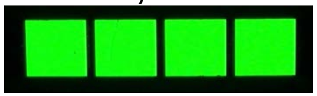
# Advances in Organic Materials for White OLEDs

Mark Thompson
*University of Southern California*

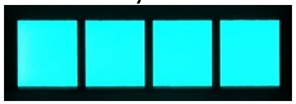
Stephen Forrest
*University of Michigan*

# Universal**PHOLED**® Technology and Materials

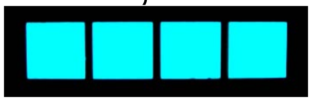
0.33, 0.63



0.17, 0.38

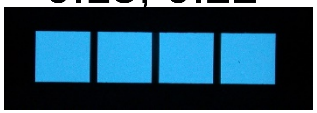


0.16, 0.37



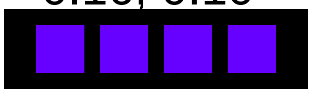
0.16, 0.29

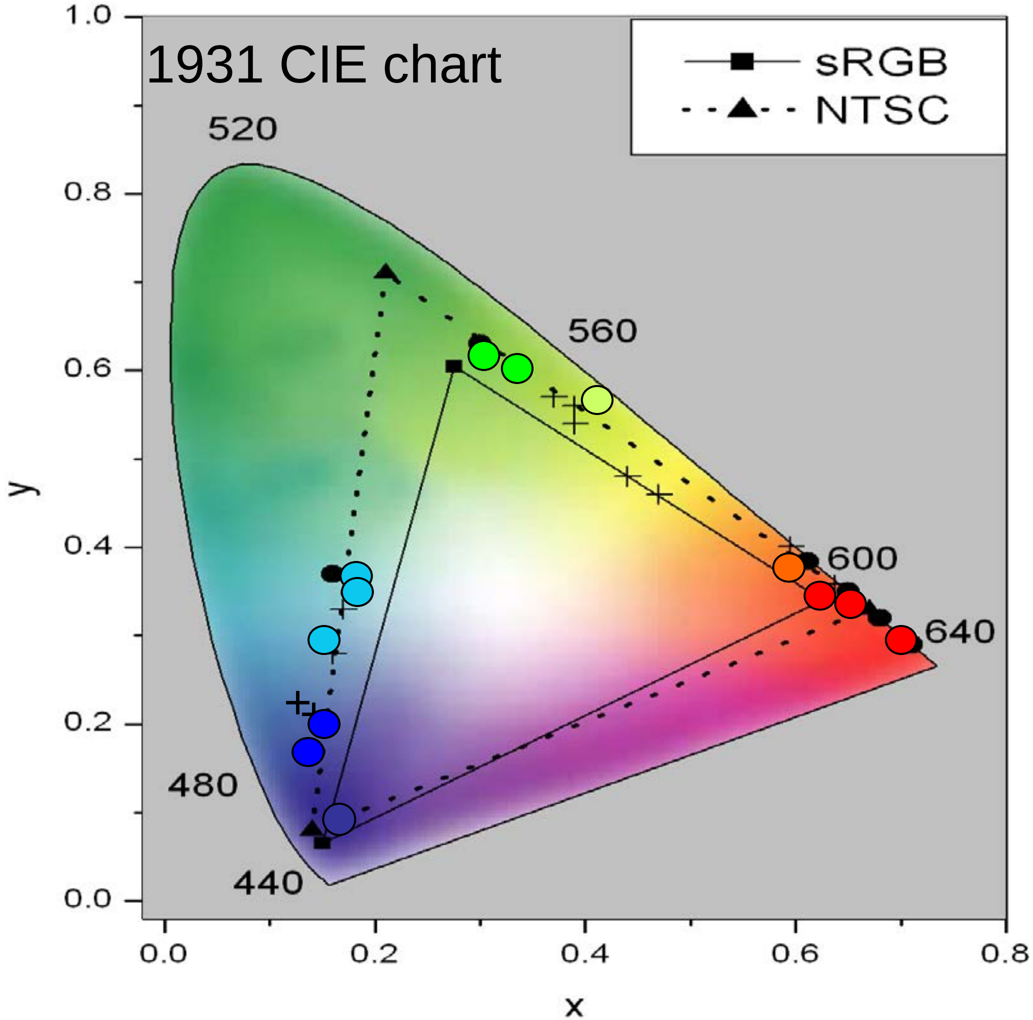
0.15, 0.22



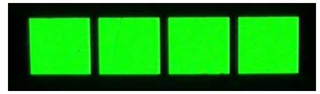
0.14, 0.13

0.16, 0.10

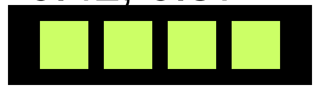




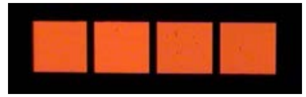

0.35, 0.61



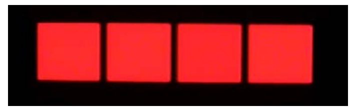
