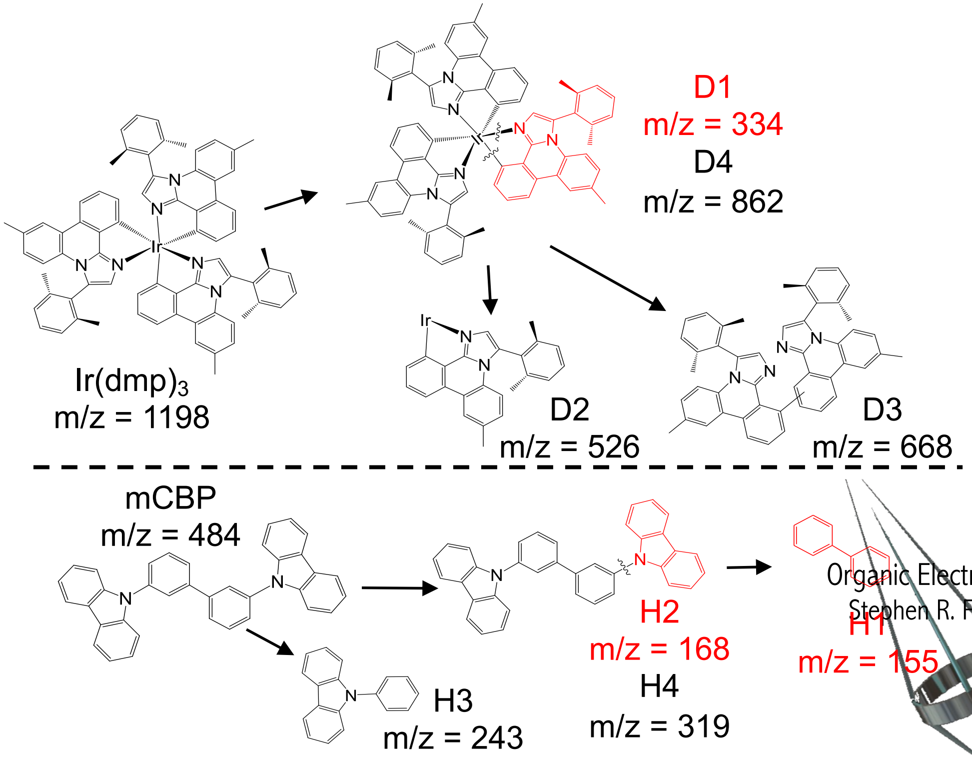


Laser Desorption Ionization-Time of Flight Mass Spectroscopy (LDI-TOF-MS)

