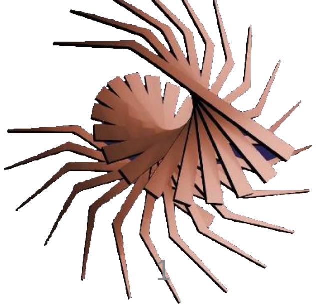
Week 10

Light Emitters 3

Outcoupling Strategies
Reliability

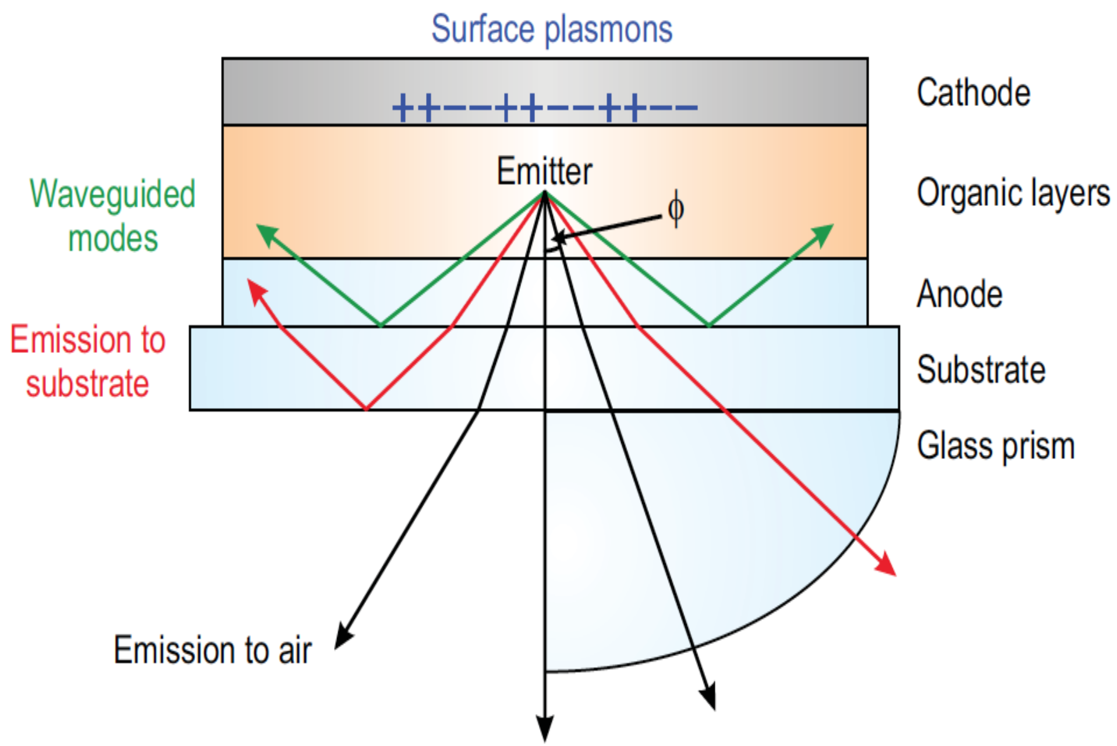
Chapter 6.9-6.11

Concepts in Organic Electronics
Stephen R. Forrest



OLEDs: Not All Light Goes to the Viewer

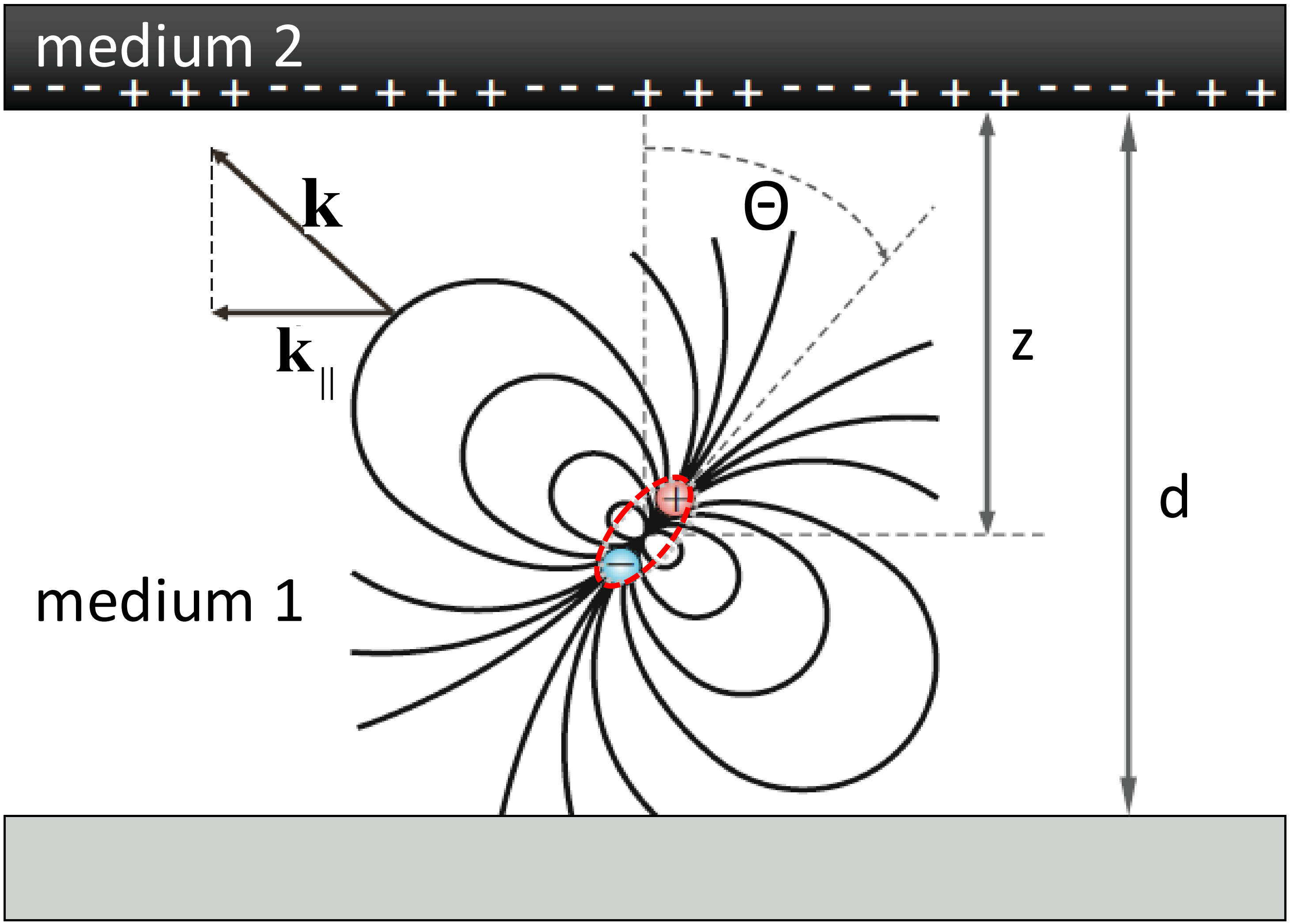
- Optical paths outcoupled with hemispherical lens



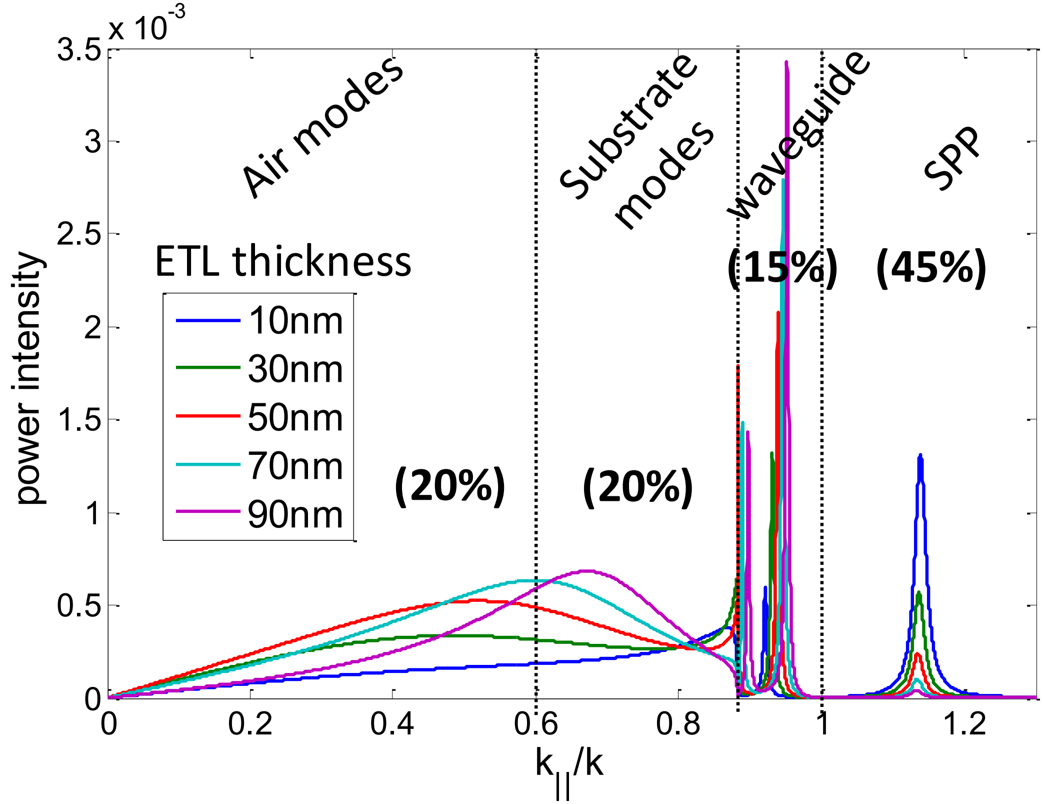
Emission into air: $n_{sub} sin\phi_{sub} = n_{air} sin\phi_{air} = sin\phi_{air}$

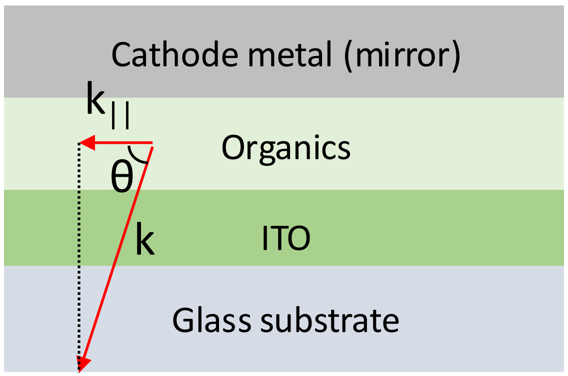
TIR condition: $\phi_{air} = 90^o \Rightarrow$ for glass substrate: $n_{sub} = 1.5 \Rightarrow \phi_{sub} = 40^o$
$\Rightarrow$ 22% of light outcoupled

Molecules are radiating dipoles in inhomogeneous media



Where do all the photons go?

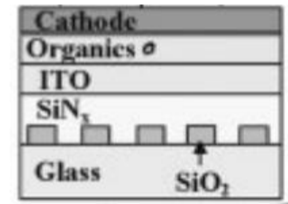


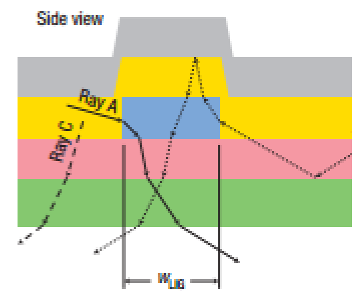


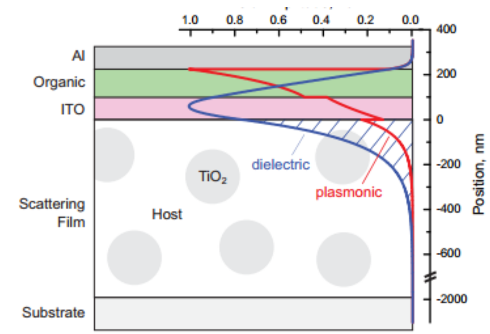
- **Air modes**: EQE first increases, then decreases with ETL thickness
- **Waveguide modes**: Only one waveguide mode TE_0 due to thin ETL (<30nm). TM_0 appears when >50nm.
- **Surface plasmon polariton modes:** Reduced with ETL thickness
- Both waveguide and SPP modes are quantized
- Total energy is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

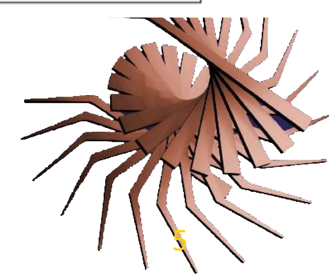
Getting all the photons out

- **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







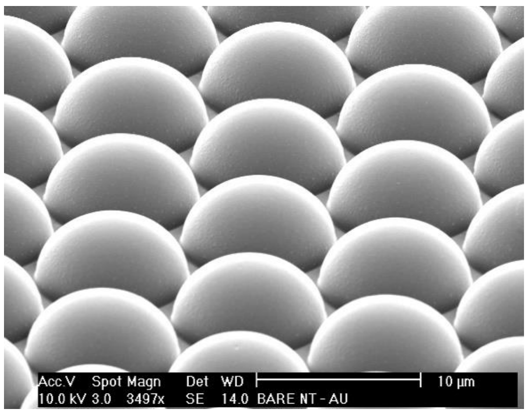


[1]Y .R. Do, et al, *Adv. Mater*. **15**, 1214 (2003).
[2]Y. Sun and S.R. Forrest, *Nat Phot*. **2**, 483 (2008).
[3]Chang, H.-W. *et al*. *J. Appl. Phys*. **113,** - (2013).