0.42, 0.57



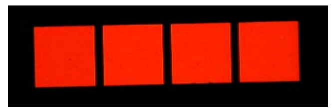
0.62, 0.38



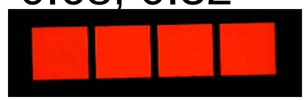
0.65, 0.35



0.67, 0.33



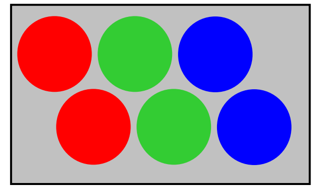
0.68, 0.32



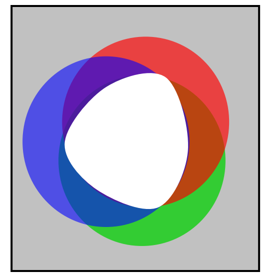
UNIVERSAL DISPLAY CORPORATION

# Color Mixing to Achieve White Emission

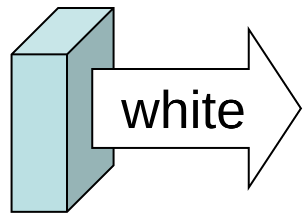
- Color mixing
- Side-by-side arrangement of RGB elements



- Transparent devices can be stacked
  - Pixels on top of pixels with a common substrate
  - Large sheets of transparent R, G and B OLEDS can be stacked to achieve white



- Mixed emitters in a single device
  - Simplifies device
  - Color balance achieved automatically
  - Several possible architectures