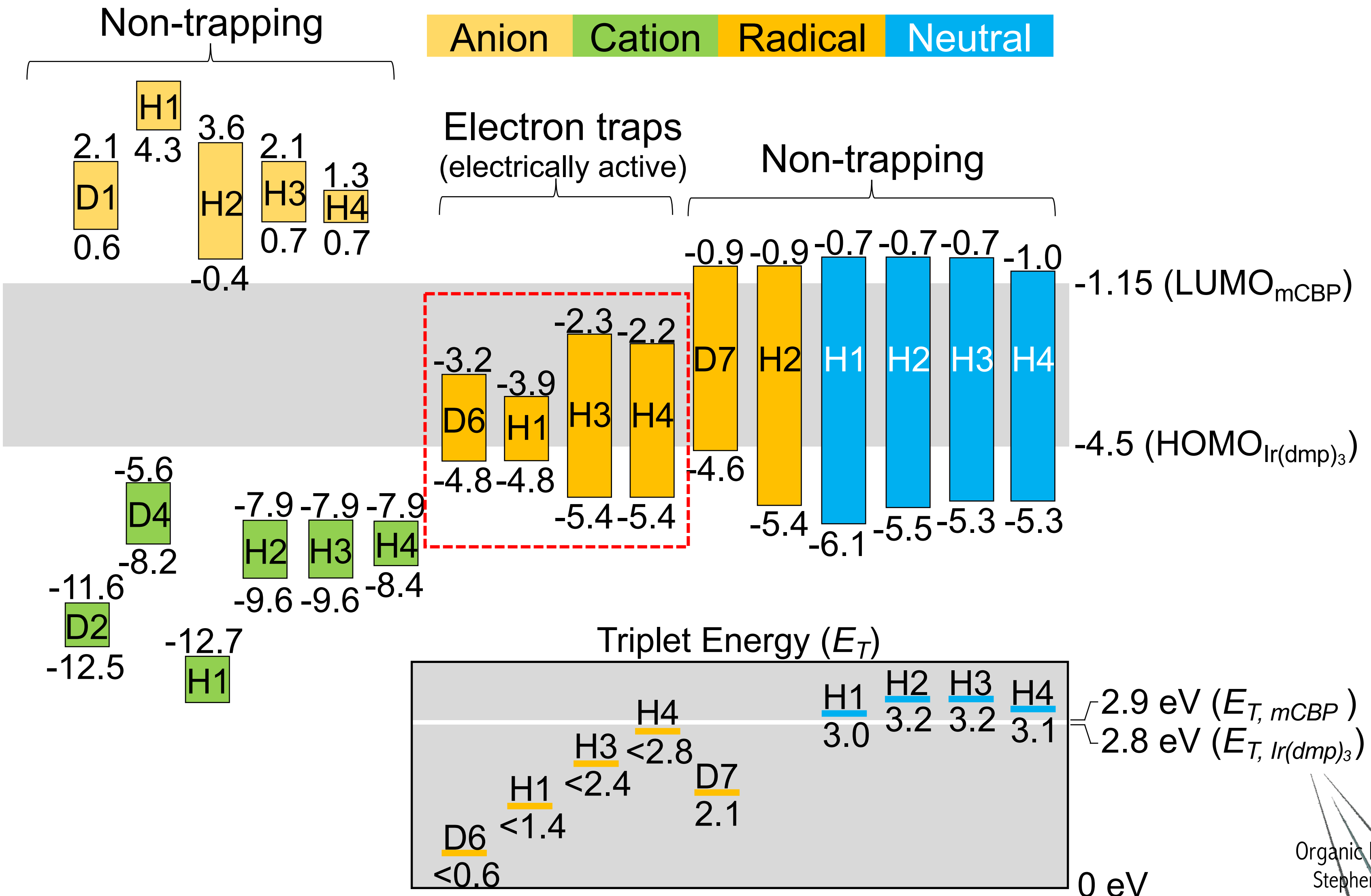
-Molecular species identification



Jeong, et al. Org. Electron., **64**, 15 2019

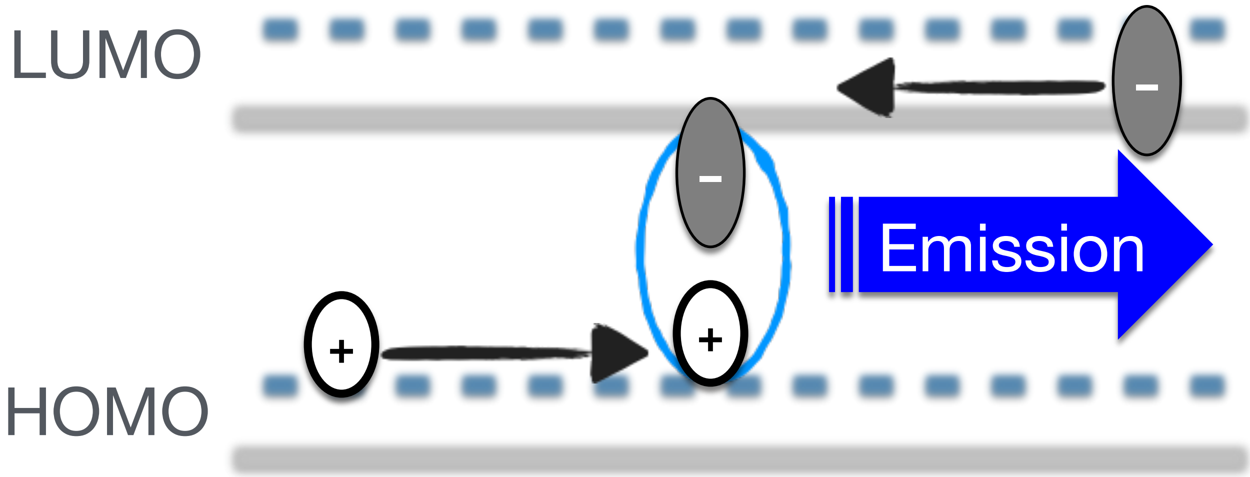


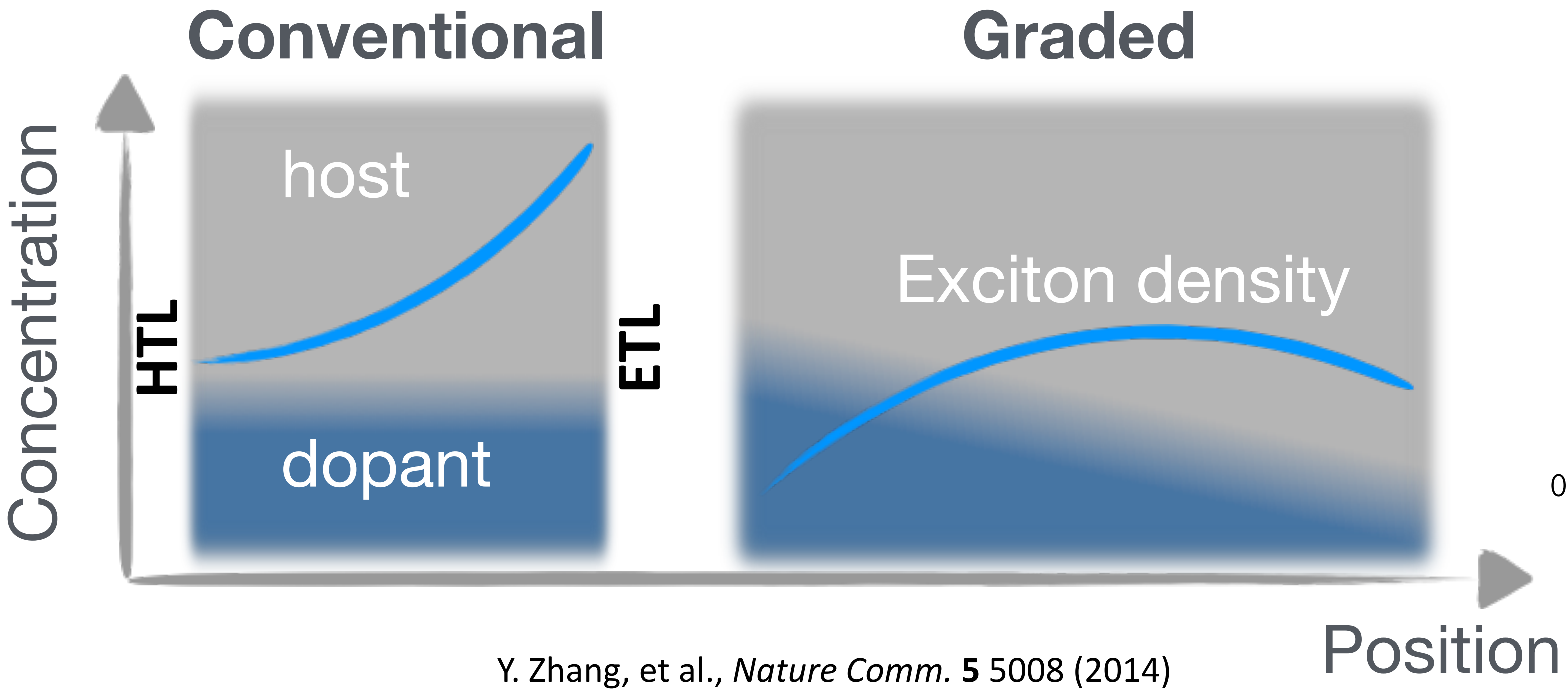
Identification of Defect Energies



Jeong, et al. Org. Electron., **64**, 15 2019

Reducing Exciton Density to Increase Lifetime

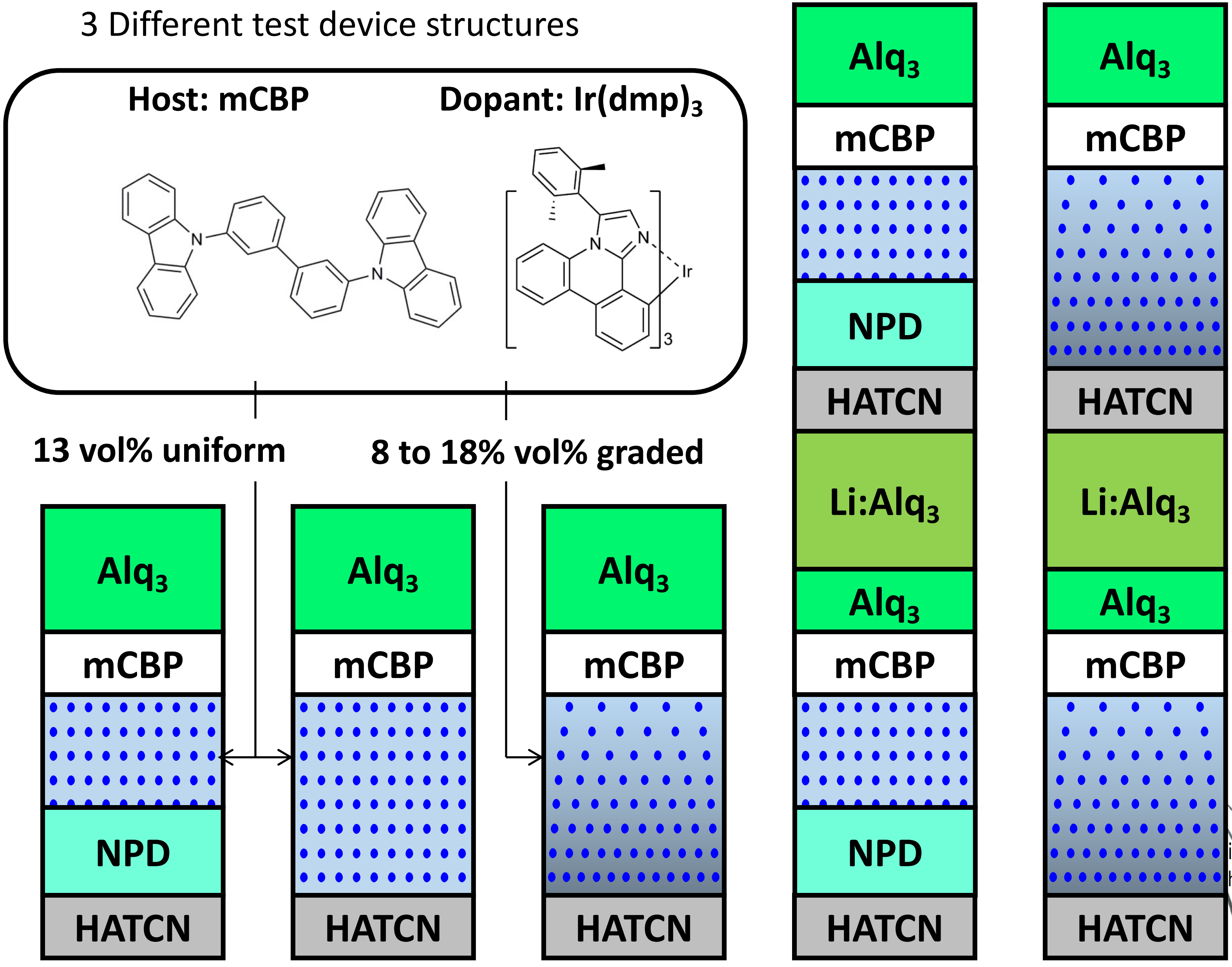




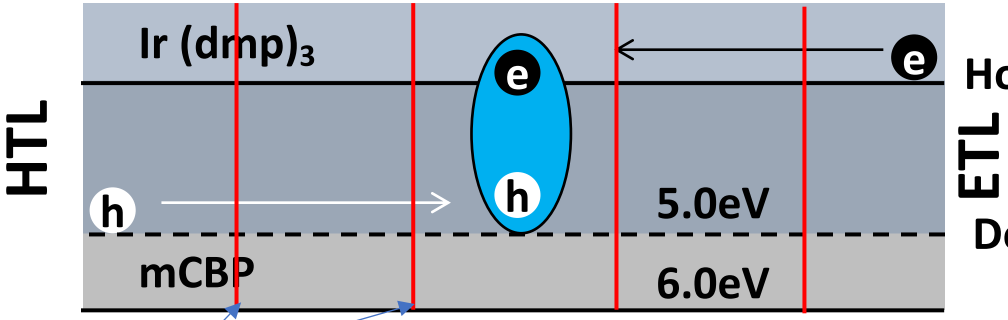
Y. Zhang, et al., *Nature Comm.* **5** 5008 (2014)

Spreading the recombination zone: Dopant/Host Grading

3 Different test device structures



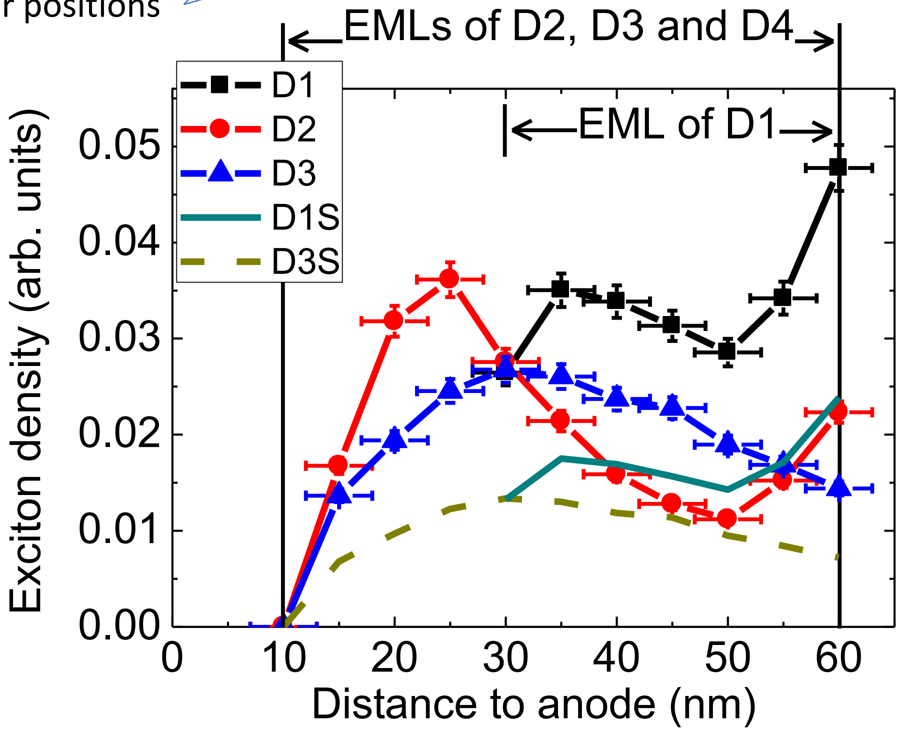
Excitons in the EML



Host conducts electrons

Dopant conducts holes

sensing layer positions

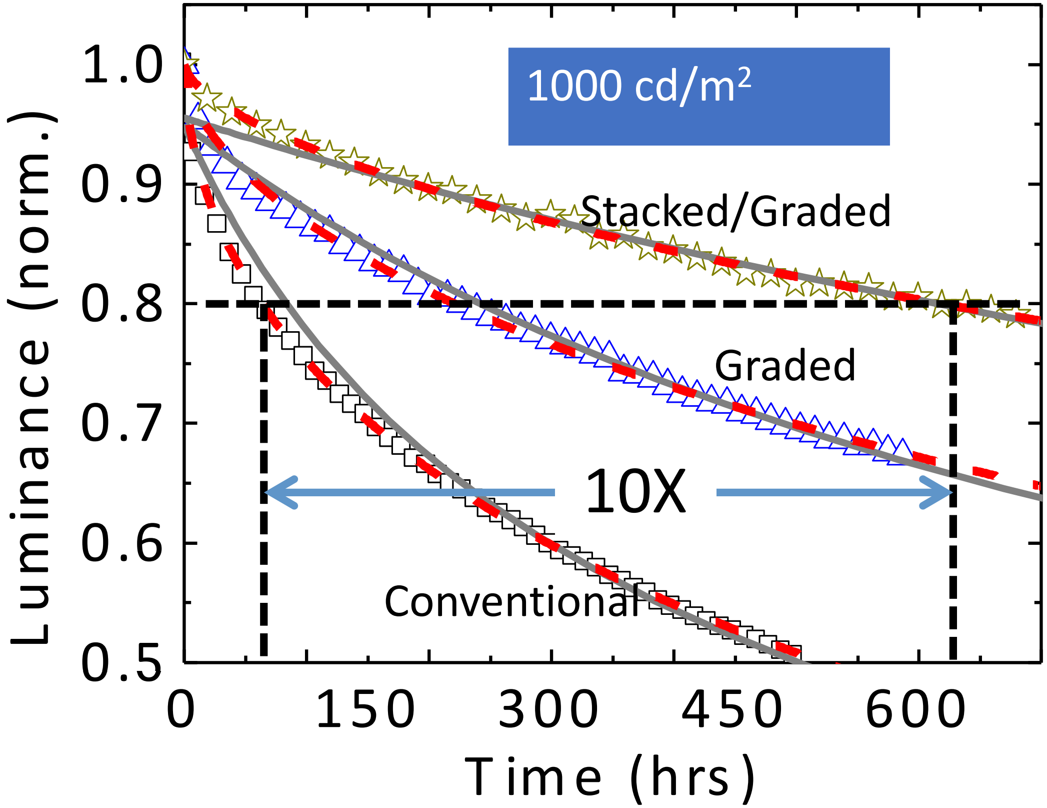


Exciton Sensing

- Red Phosphor (PQIr)
- 1.5 nm thick
- Placed at 5 nm intervals in EML
- Measure red emission intensity

Y. Zhang, et al., *Nature Comm.* **5** 5008 (2014)

10 X Lifetime Improvement Over Conventional



Y. Zhang, et al., *Nature Comm.* **5** 5008 (2014)

Stacking is essential!