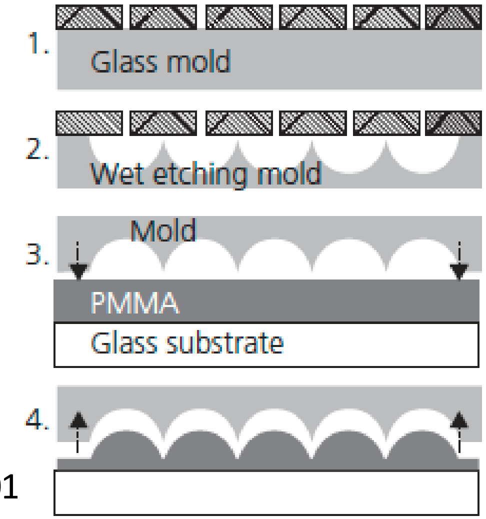
Substrate Mode Outcoupling: ~2X Improvement

η_{ext}~40%

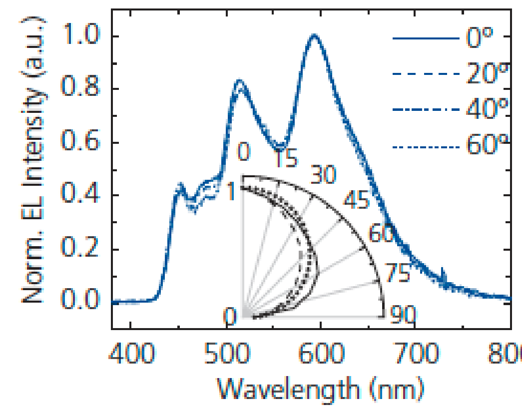
Microlens arrays: Polymer hemispheres much smaller than pixel



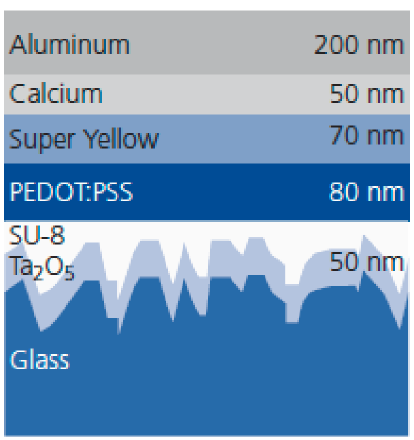
Möller, S. & Forrest, S. R. *J. Appl. Phys.*, **91,** 3324 (2001

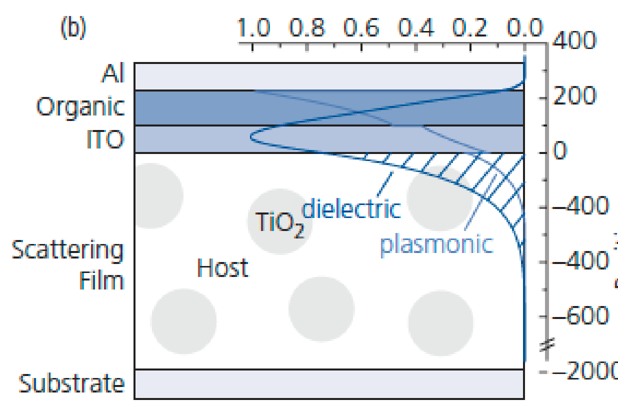


Fabrication sequence



Spectrum angle independent





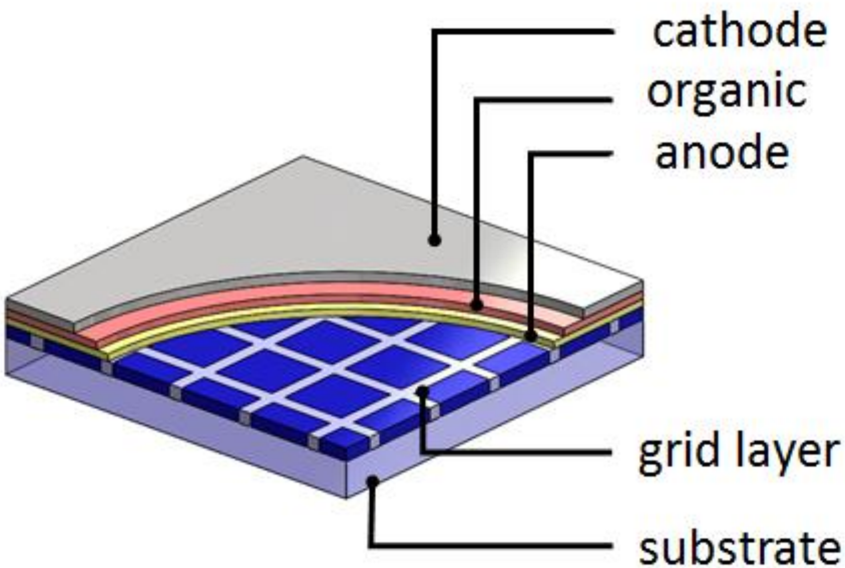
Scattering and surface roughness also can reduce substrate modes

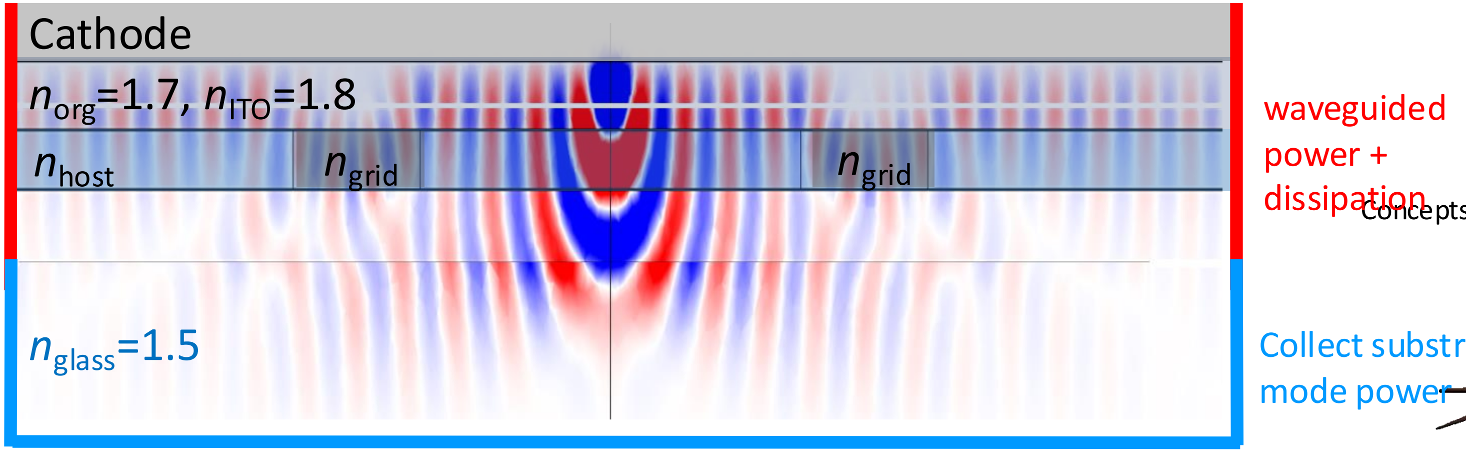
Reidel, et al., Opt. Express **18** A631 (2010)

Chang, et al., J. Appl. Phys., **113** 204502 (2013)

A better approach: Sub-Anode Grid

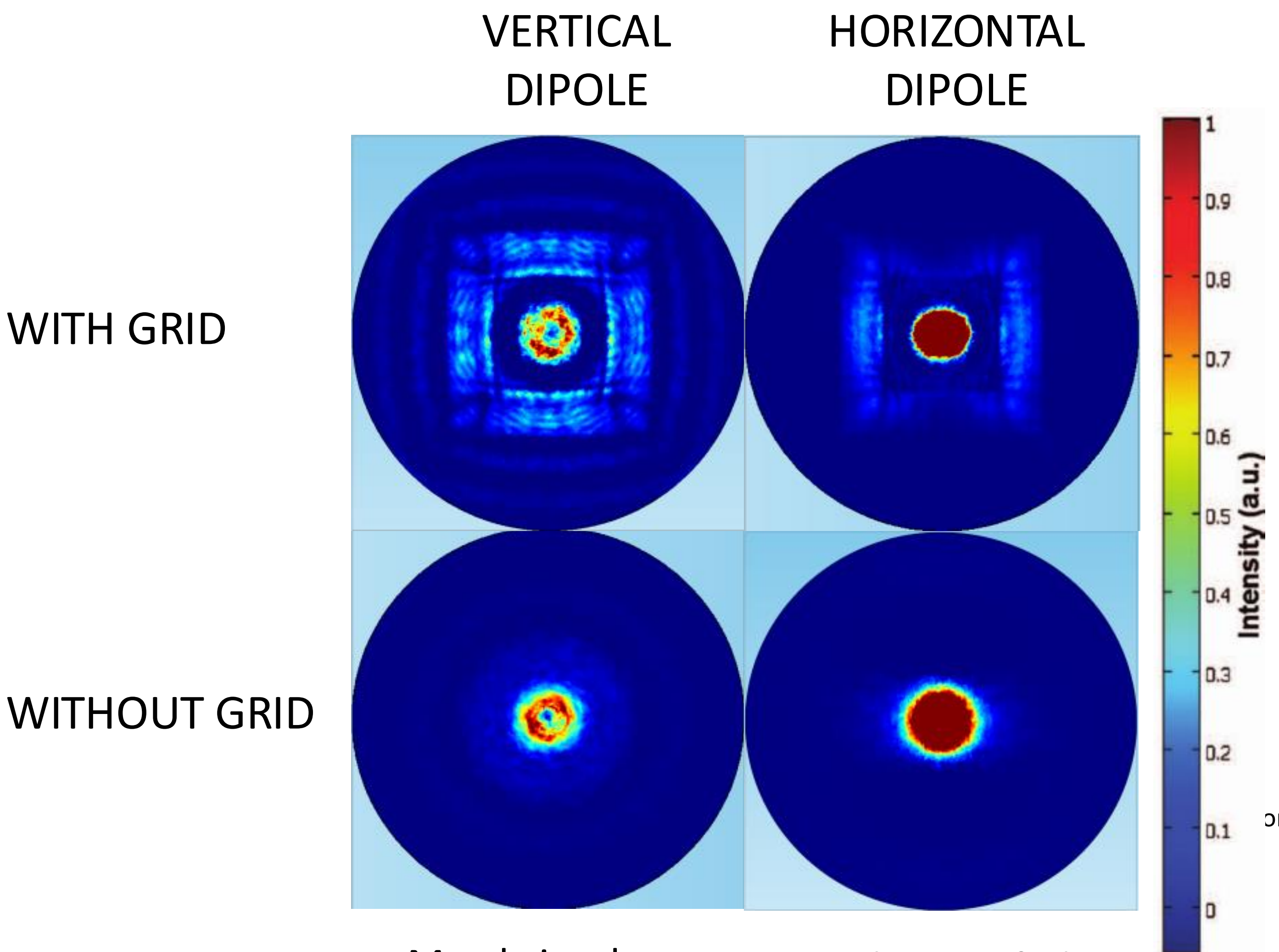
- A multi-wavelength scale dielectric grid between glass and transparent anode (sub-anode grid)
- The grid is removed from the OLED active region
- Waveguided light is scattered into substrate and air modes





Qu,et al., *Nature Photonics* , **9**, 758 (2015)