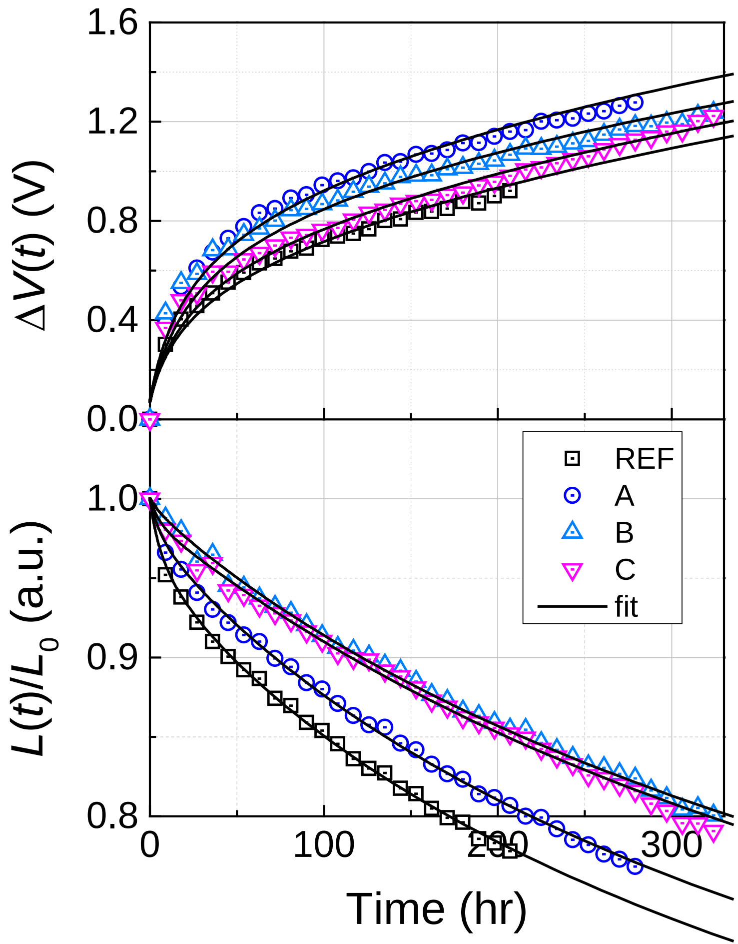

- **In all cases the White OLED lifetimes are limited by the blue components**

# Efficiency and Operational Lifetime of PHOLEDs

## Phosphorescent dopants

| Color | CIE | LE (cd/A) | $t_{50}$ (hrs) |
|---|---|---|---|
| **Red** | **[0.64, 0.36]** | **30** | **900,000** |
| **Green** | **[0.31, 0.63]** | **85** | **400,000** |
| **Blue** | **[0.14, 0.12]** | **High** | **short** |

Universal Display Corp.

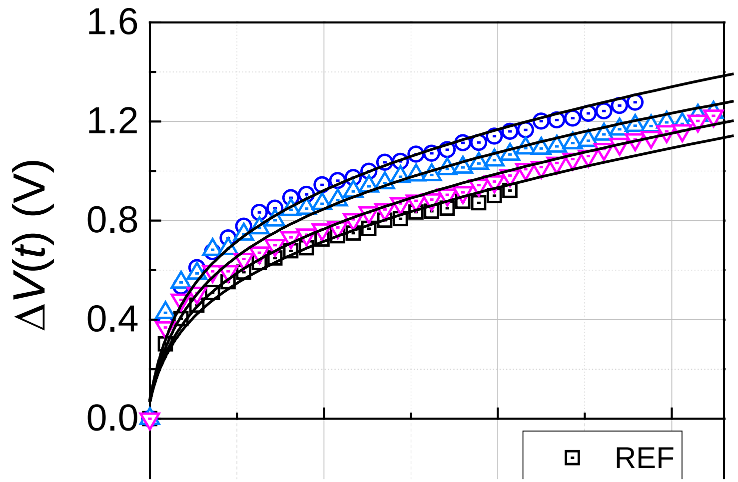

Commercial lighting panels use sky-blue dopant to extend lifetime, but the WOLED lifetime is still limited by blue.

# Efficiency and Operational Lifetime of PHOLEDs

## Phosphorescent dopants

| Color | CIE | LE (cd/A) | $t_{50}$ (hrs) |
|---|---|---|---|
| Red | [0.64, 0.36] | 30 | 900,000 |
| Green | [0.31, 0.63] | 85 | 400,000 |
| Blue | [0.14, 0.12] | High | short |

Triplet exciton lifetime – μs



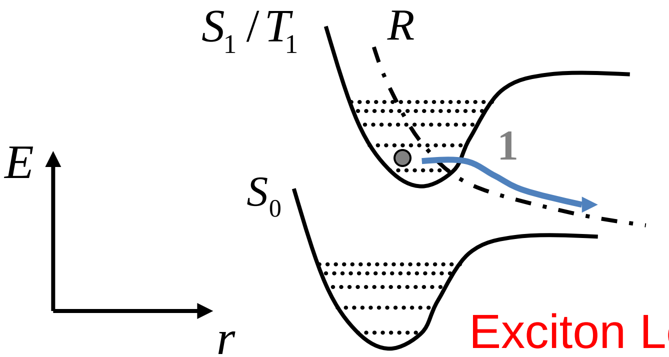

Is there enough energy in the $T_1$ exciton to break bonds?