Panel **15 cm x 15 cm** **82% fill factor**	**2 Unit WSOLED**
Luminance [cd/m^2]	**3,000**
Efficacy [lm/W]	**48**
CRI	**86**
Luminous Emittance [lm/m^2]	7,740
1931 CIE	(0.454, 0.426)
LT$_{70}$ [hrs]	**13,000**

P.Levermore et al, **SID Digest**, 2011.

Dopant Grading: Is it Good Enough?

using acceleration factors to predict lifetime

- Luminance to achieve sRGB color gamut for G is 10X that for B
- ⇒B sub-pixel L_0=100 cd/m^2 (c.f. G with L_0>1,000 cd/m^2)
- ⇒B lifetime to T50=70,000 hr.
- Adopting Degradation acceleration factor: n =1.55 with

$$T50(100\text{cd/m}^2) = T50(1000\text{cd/m}^2) \times \left[\frac{1000\text{cd/m}^2}{100\text{cd/m}^2} \right]^n$$

- ⇒B PHOLED lifetime to T50 = 1.3×10^5 hr.
- Commercial G PHOLED lifetime = 10^6 hours at L_0 = 1000 cd/m^2.

Not blue enough, T95 is required

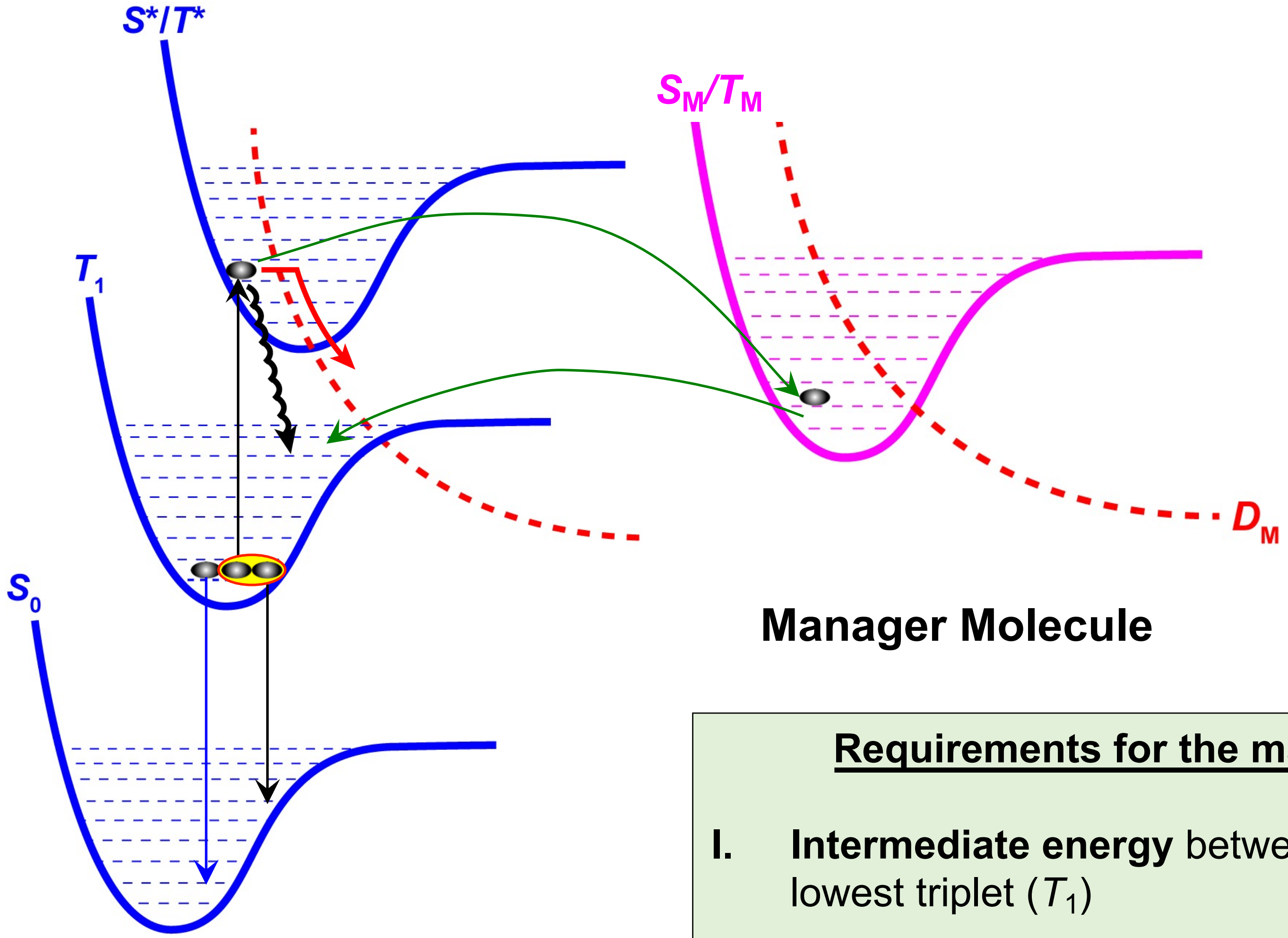
Dopant Grading for Lighting: Is it OK?

- Current state of stacked WOLED: T70=13,000 hrs
- Mostly limited by blue lifetime
- Only light blue required
- Estimated increase in lifetime for stacked blue at lighting brightness: ~4X
- Lifetime of blue lighting using grading: 50,000 hr

This is almost good enough

Hot excited state management:

Eliminating the highest energy excited states



Manager Molecule

Blue Dopant/Host Molecules

Lee, et al. Nat. Comm. 8, 15566 (2017)

Requirements for the manager molecule

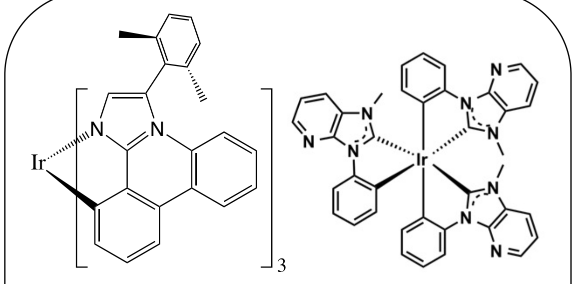
I. **Intermediate energy** between hot state (T^*) and lowest triplet (T_1)

II. **Molecular stability**

III. **Fast energy transfer** from dopant/host to manager

Managed blue PHOLEDs

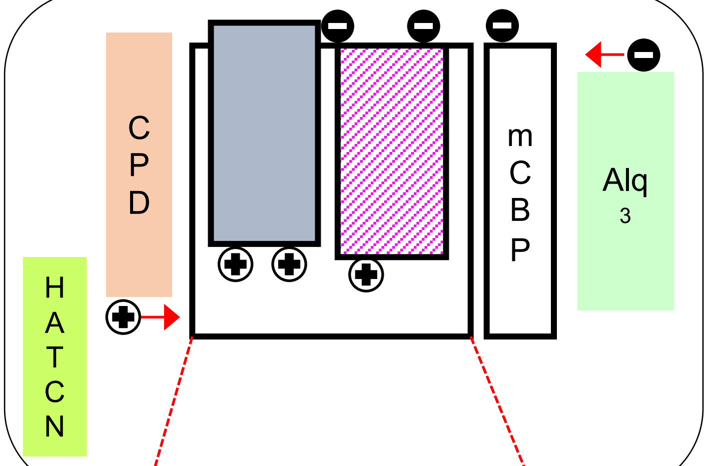
EML materials



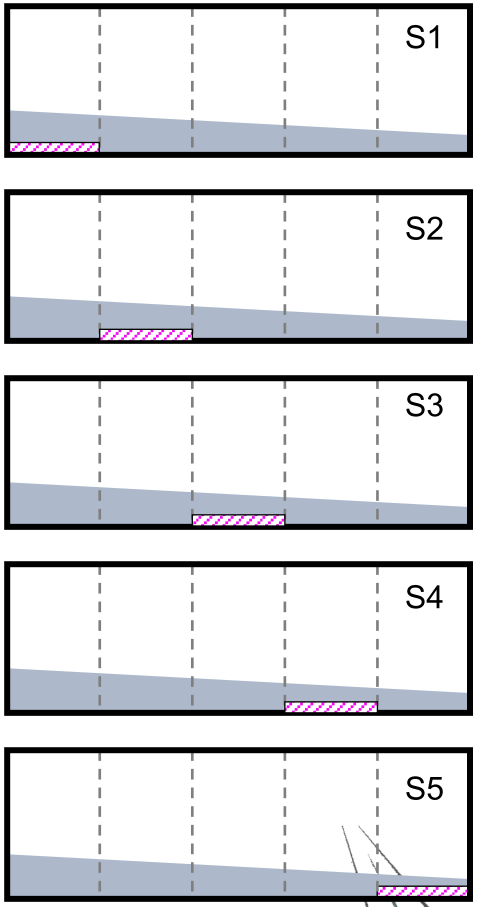
Blue dopant
Ir(dmp)$_3$
E_T = 2.8 eV

Manager
mer-Ir(pmp)$_3$
E_T = 3.1 eV

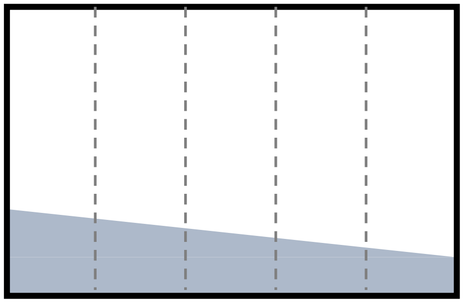
Energetics and charge transport



Managed EML (M1–M5)

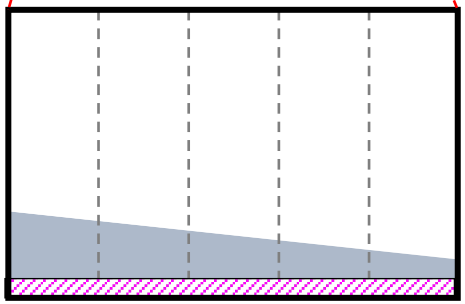


Graded EML (GRAD)



■ : 18−8 vol%

Managed EML (S0)