Emission field calculations

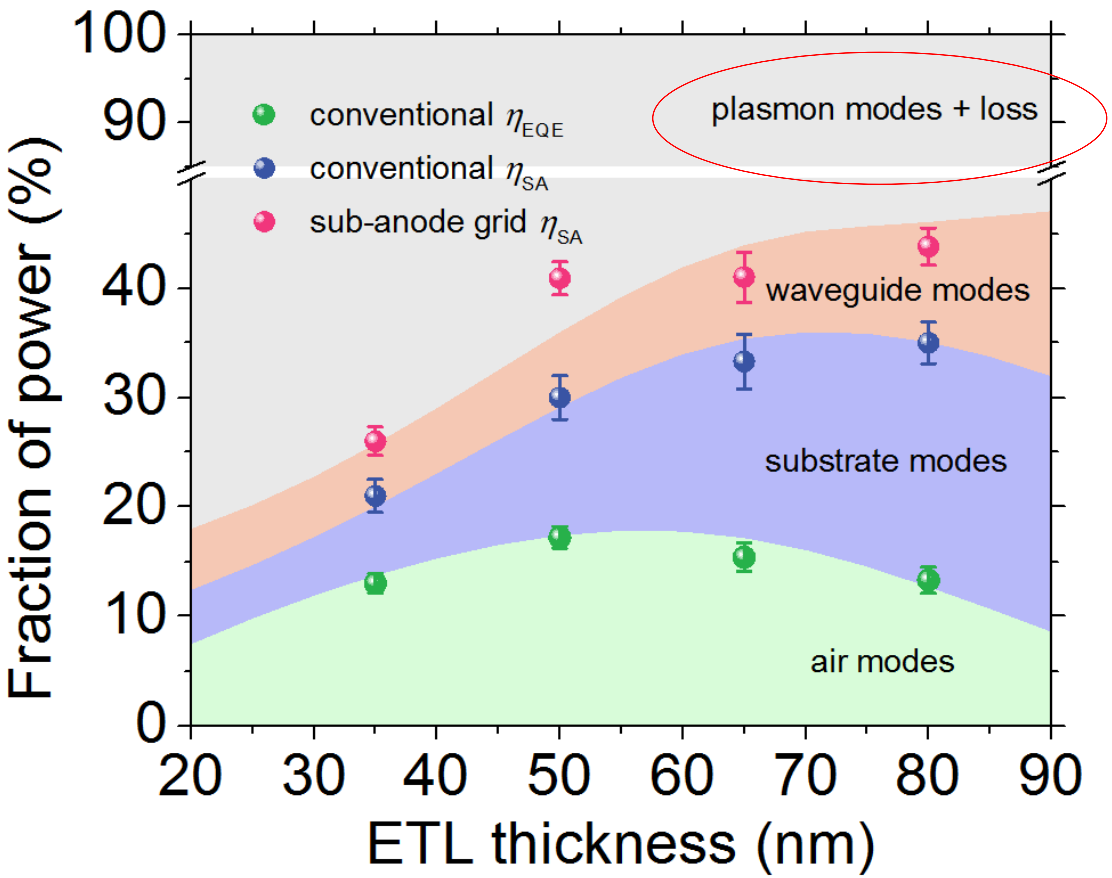


Mostly in-plane (Waveguided)

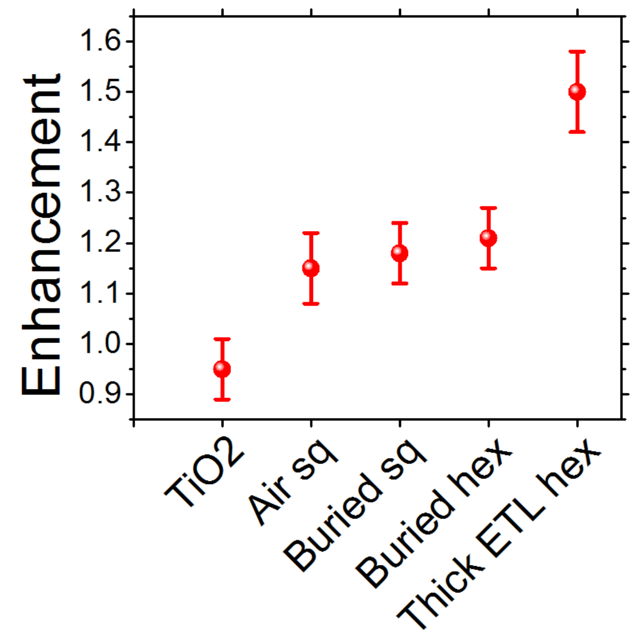
Mostly out-of-plane (Glass + air)

Qu,et al., *Nature Photonics* , **9**, 758 (2015)

Optical Power Distribution



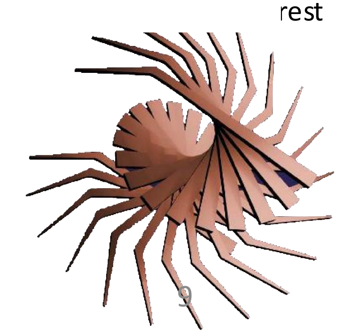
2nm MoO_3/40nm CBP/15nm CBP:Ir(ppy)$_3$/xnm TPBi/1nm LiF/Al



Thick-ETL organic structure:

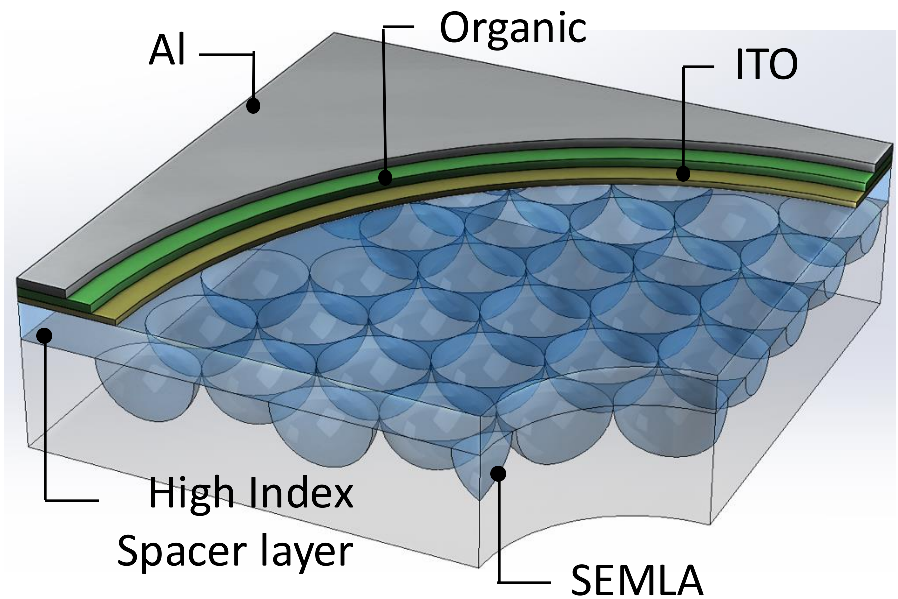
340nm grid/70nm ITO/2nm MoO_3/40nm TcTa/15nm CBP: Ir(ppy)$_3$/10nm TPBi/230nm Bphen:Li/Al

nics
rest



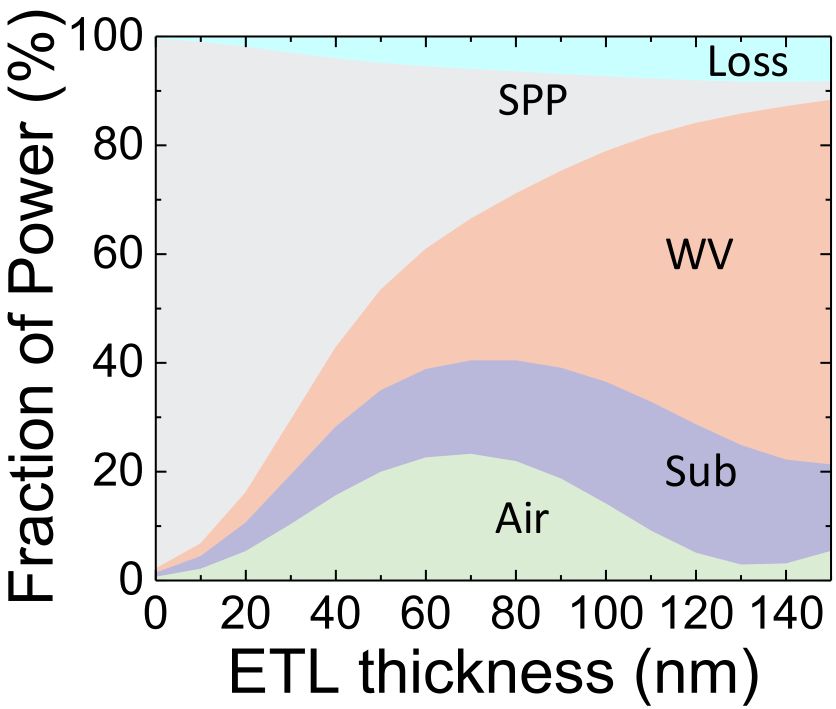
Qu,et al., *Nature Photonics* , **9**, 758 (2015)

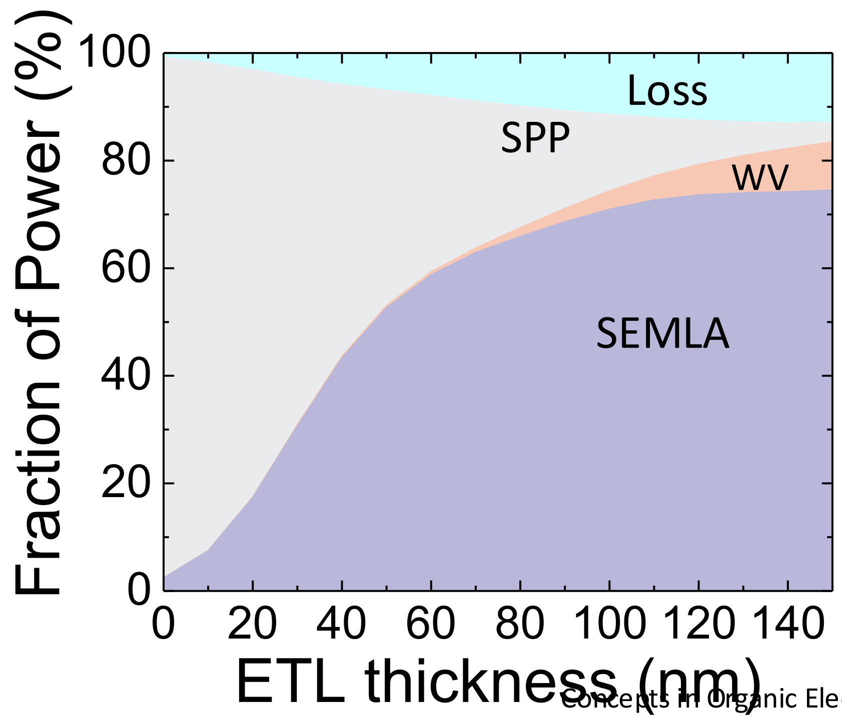
Getting All the Light Out: Sub-Electrode Microlens Array (SEMLA)



Qu, Y., et al. ACS Photonics, **5**, 2453 (2018).

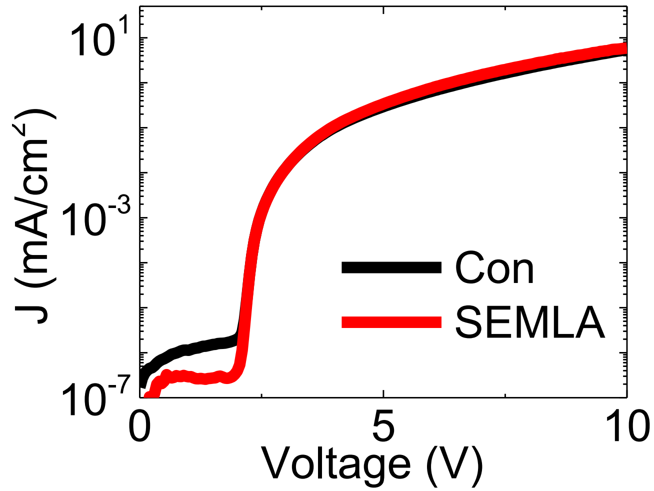
SEMLAs Change the Outcoupling Landscape

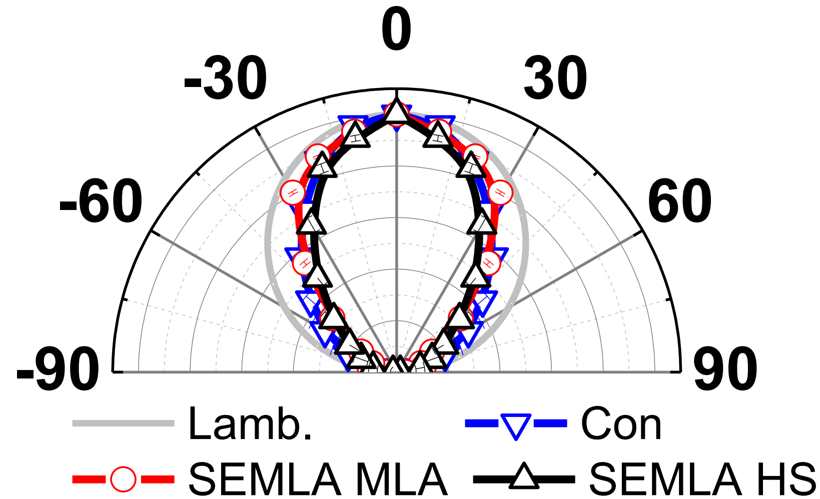


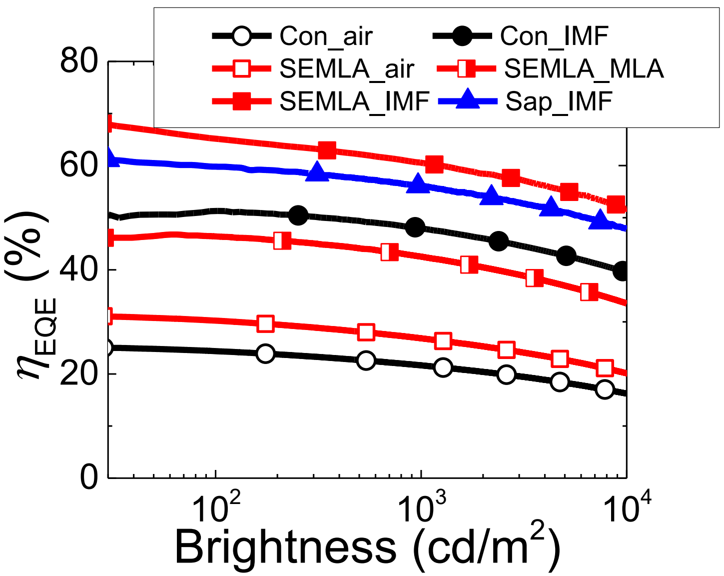


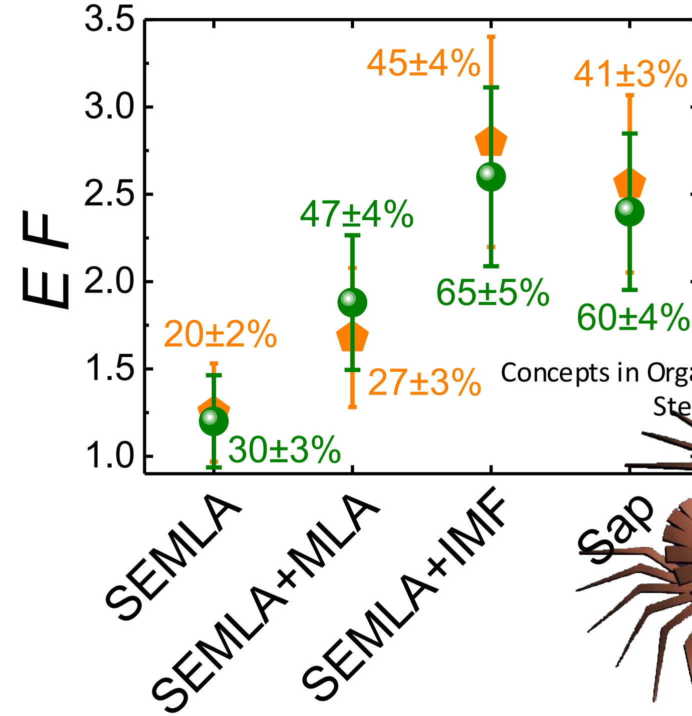
Qu, Y., et al. ACS Photonics, **5**, 2453 (2018).

SEMLA Performance









Concepts in Organic Electronics
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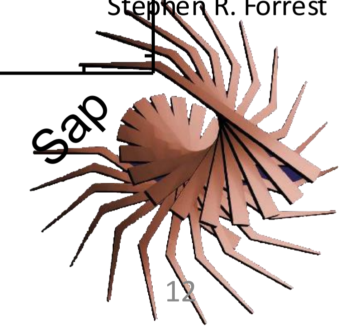
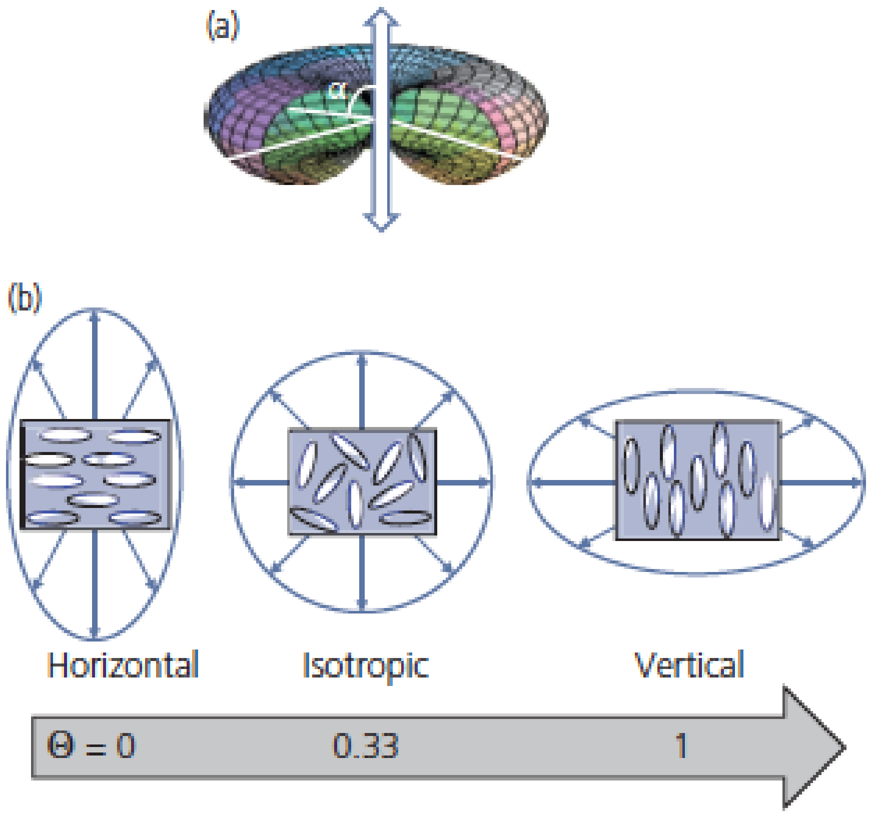
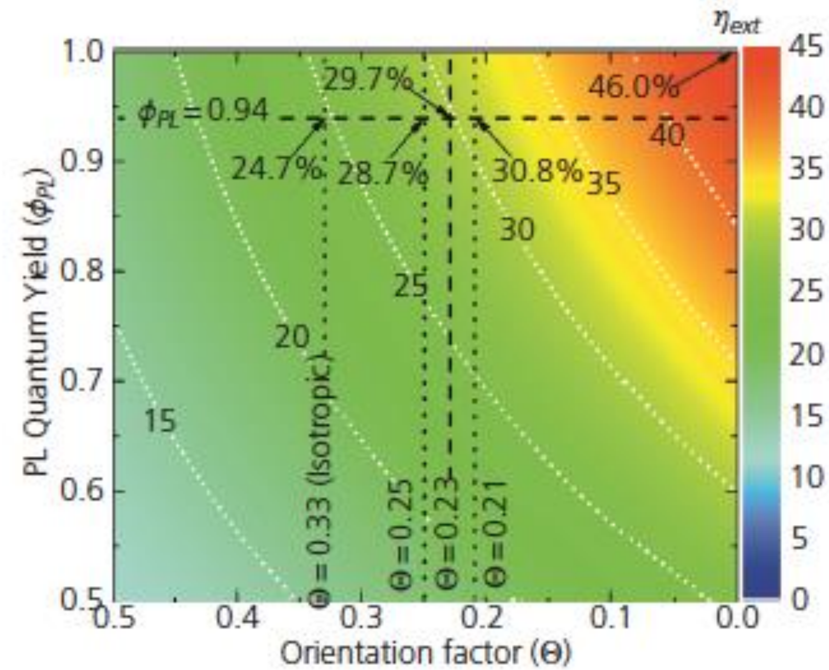


Qu, Y., et al. ACS Photonics, **5**, 2453 (2018).

Dipole orientation significantly affects outcoupling

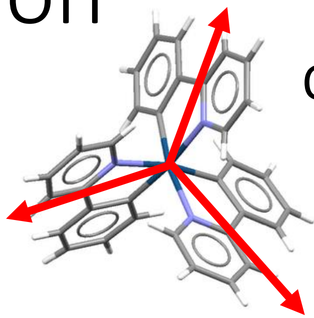




Stephen R. Forrest

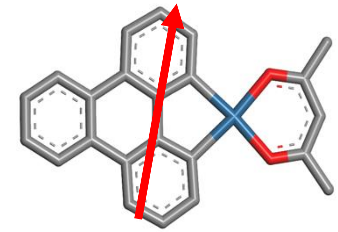
Ratio of light emitting by vertical to horizontal dipoles: $\Theta = \dfrac{TM_{\parallel}}{TE_{\perp} + TM_{\perp} + TM_{\parallel}}$

Outcoupling Enhancements by Molecular Orientation



Isotropic Orientation

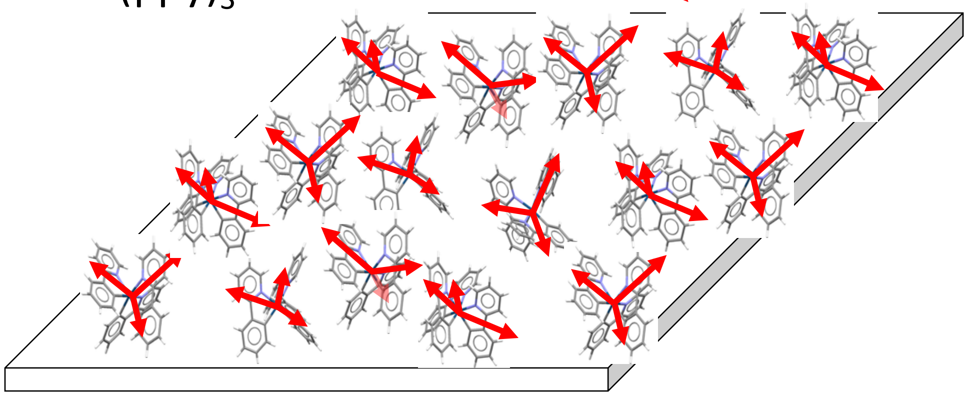
Horizontal Orientation

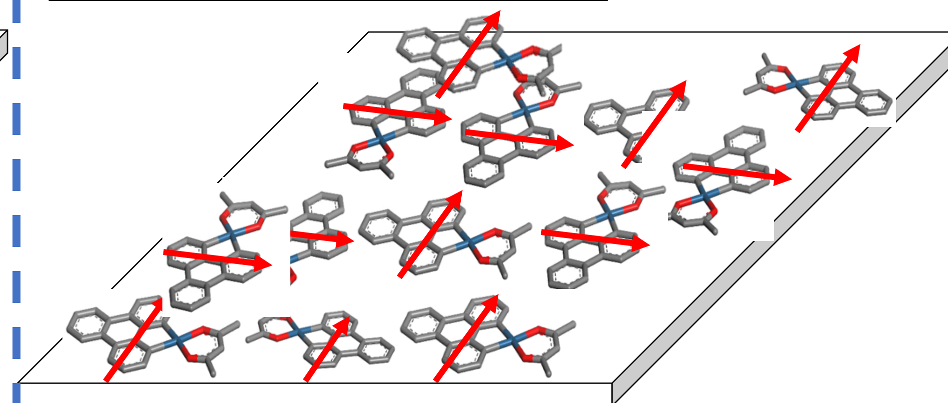


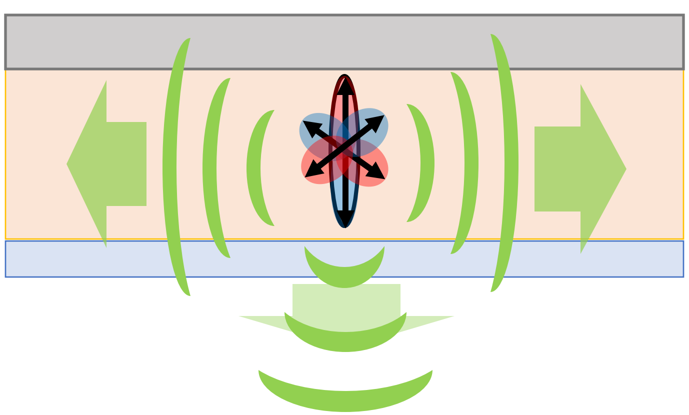
Prevents coupling to SPPs and waveguide modes

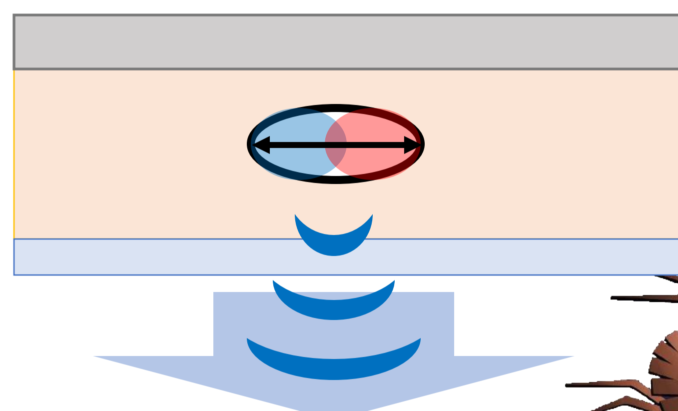
Pt(dbq)(acac)