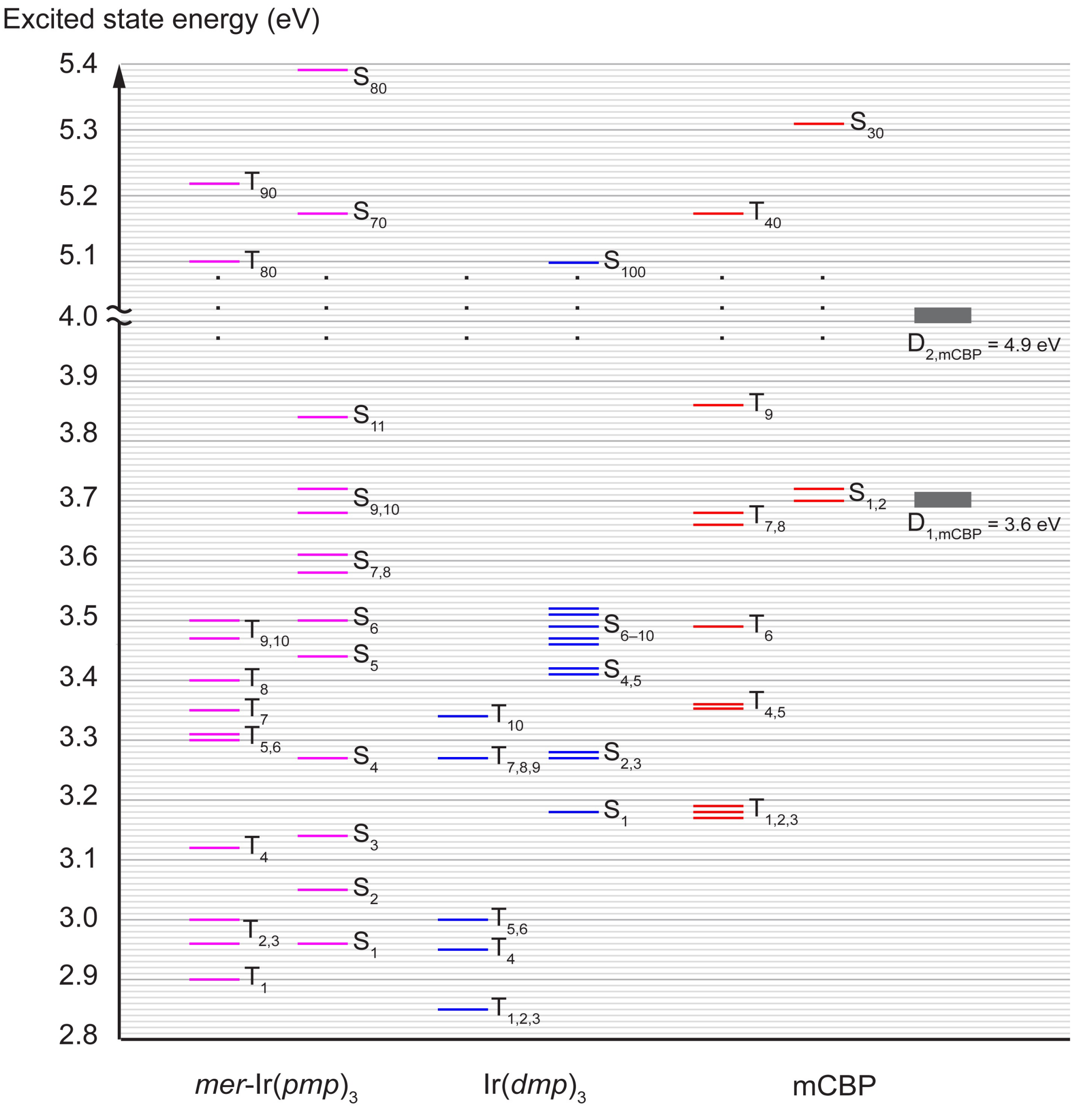


■ : 15−5 vol%

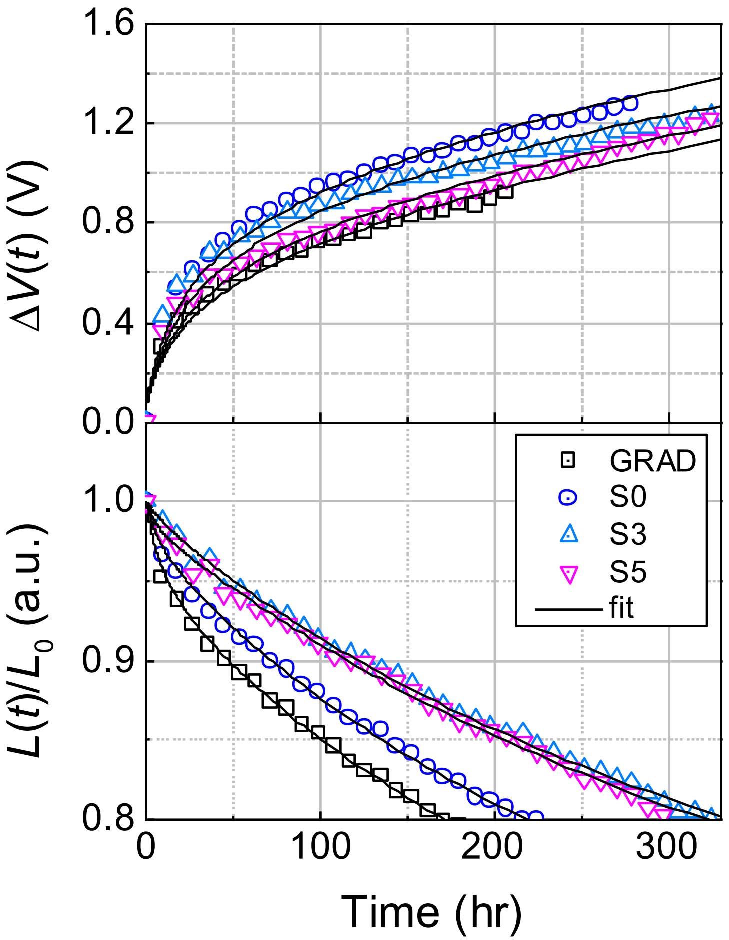
▨ : 3 vol%

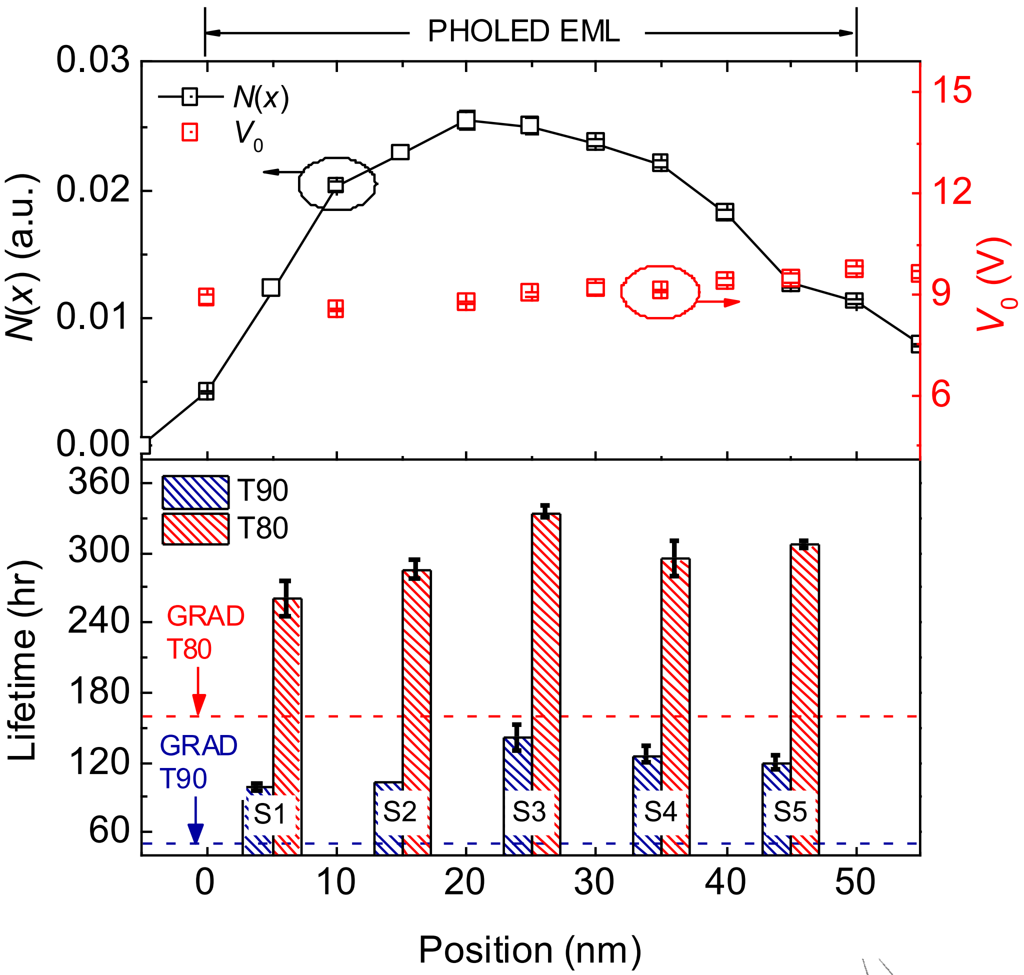
Place manager at 10 nm sections of EML

Plenty of Energy Levels to Access in the Management Process



Lifetime Improvements and TTA/TPA Model

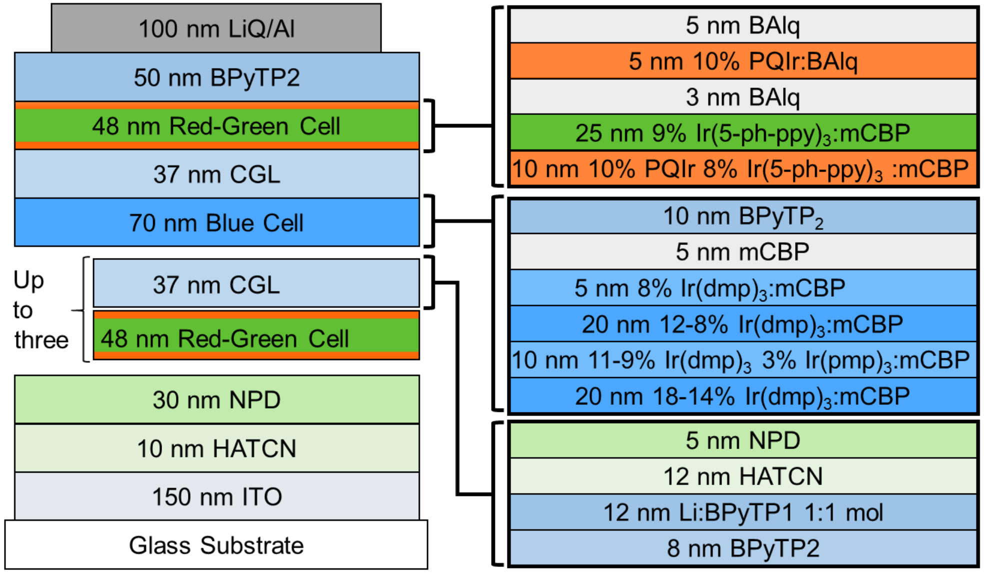




- Greatest improvement in lifetime when manager at position of highest exciton density (S3)
- Fractional increase in lifetime decreases with time
  - Greater at T90 than T80 ⇒manager depletion

Lee, et al. Nat. Comm. 8, 15566 (2017)

Putting Grading Excited State Management to Work: Long lived all phosphor stacked WOLEDs



100 nm LiQ/Al
50 nm BPyTP2
48 nm Red-Green Cell
37 nm CGL
70 nm Blue Cell
Up to three
  37 nm CGL
  48 nm Red-Green Cell
30 nm NPD
10 nm HATCN
150 nm ITO
Glass Substrate

5 nm BAlq
5 nm 10% PQIr:BAlq
3 nm BAlq
25 nm 9% Ir(5-ph-ppy)$_3$:mCBP
10 nm 10% PQIr 8% Ir(5-ph-ppy)$_3$:mCBP

10 nm BPyTP$_2$
5 nm mCBP
5 nm 8% Ir(dmp)$_3$:mCBP
20 nm 12-8% Ir(dmp)$_3$:mCBP
10 nm 11-9% Ir(dmp)$_3$ 3% Ir(pmp)$_3$:mCBP
20 nm 18-14% Ir(dmp)$_3$:mCBP

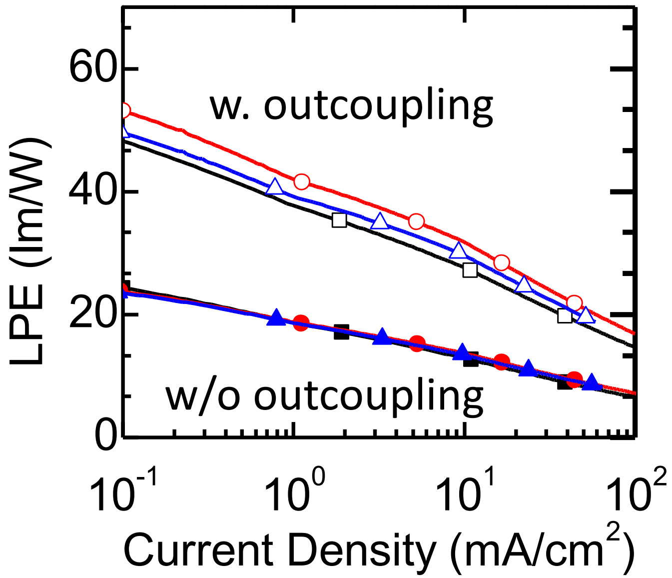
5 nm NPD
12 nm HATCN
12 nm Li:BPyTP1 1:1 mol
8 nm BPyTP2

Photo illustrating good color rendering of the SWOLEDs in this report. The luminaire comprises 36 pixels (2 mm^2) operated at 50-100k nits

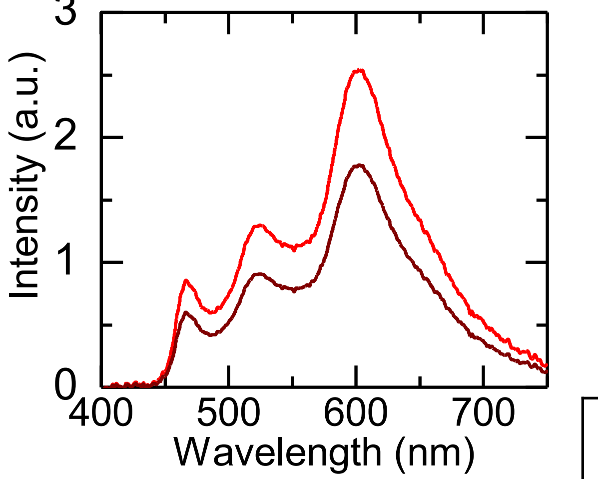
- Max Luminance > 200,000 nits
- 50 lm/W max
- CCT = 2780K
- CRI=89

Coburn et al., ACS Photonics 5, 630 (2017)

All Phosphor SWOLED Performance



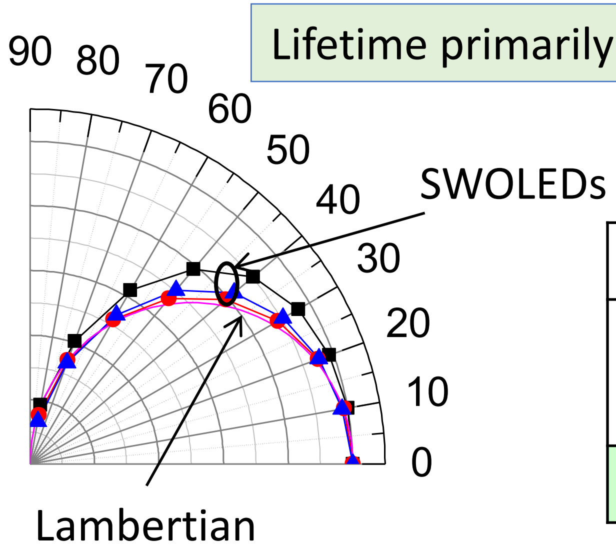
Spectral shifts after aging



T70	SWOLED
ΔCCT	-360 K
ΔCRI	-0.8
ΔCIE	(0.03,0)

SWOLED Architecture	**Blue degradation @ WOLED T70:**
Conv	T28
Grad-Managed	T48

Lifetime primarily limited by R/G sections



	With outcoupling		
	T70 1000 nit (x10^3 hr)	T70 3000 nit (x10^3 hr)	ΔV/V$_0$ (T70) (%)
SWOLED	80±40	14±5	~+10%

Coburn et al., ACS Photonics 5, 630 (2017)

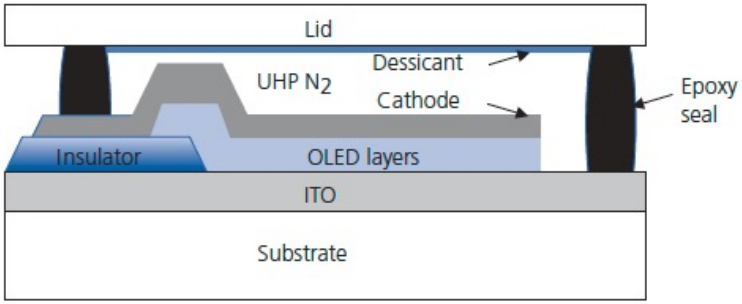
What we learned about OLEDs

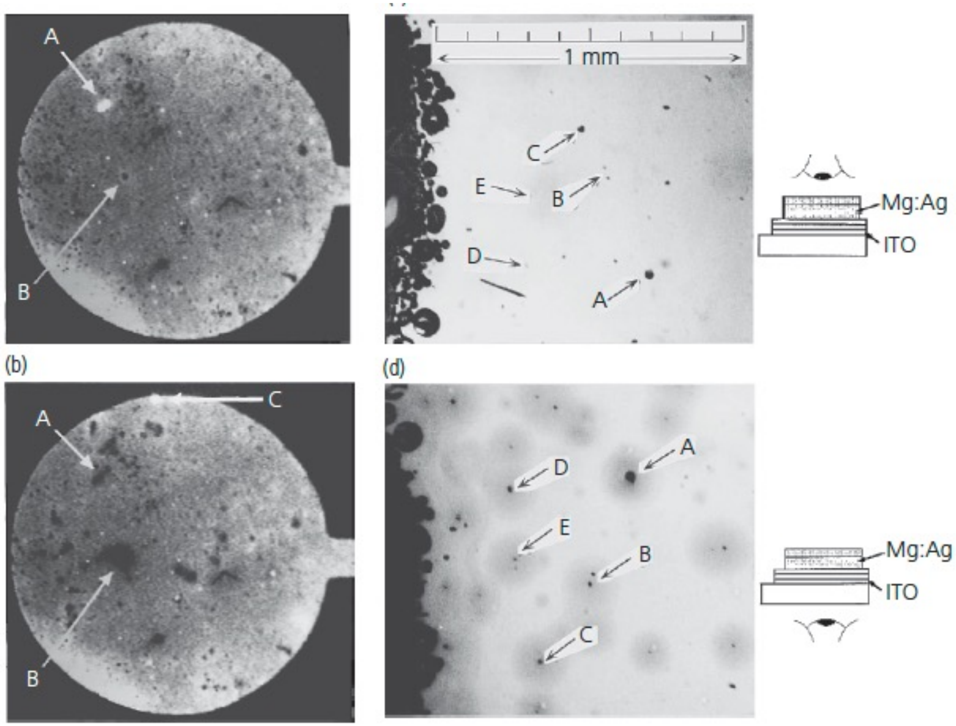
- Chromaticity and the perception of color is quantified based on eye response (photometic quantities)
- OLEDs reach highest efficiency when both singlets and triplets are harvested (heavy metal complexes and TADF molecules)
- Optimized OLEDs have many layers serving purposes ranging from charge conduction, contacting to electrodes, to light emission
- Outcoupling methods essential to view substrate and waveguide modes while limiting surface plasmons
- Degradation of OLEDs particularly severe for blue due to bimolecular annihilation
- Lighting requires broad spectral emission using multilayer devices or excimer emission
- OLEDs provide uniform, area lighting vs. specular LED lighting

Packaging Matters

(see Ch. 5)

- Without packaging, there is rapid degradation of OLED luminance
- Dark spot defect formation of contacts more rapid in atmosphere than when packaged in inert (e.g. N_2) gas.





- Dark spot formation on cathode as seen from the top and bottom sides
- Defect bright EL spots soon become dark
- Defects appear to be due to dust on substrate penetrating device active region

Burrows et al., Appl. Phys. Lett., 65, 2922 (1994)

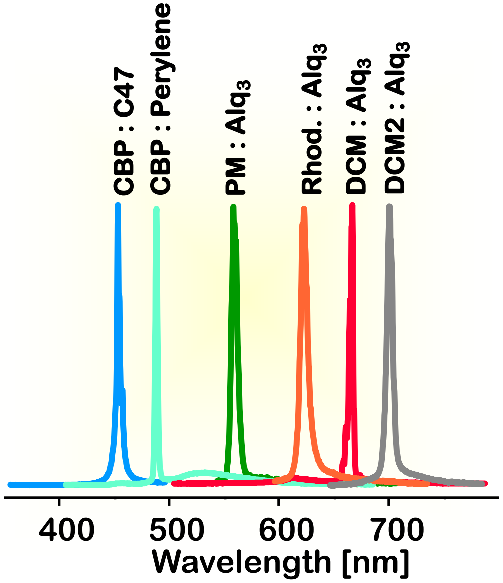
Organic Lasers

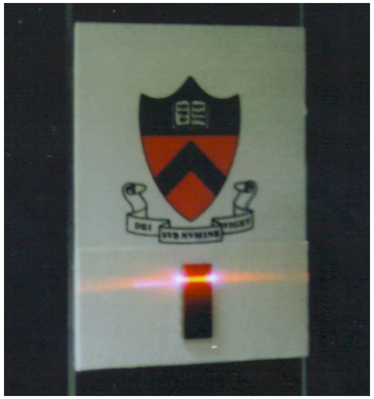
- High intensity, monochromatic sources
- To date, only optical pumping has unambiguously shown lasing
- Large triplet and electrode losses, and low mobilities (hence low current) hamper electrical pumping