Ir(ppy)$_3$





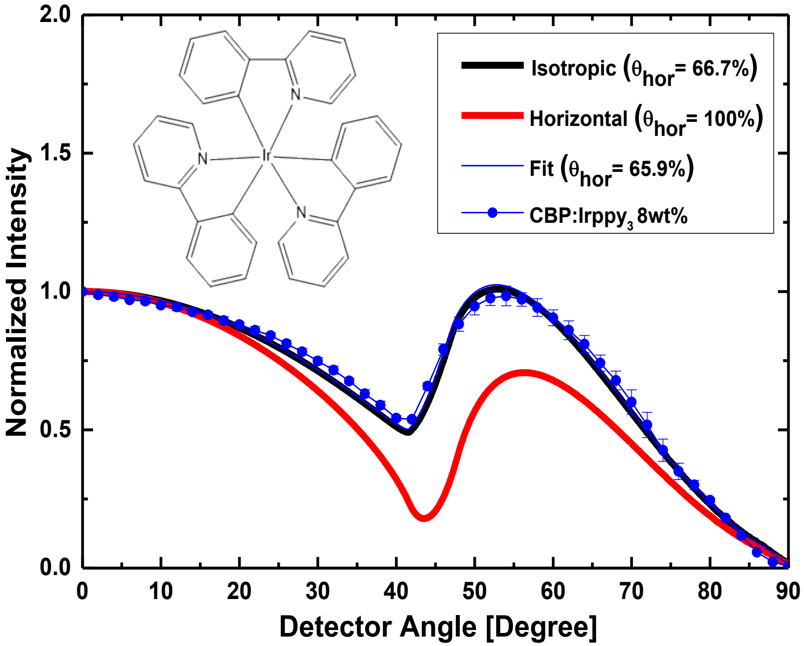




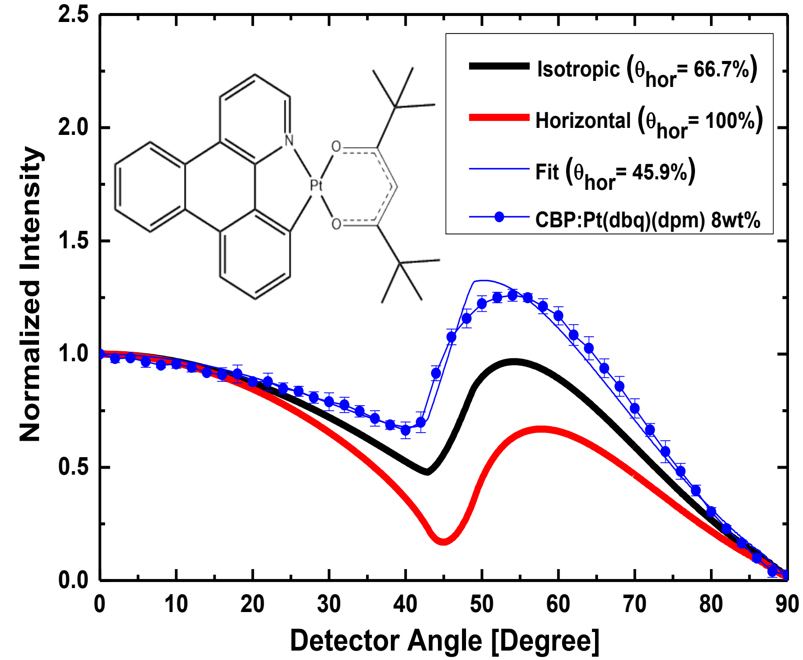
Dihedral molecules (e.g. Pt-complexes) more likely to align than pseudo-octahedral (tris-Ir complexes)

Example results

Ir(ppy)$_3$



Pt(dbq)(dpm)

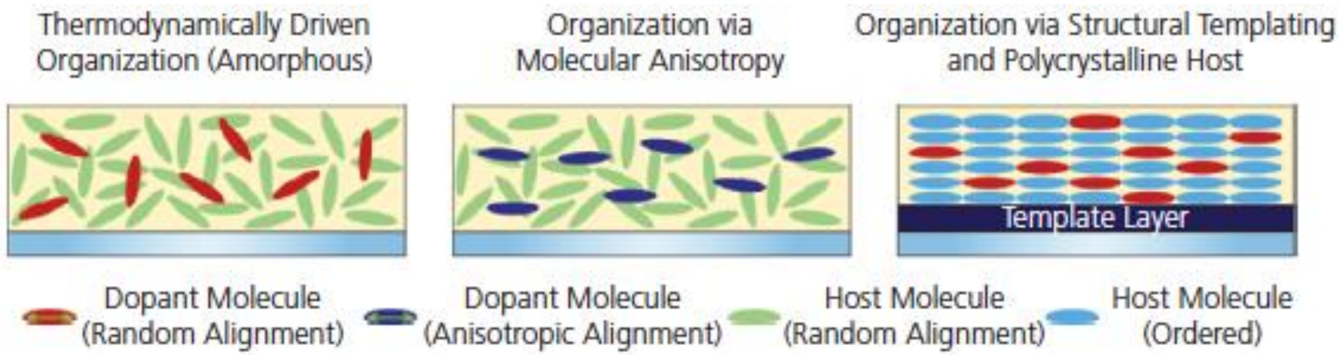


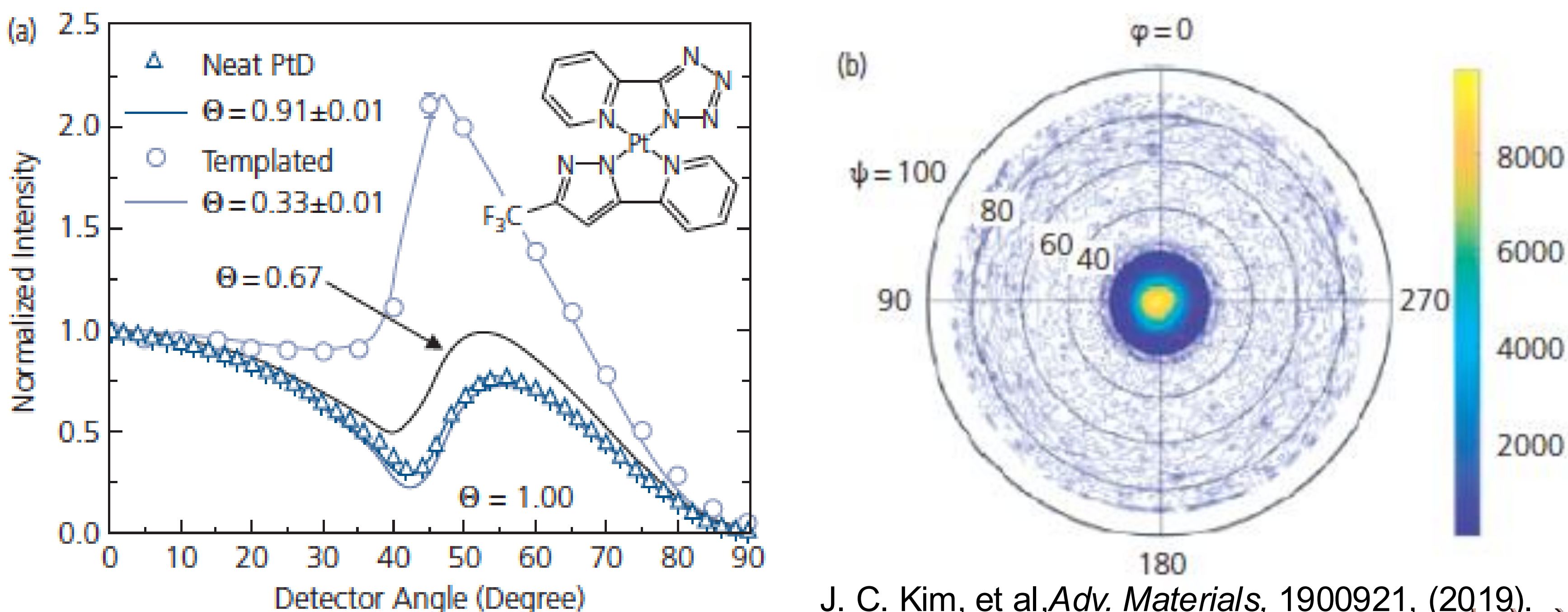
Ratio of light emitting by vertical to horizontal dipoles: $\Theta = \dfrac{TM_{\parallel}}{TE_{\perp} + TM_{\perp} + TM_{\parallel}}$

Approach challenges

- Added constraints on molecular design
- Added constraints on process (growth) conditions: may not align as expected
- Added constraints on device architecture
- Alignment is never “perfect”: limits improvements

Templating can drive orientation

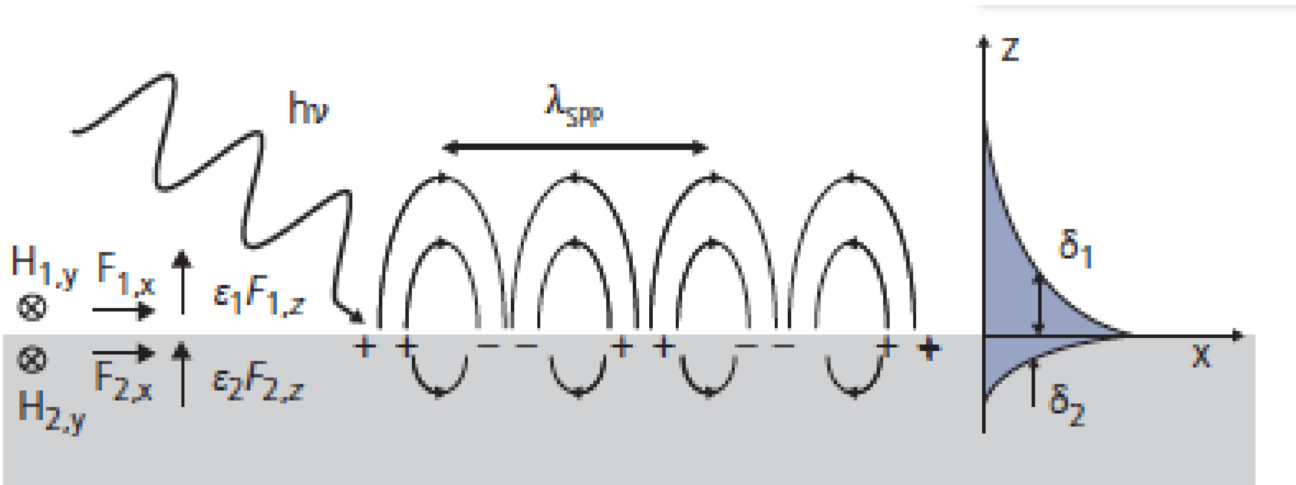




J. C. Kim, et al, *Adv. Materials,* 1900921, (2019).

Surface Plasmon Polariton (SPP) Modes: A 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

W. L. Barnes, et al., Nature, **424** 824 (2003)

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**:

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

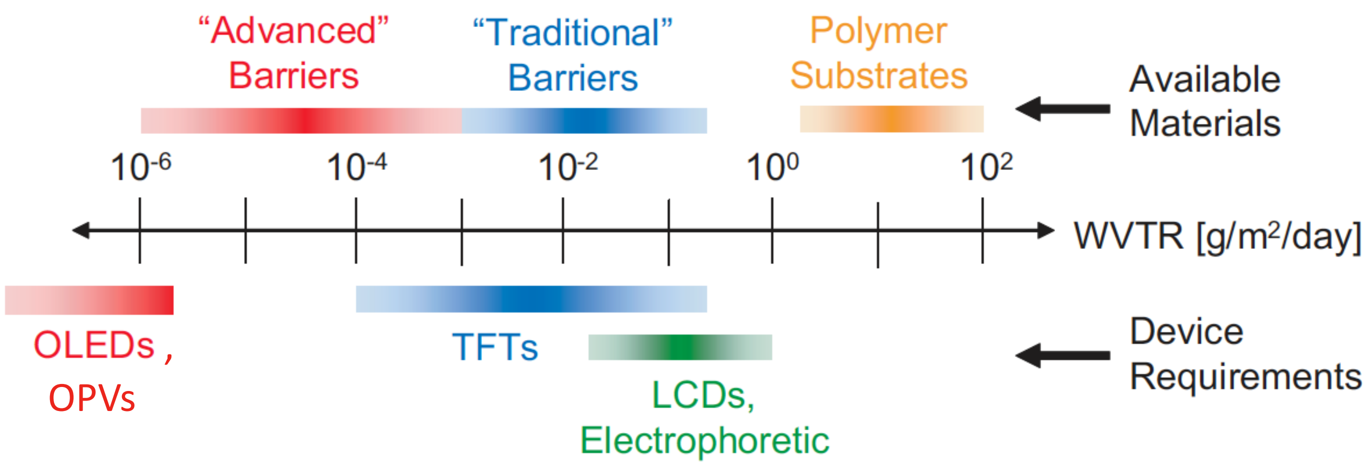
τ, β = empirical constants

- 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**)