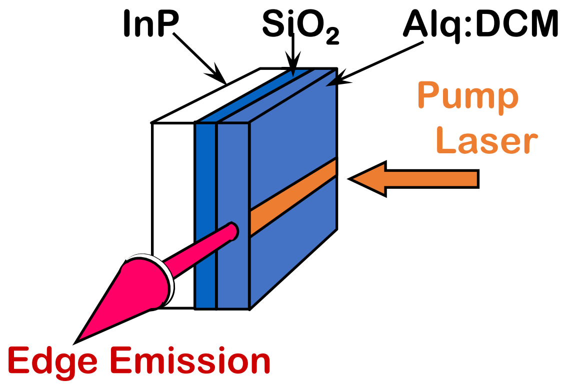
How to identify a laser

- A clear threshold between spontaneous and stimulated emission evident from an abrupt increase in output slope efficiency
- A significant narrowing of the spectral linewidth at threshold. Single mode lasers show linewidths ~1Å, multimode lasers will have multiple emission lines coincident with the gain (PL) spectrum of the material, and whose separation is $\Delta\lambda \sim 1/L$, the cavity length
- A well-defined output beam
- Temporal and spatial coherence of the output beam

Features of Organic Lasers



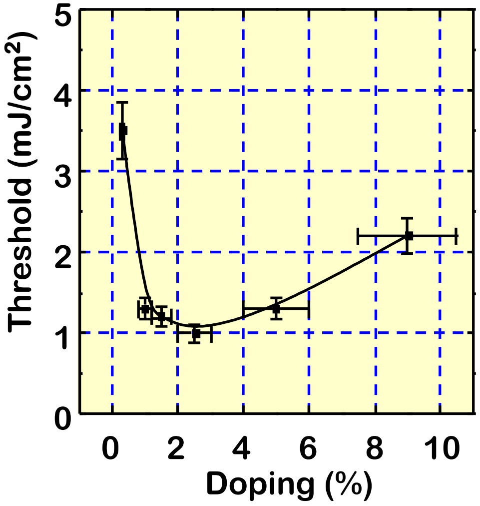




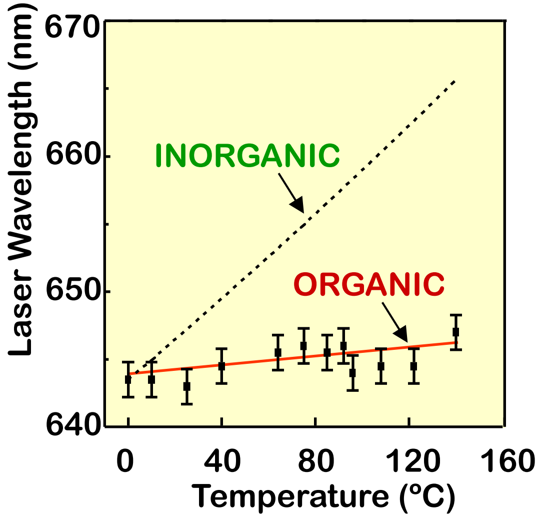
Kozlov, *et al.*, *Nature* **389**, 362 (1997).

- Material Tunability
- Freedom from Epitaxial Limitations
- Natural Quantum Dots

Low Lasing Threshold

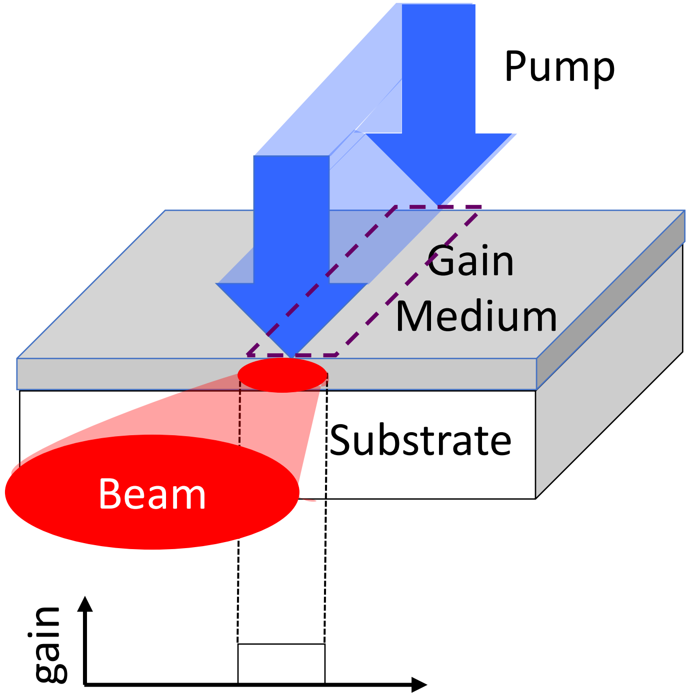


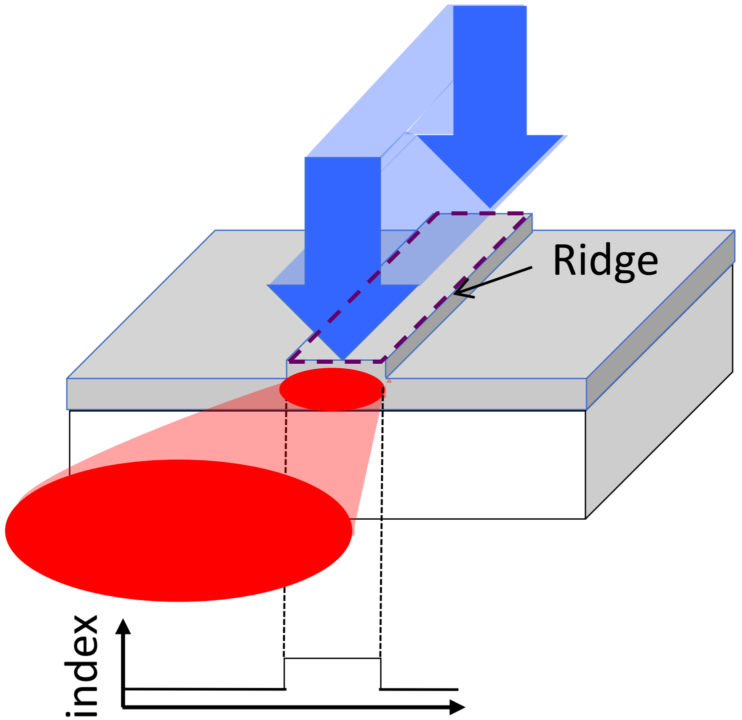
Temperature Insensitivity



Kozlov, *et al.*, *Appl. Phys. Lett.* **71**, 2575 (1997).

Gain vs. Index Guided Lasers

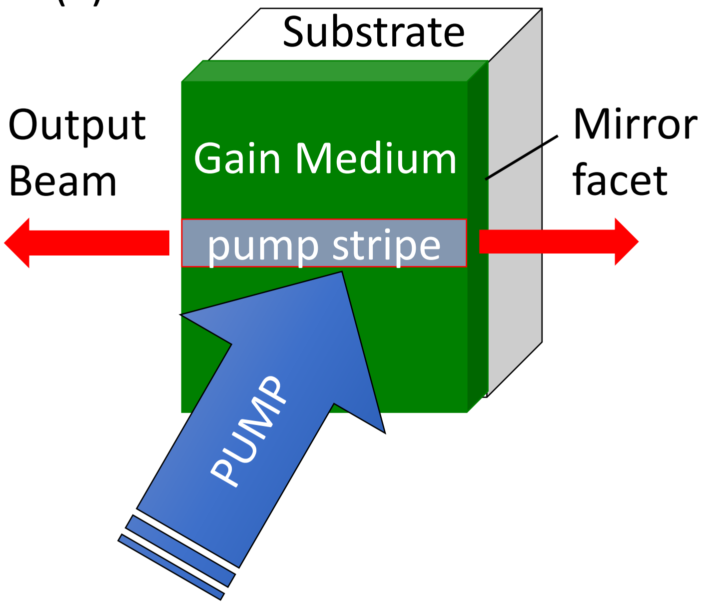




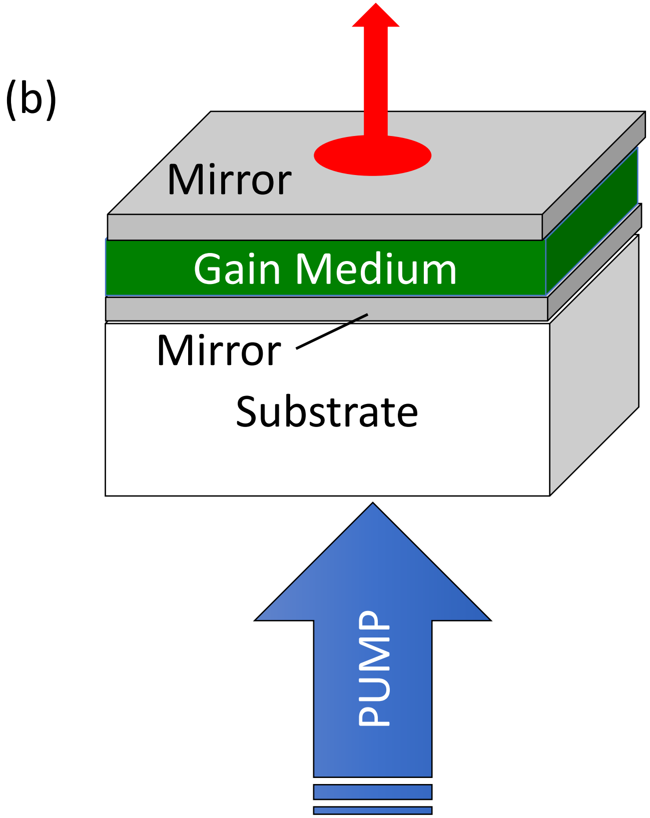
Gain guiding
- Simple
- Can lead to high thresholds
- Can lead to modal instabilities

Index guiding
- More complex
- Can reduce thresholds
- Has modal instabilities only at very high power

Optically pumped lasers



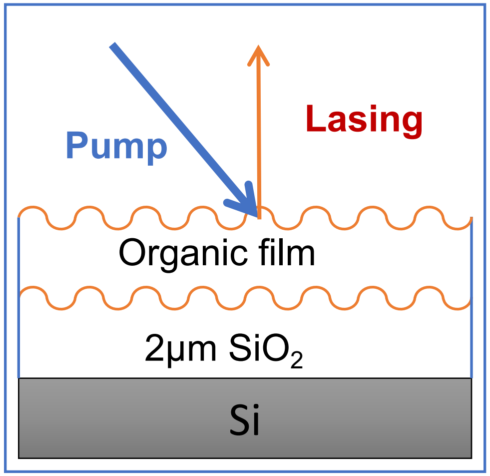
Longitudinal Configuration

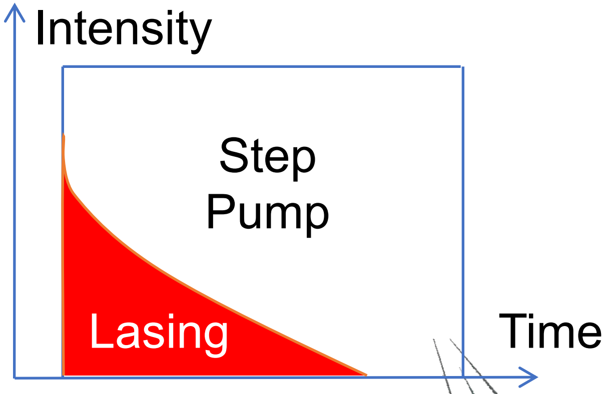


Vertical Cavity Surface Emitting Laser (OVCSEL)

Pulsed Organic Lasers

- Why does organic lasing last only <100ns?
  - ❑Initially (<10ns)
    - ➢ Negligible T
    - ➢ Gain=Loss
  - ❑Later (>100ns)
    - ➢ T builds up
    - ➢ Gain ↓ : S-T quenching
    - ➢ Loss ↑ : T absorption
  - ➢Same source of loss prevents electrically pumped laser action

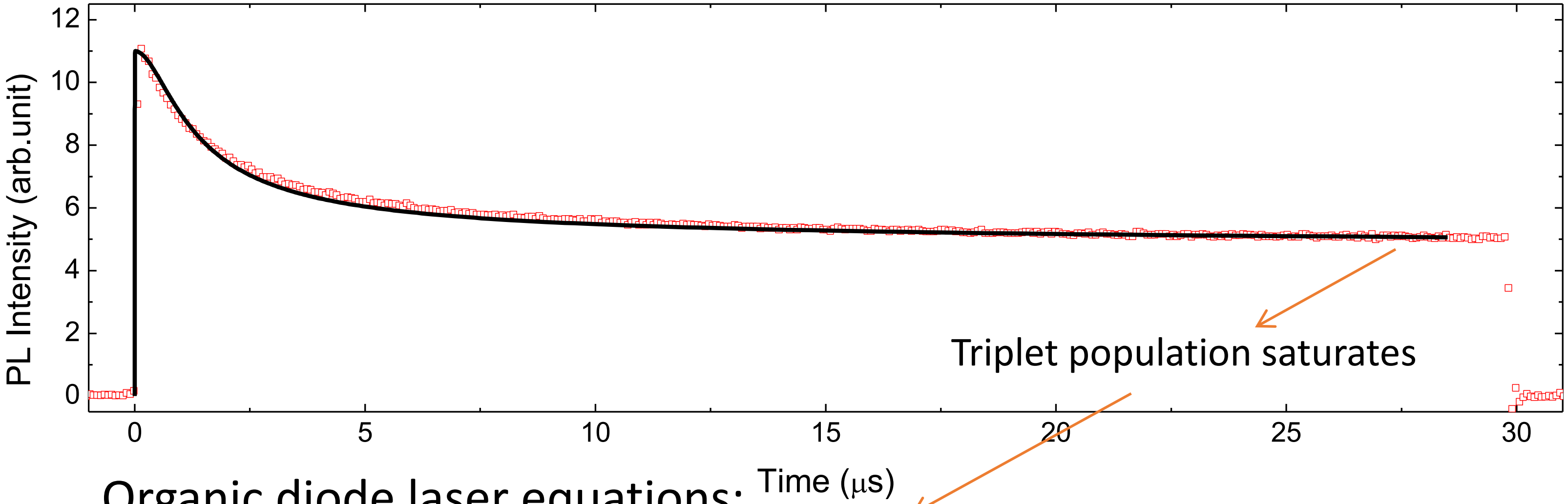




Giebink & Forrest, *Phys. Rev. B* **2009**, *79*, 073302

Lehnhardt, et al. *Phys. Rev. B* **2010**, *81*, 165206

Triplet saturation and CW threshold



Triplet population saturates

Organic diode laser equations:

Threshold: $g_{net}(t)=\Gamma\sigma_{stim}S(t)-\alpha_{cav}-\Gamma\sigma_{TT}T_G(t)\geq 0$ (gain condition)

S-T

T abs

Pulsed threshold

$$I_{PS}=e_p d(k_S+k_{ISC})\frac{\alpha_{CAV}}{\eta\Gamma\sigma_{stim}}$$

CW threshold

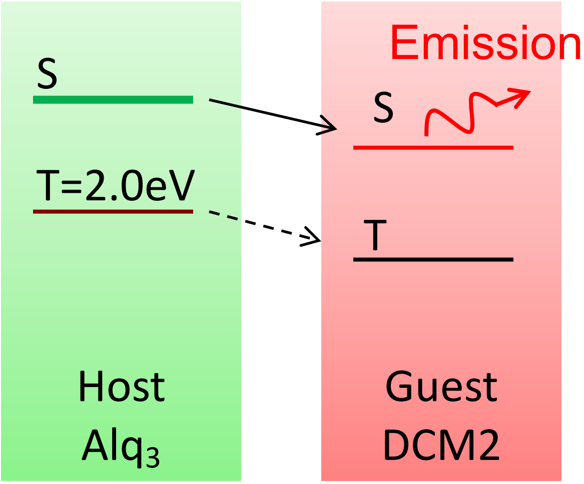
$$I_{CW}=e_p d(k_S+k_{ISC}+k_{ST}T_\infty)\frac{\alpha_{CAV}+\Gamma\sigma_{TT}T_\infty}{\eta\Gamma\sigma_{stim}}$$

	I_{PS} (kW/cm^2)	T_∞ (10^{18}cm^{-3})	I_{CW} (kW/cm^2)
DCM2:Alq$_3$	0.93	5.0	32

Above damage threshold

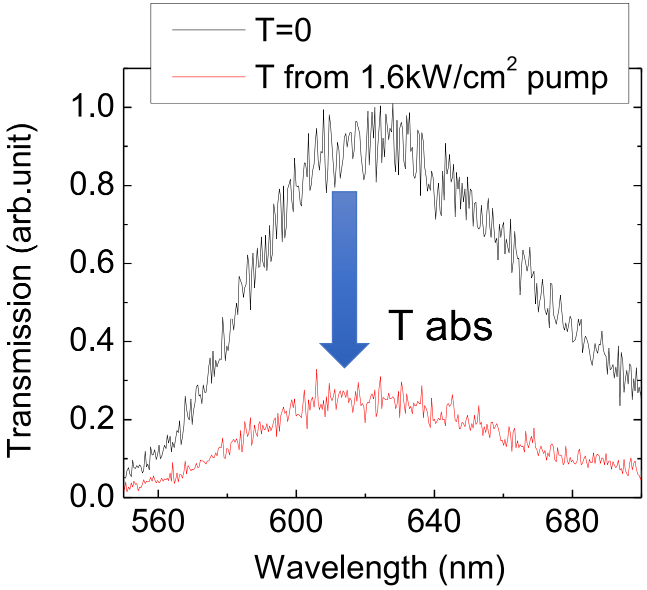
Zhang & Forrest, Phys. Rev. B, **84,** 241301 (2011)

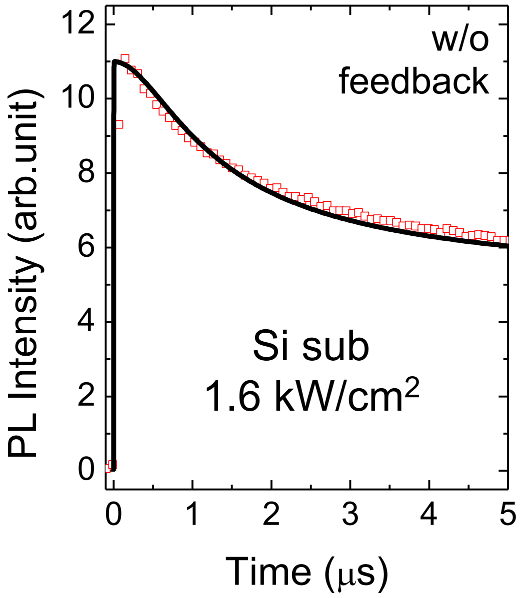
Example Laser -- DCM2:Alq$_3$

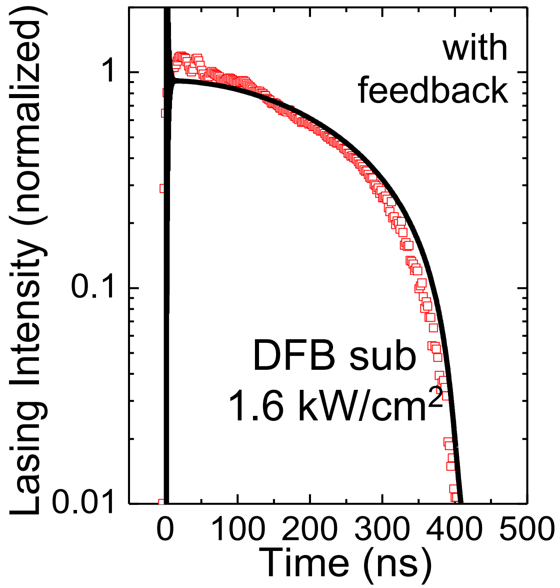


- PL fit follows S-T quenching
  - ❑ $S^*+T^* \rightarrow S_0+T^{**}$
- Lasing fit follows S-T and T absorption
  - ❑ $P+T^* \rightarrow T^{**}$
- Lasing condition

$$g_{net}(t)=\Gamma\sigma_{stim}S(t)-\alpha_{cav}-\Gamma\sigma_{TT}T_G(t)\geq 0$$