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

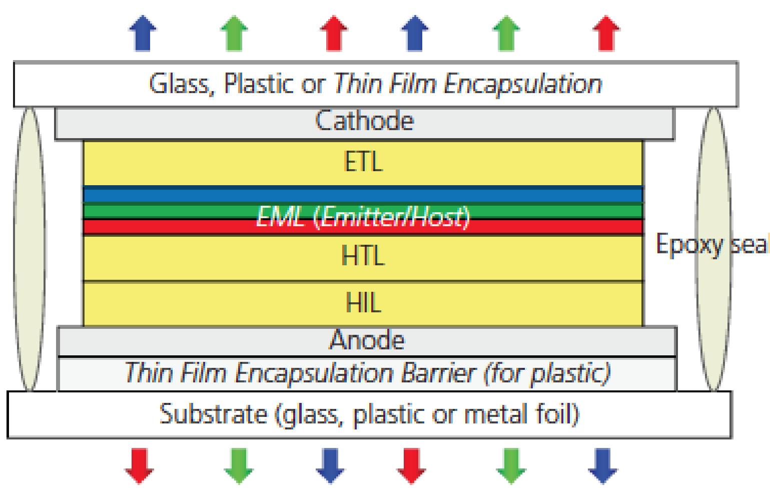
n = empirical acceleration factor

Packaging required for long lifetime



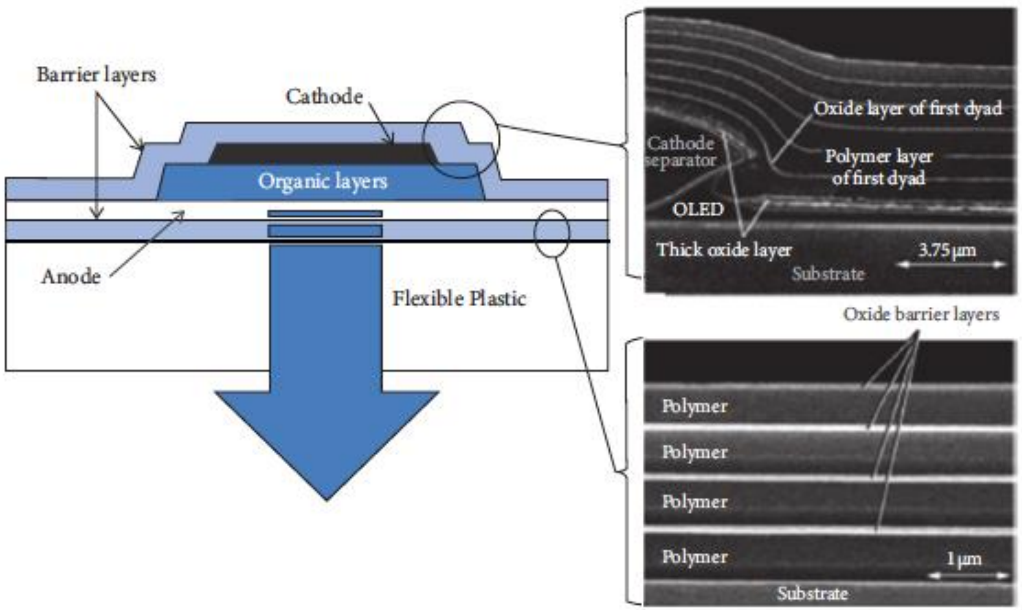
Lewis, Mater. Today, **9**, 38 (2006)

Water vapor transfer rate determines package quality and use



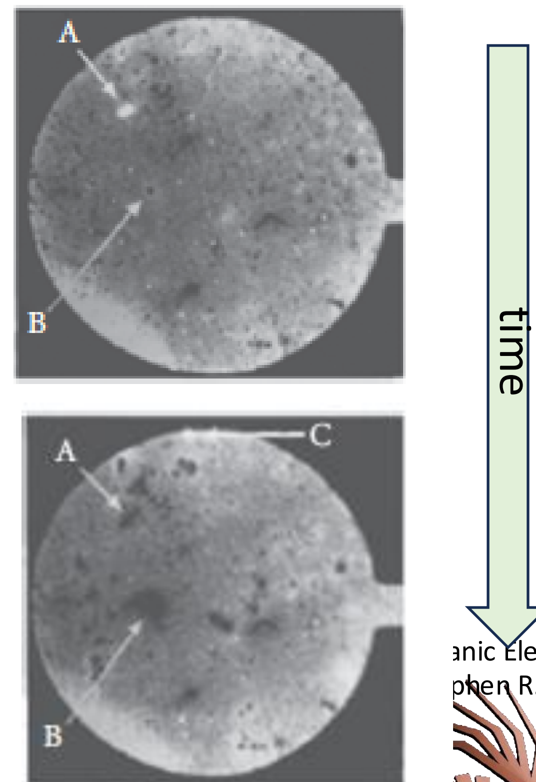
Common OLED epoxy sealed packaging scheme

Encapsulation and Dark Spot Formation



C.-S. Suen and X. Chu, Solid State Technology (2008) **51,** 36

Extrinsic degradation due to dark spot formation over time in unencapsulated devices



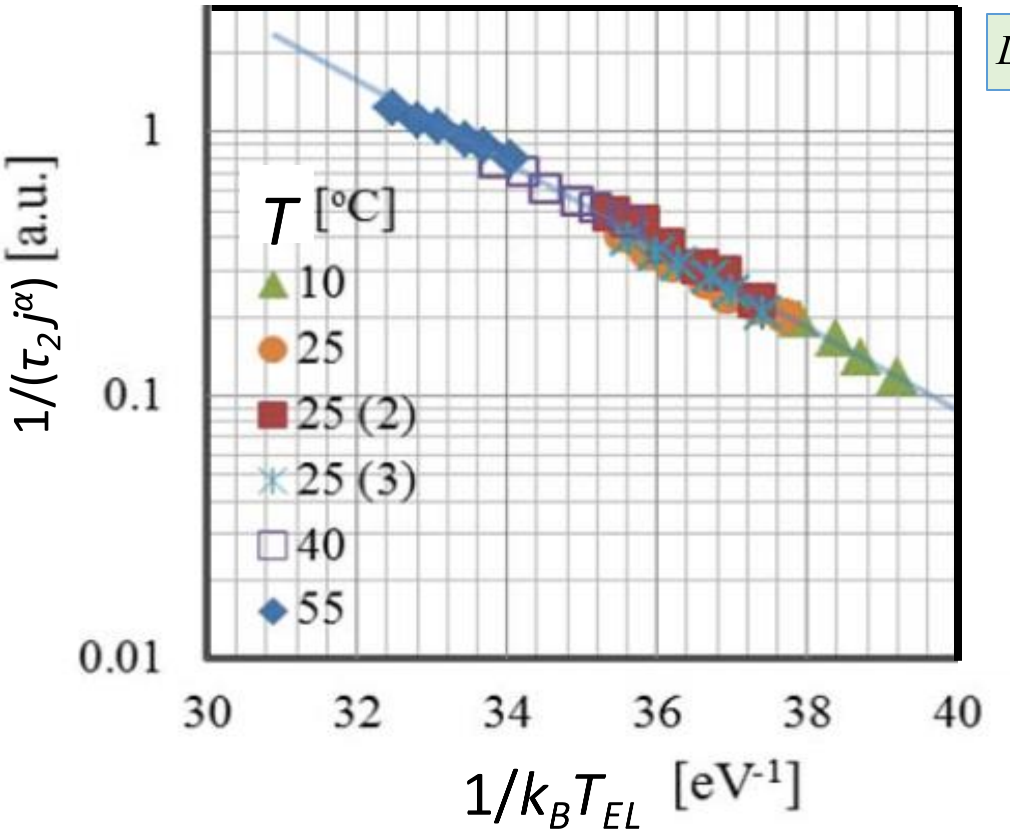
Alq_3 EL images

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

Accelerated Degradation Methodologies

Example data: Green PHOLED

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

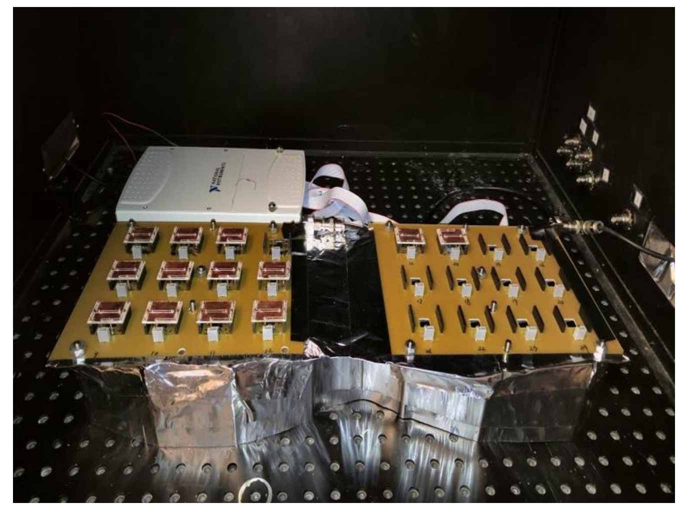


Sum of lifetimes is alternative empirical relation:

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

ΔE_{A0}=thermal activation of degradation

α = current acceleration factor

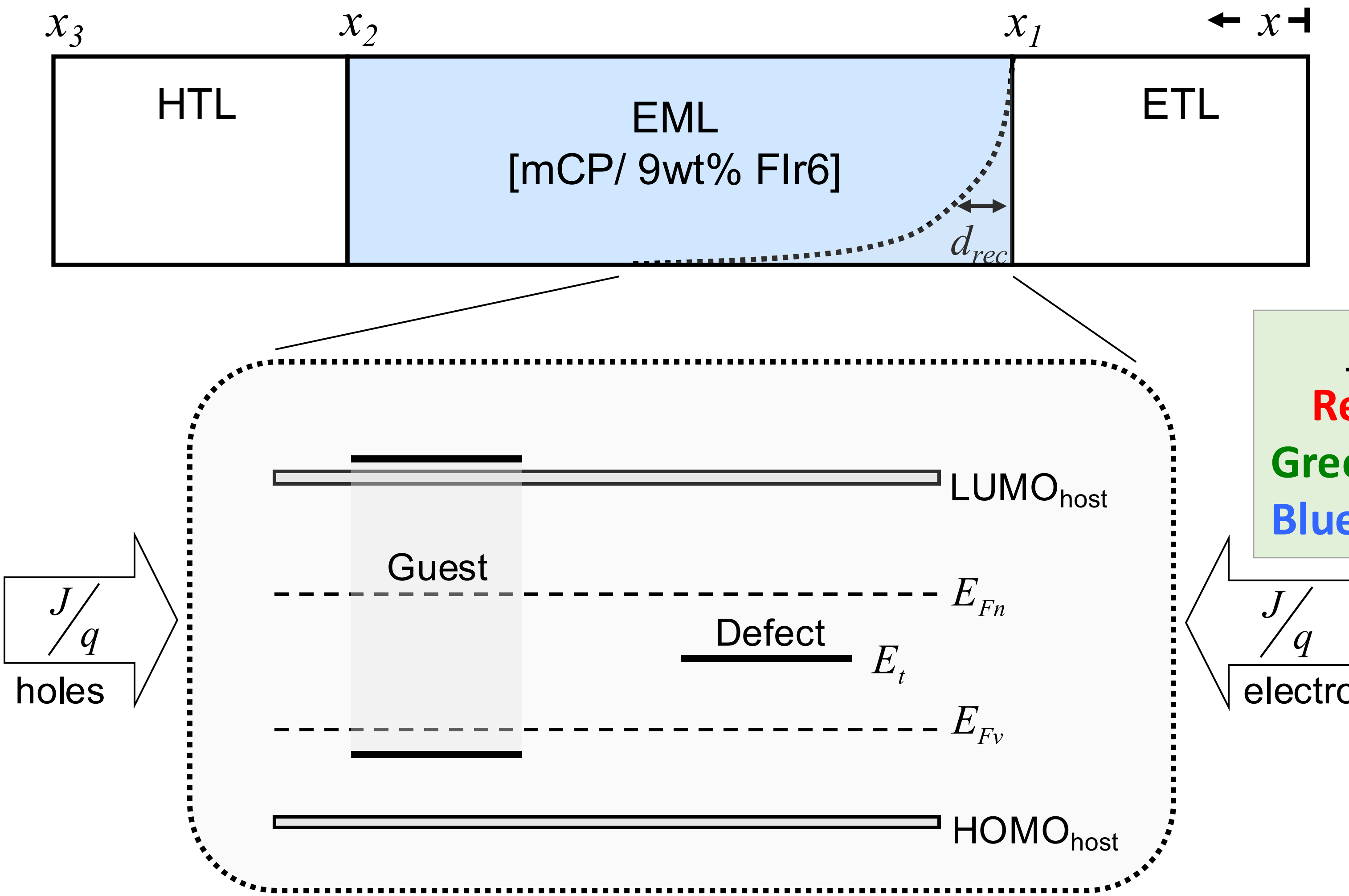


Measuring populations of identical devices

Combining all degradation sources:

$$LTx(L_0, T_0) = LTx(L_{tst}, T_{tst}) \left[\frac{L_{0tst}}{L_0}\right]^n exp\left(-\frac{\Delta E_A}{k_B}\left(\frac{1}{T_{tst}} - \frac{1}{T_0}\right)\right).$$

Intrinsic Lifetime Limits of OLEDs



Energy Scale

Red light: ~ 2 eV

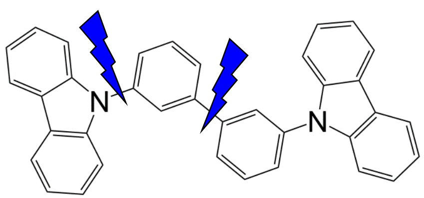
Green light: ~2.3 eV

Blue light: ~ 2.9 eV

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

Degradation Routes

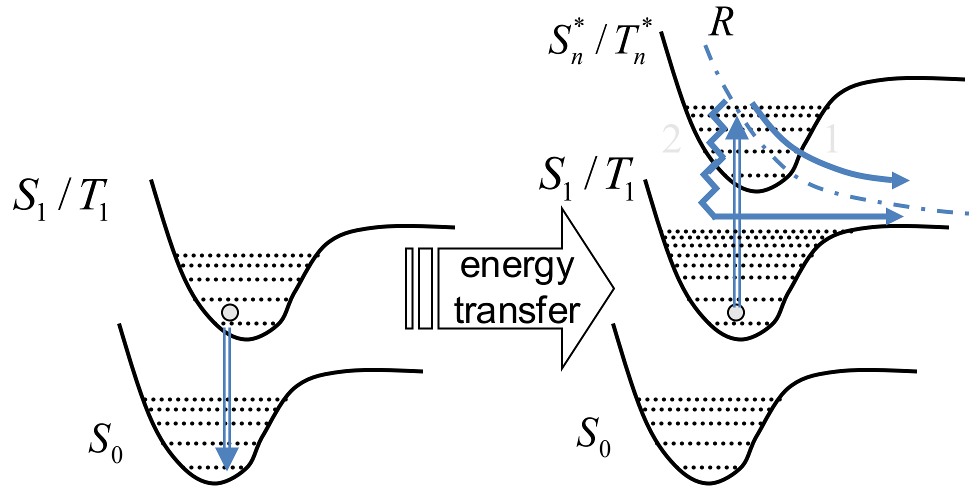
- Energetically Driven
  - Lifetime: R>G>B
- Two particle interactions lead to luminance loss
  - Exciton on phosphor, polaron on host
  - Exciton-exciton also possible