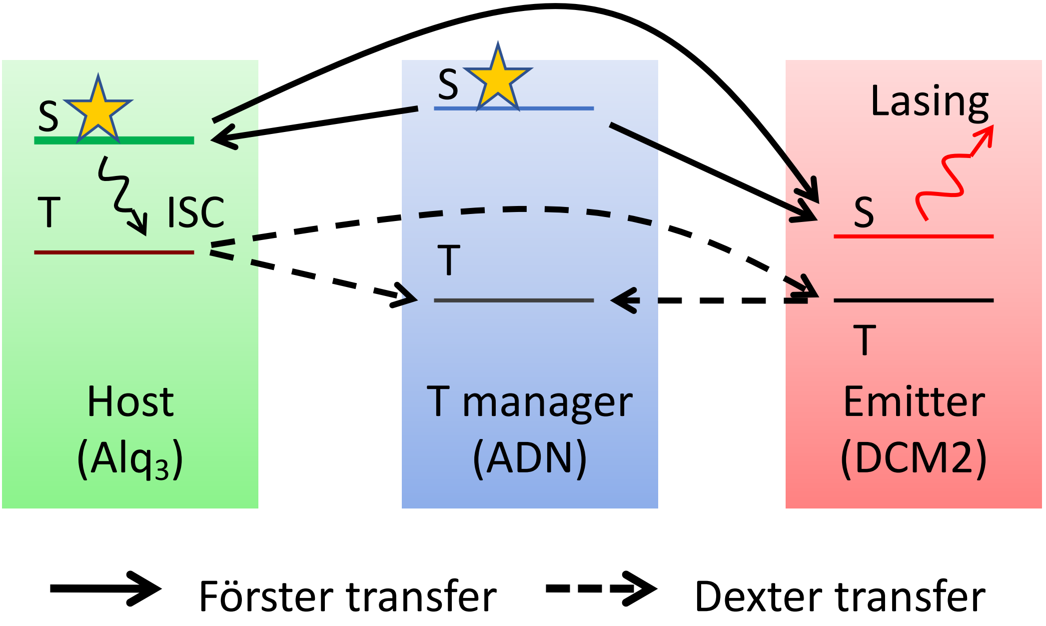




Lasing turns off once triplet loss exceeds gain

The Triplet Management Concept

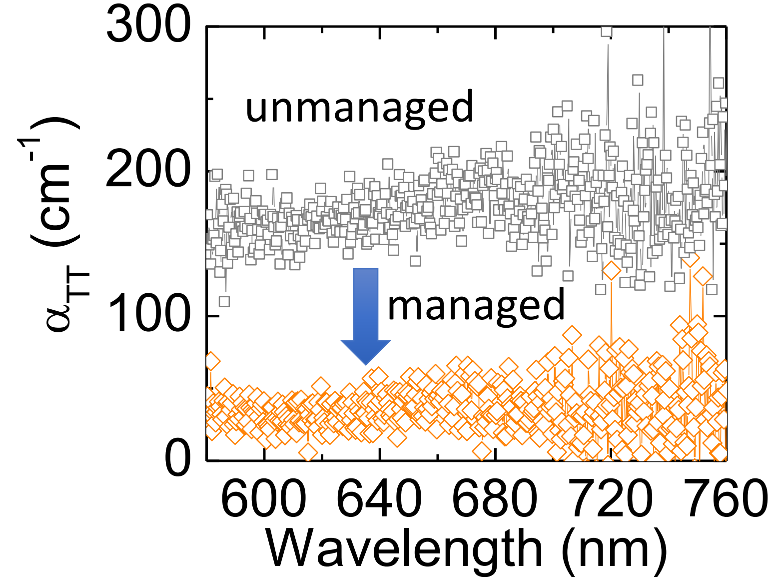
- Introduce a 3rd molecule into the gain region that quickly removes triplets⇒reduced absorption loss
- Same concept works in fluorescent OLEDs to reduce rolloff due to accumulation of triplets at high intensity



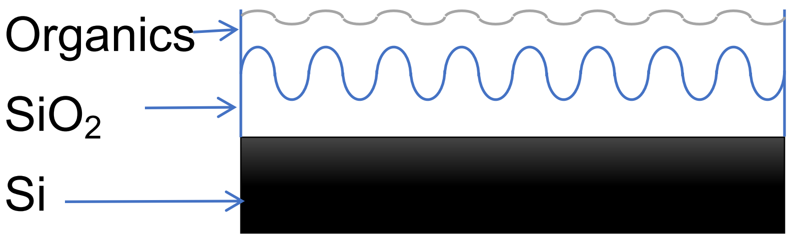
Example gain region composition

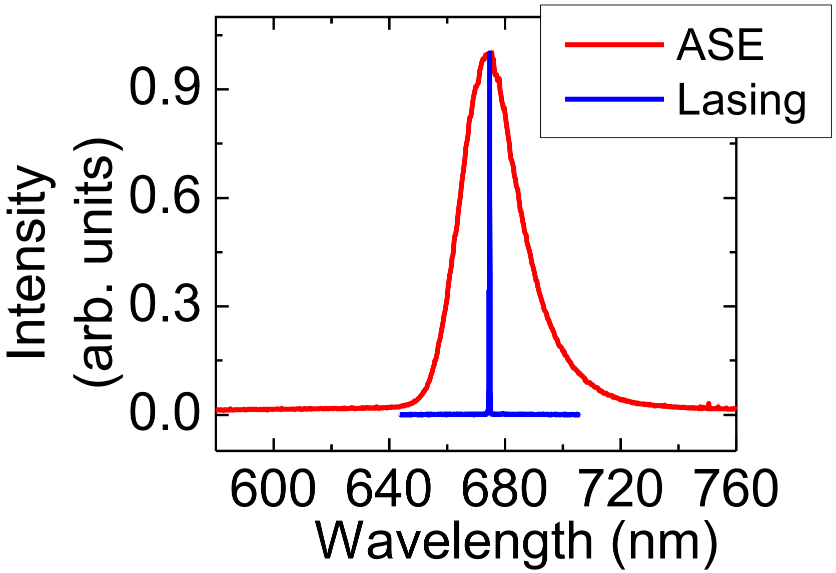
T absorption and lasing with T management

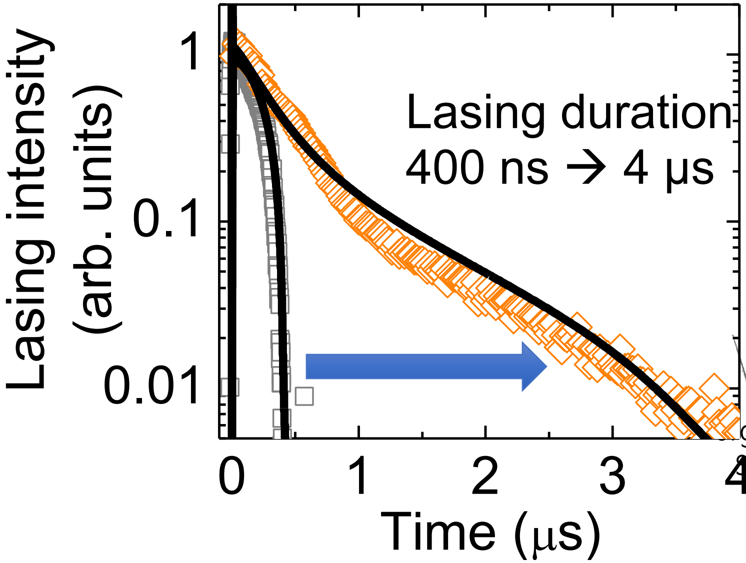
Alq$_3$:DCM2



Organic laser with 2nd order distributed feedback structure



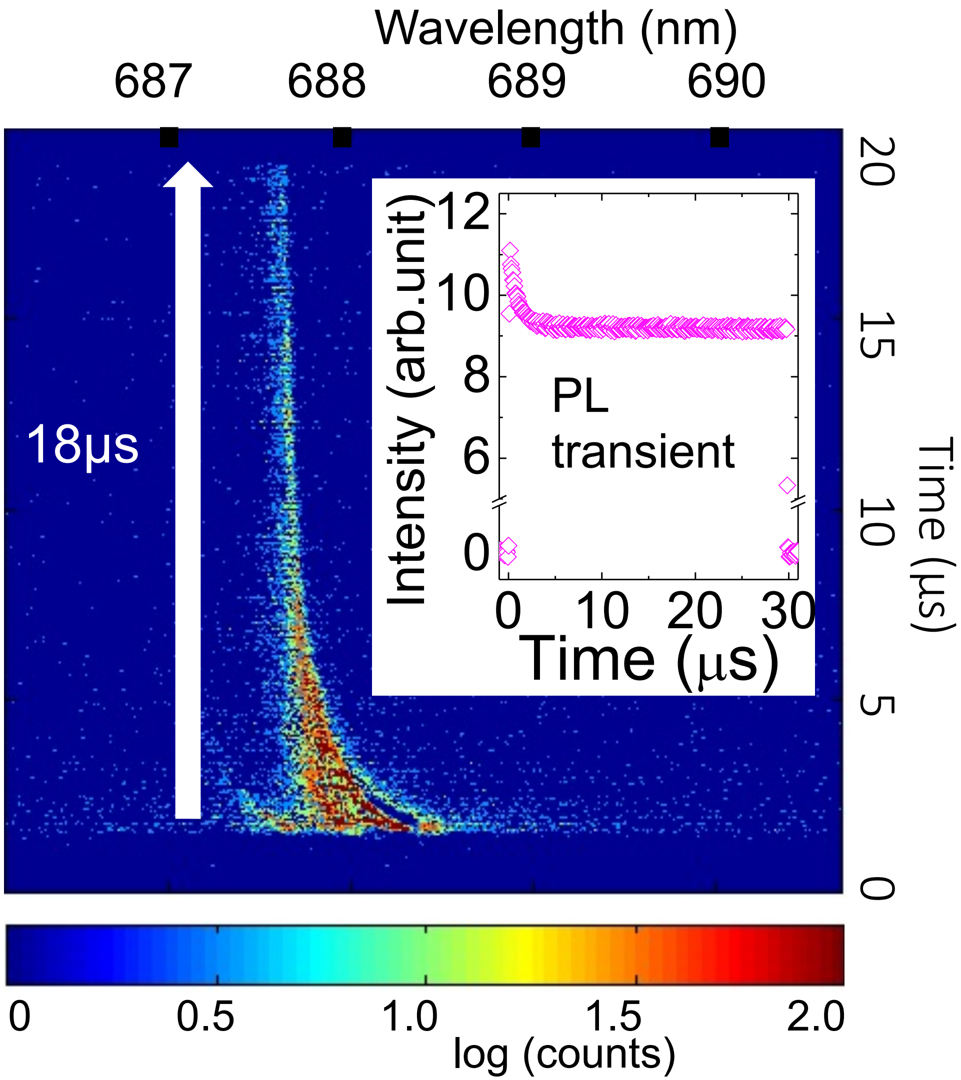




Lasing duration
400 ns → 4 μs

Zhang & Forrest, Phys. Rev. B, **84,** 241301 (2011)

Management Allows CW Lasing Above the CW threshold



- ☐ Condition
  - ➢ $2.4kW/cm^2$, 10Hz/18µs
  - ➢ Integrate 1000 pulses
  - ➢ Degradation limited
- ☐ **Single pulse → 100 µs**
- ☐ Wavelength shift due to triplet induced index change

$$m\lambda=2n_{eff}\Lambda$$

- ☐ CW lasing not limited by T

Zhang & Forrest, Phys. Rev. B, **84,** 241301 (2011)

What we have learned

- OLEDs are the leading application of organic electronics due to their features of:
  - Color versatility due to chemical modification
  - 100% internal efficiency in PHOLEDs and TADF molecules
  - Stability over long term operation (except in the blue)
  - Thin film, flexible form factors allowing for their use in mobile applications
  - Very attractive lighting colors and luminance characteristics
  - But...optical outcoupling losses and long lived PHOLEDs and TADF devices are remaining challenges to be solved.
- Organic lasers are excited primarily via optical pumping with features of:
  - Wavelength agility
  - Extraordinary temperature stability of its threshold and spectral properties
  - But...electrical pumped lasing remains a challenge due to large triplet and contact losses.