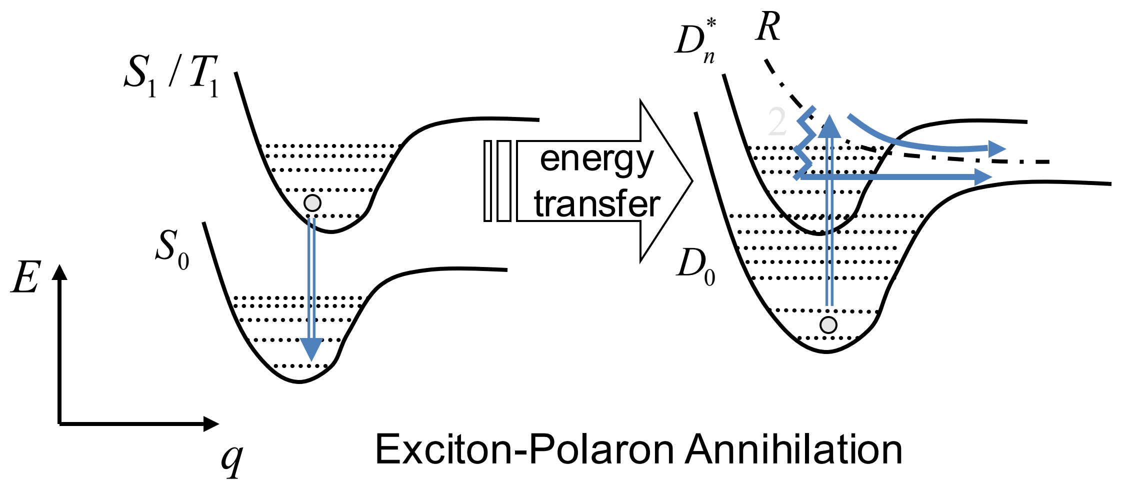
Bond	BE(eV)	Bond	BE(eV)
C-C	3.64	N-N	1.69
C-H	4.28	N-O	2.08
C-O	3.71	N-H	4.05
C-N	3.04	O-O	1.51
C-F	5.03	H-H	4.52

Bond cleavage

Broken bonds? → Defects!



Exciton-Exciton Annihilation

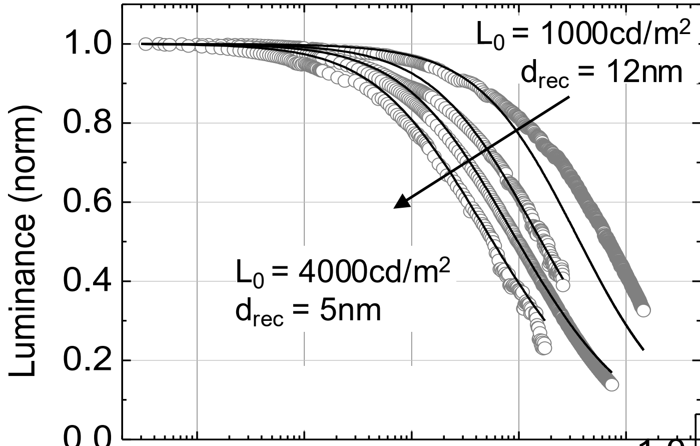


Exciton-Polaron Annihilation

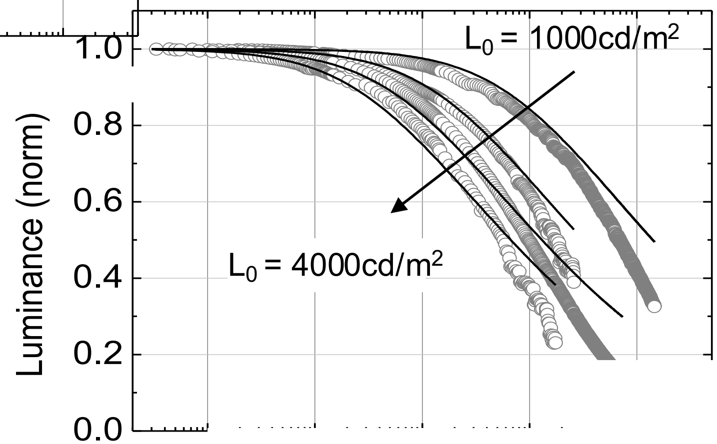
Triplet energy (~2.8 eV) + polaron (~3.3 eV) = hot polaron (≥ 6 eV)

Luminance Decay vs Time

- Blue PHOLED
- Prepared and packaged using industry std.

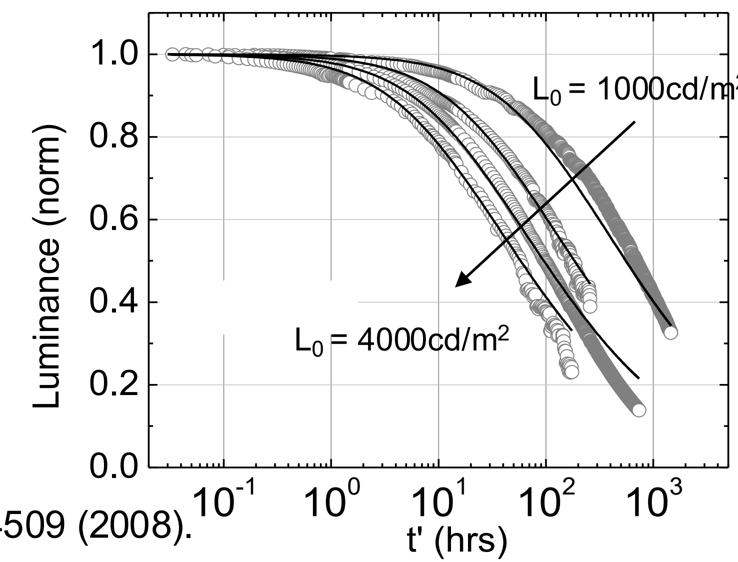


Exciton Localization



Exciton-Exciton Annihilation

Exciton-Polaron Annihilation

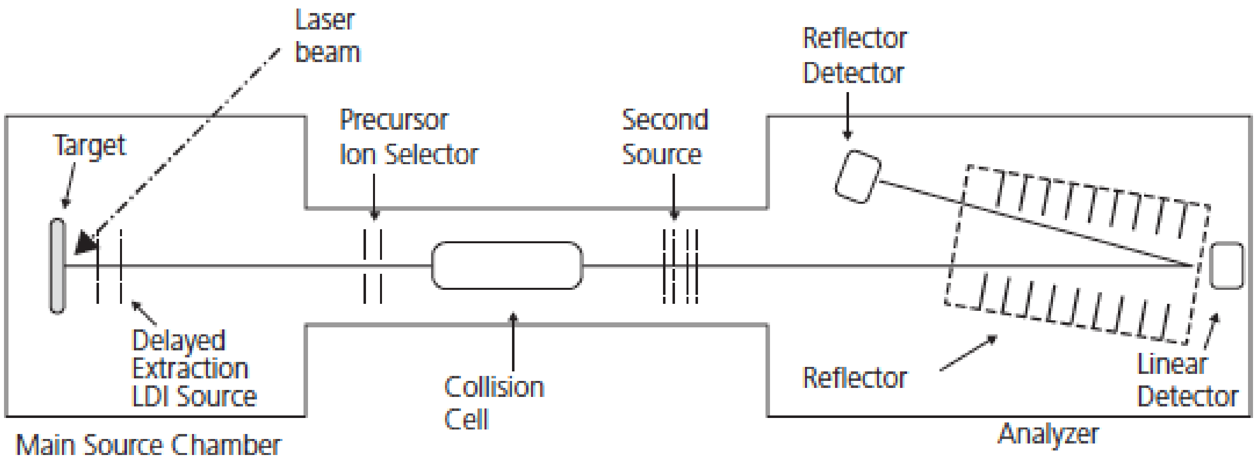


Defect Generation Rates

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

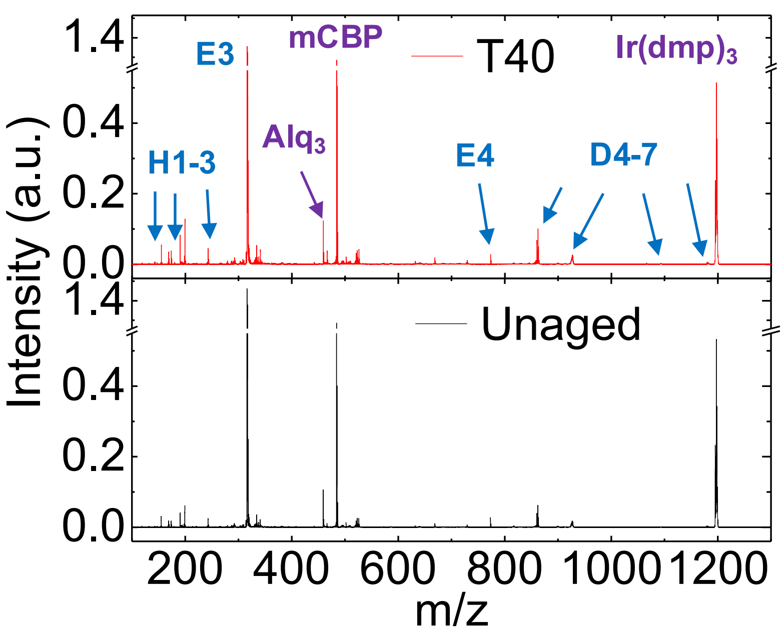
Giebink, et al., *J. Appl. Phys.*, **103**, 044509 (2008).

Evidence for Defect Formation: Molecular Fragmentation

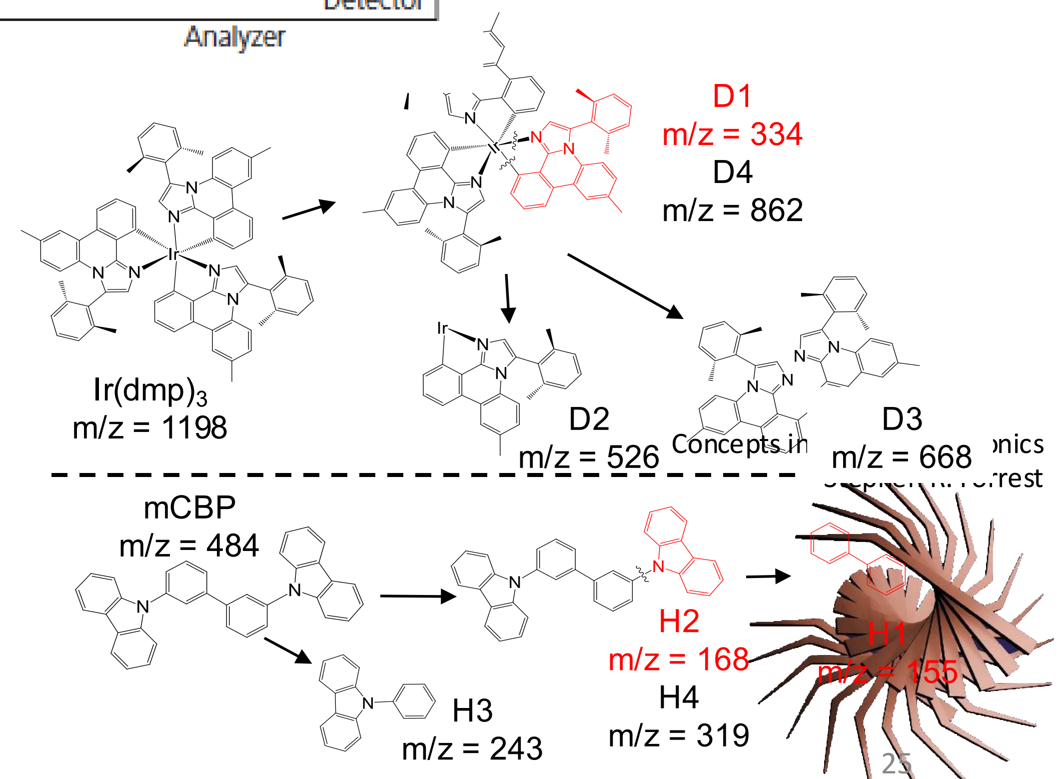


Laser Desorption Ionization-Time of Flight Mass Spectroscopy (LDI-TOF-MS)

-Molecular species identification



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



Ageing by high energy (blue) triplet annihilation

Rate of Non-radiative Defect formation: $P_{TPA} = \dfrac{3K_X\tau_r}{4\pi r_C^3}$

r_C = triplet capture radius

τ_r = radiative lifetime of the triplet

Triplet-polaron and triplet-triplet annihilation most responsible for blue PHOLED degradation

Conclusions

•Q~10^{18} cm^{-3} ➡ 50% increase in quenching

•At 1000 cd/m^2, formation rate = $10^{12} cm^{-2}s^{-1}$

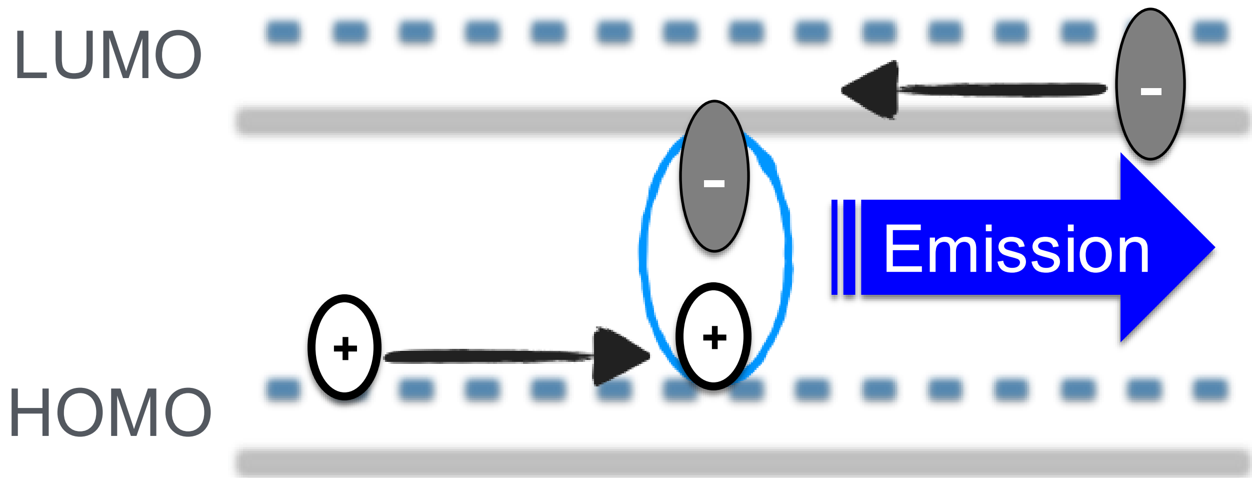
-1 in 5 x10^8 E-P encounters leads to defect

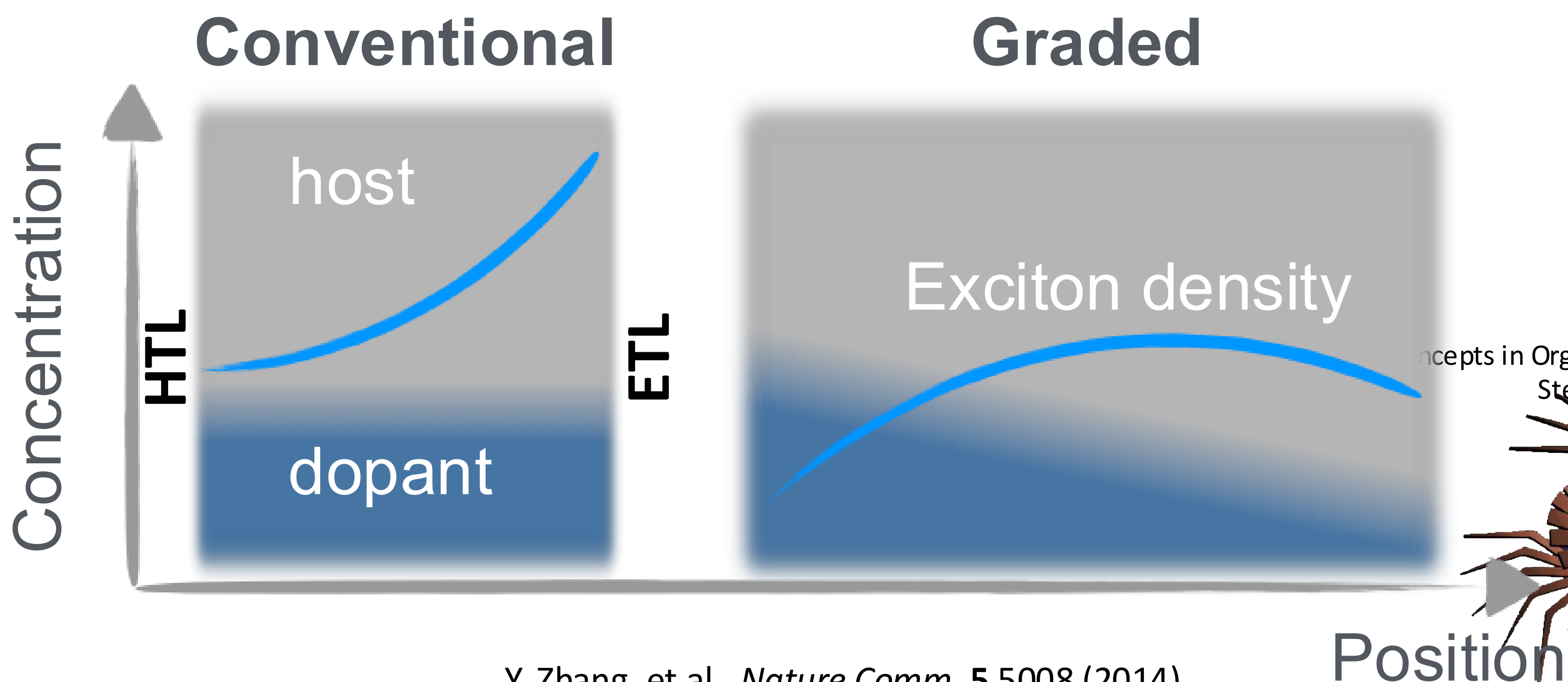
-Increasing recombination zone width extends lifetime

- Guest triplets/host polarons most active

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

Reducing Exciton Density to Increase Lifetime

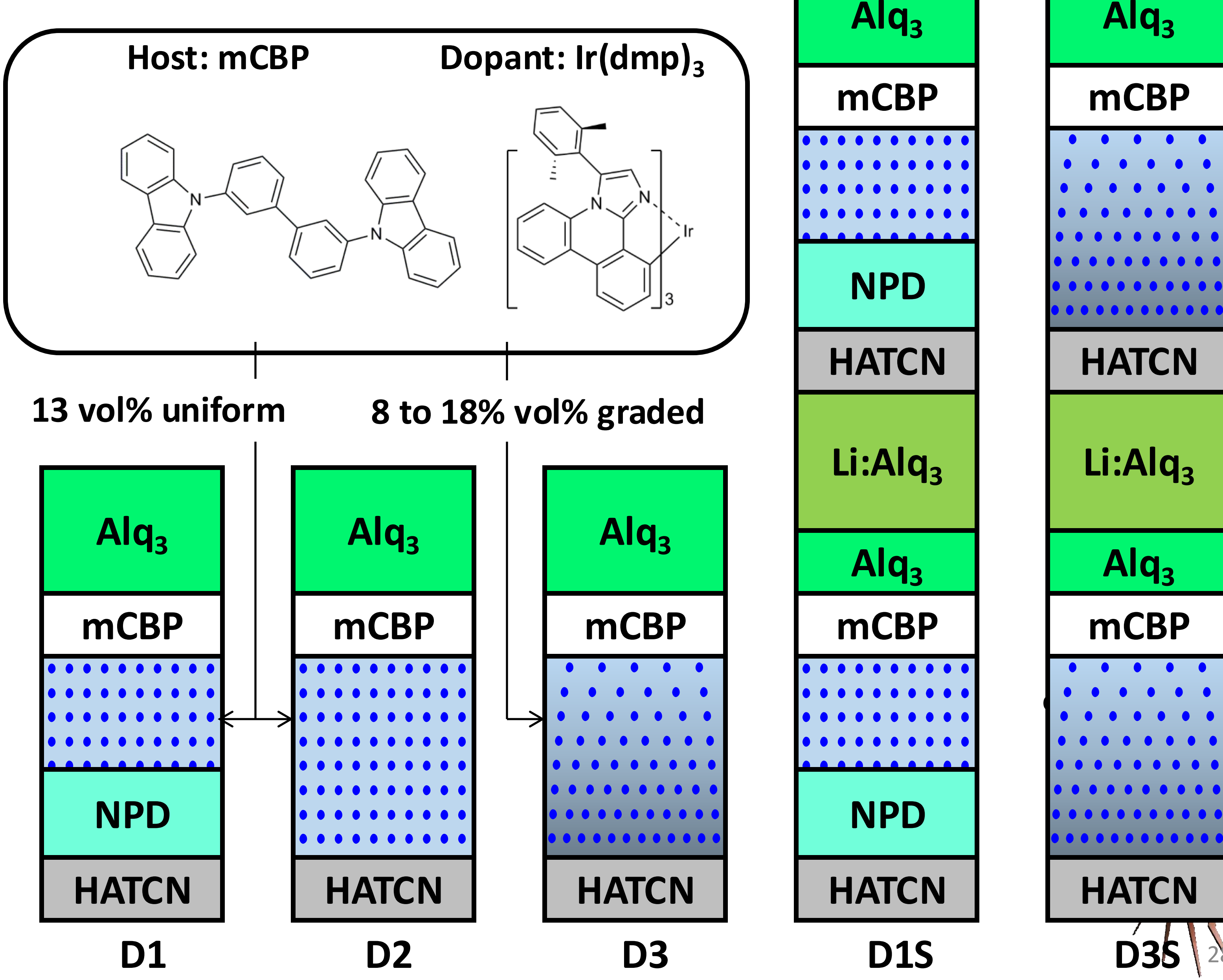




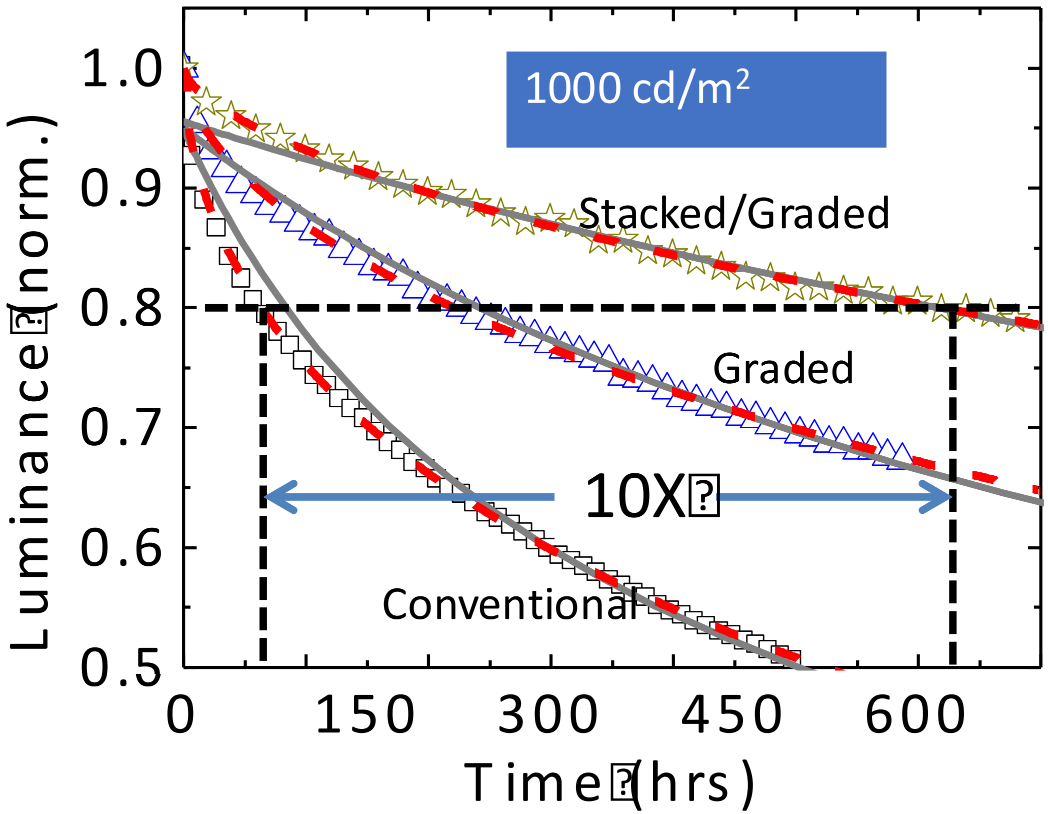
Y. Zhang, et al., *Nature Comm.* **5** 5008 (2014)

Spreading the recombination zone: Dopant/Host Grading

3 Different test device structures



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/m²]	**3,000**
Efficacy [lm/W]	**48**
CRI	**86**
Luminous Emittance [lm/m²]	7,740
1931 CIE	(0.454, 0.426)
LT_{70} [hrs]	**13,000**

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

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