| Color | $\lambda_{max}$ (nm) | Energy (eV / kcal) |
|---|---|---|
| Red | 600 | 2.07 / 48 |
| Green | 520 | 2.40 / 56 |
| Blue | 460 | 2.70 / 63 |

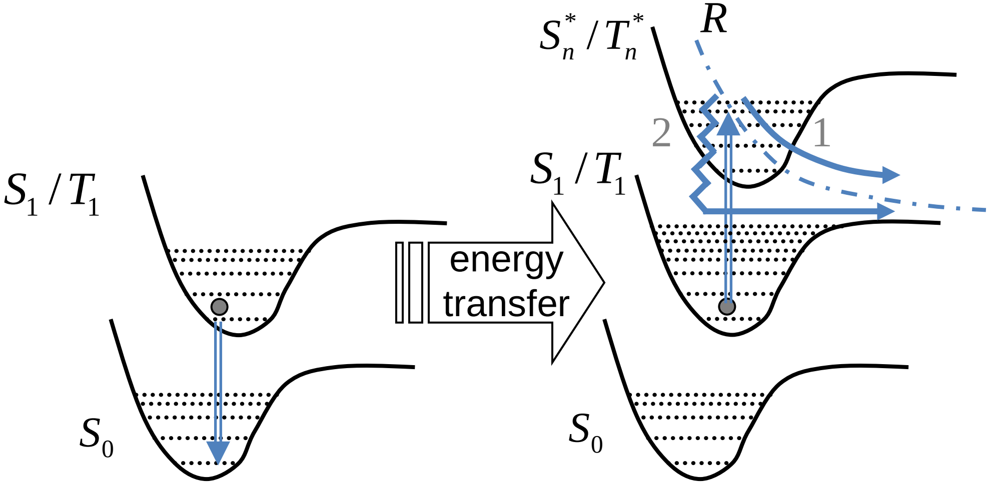
| Bond | Energy (eV / kcal) |
|---|---|
| C-H | 3.6-4.1 / 85-100 |
| C-C | 3.0-4.0 / 70-95 |
| C-N | 3.0-4.0 / 70-95 |
| Ir-C | 3.4 / 80 |

Make emitters with bonds at the upper ends of the ranges. Is that good enough?

# Degradation Routes




Exciton Localization



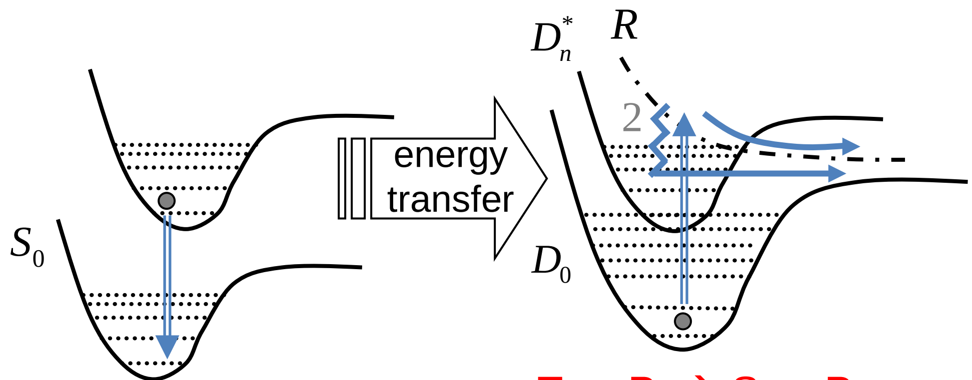

$T_1 + T_1 \rightarrow S_0 + S_n^*/T_n^*$

Exciton-Exciton Annihilation

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

Fitting kinetic data through several half-lives suggests that bimolecular process (TTA and TPA) are the most important.

$$Rate_{annhilation} = k[T_1][T_1,P^-]$$



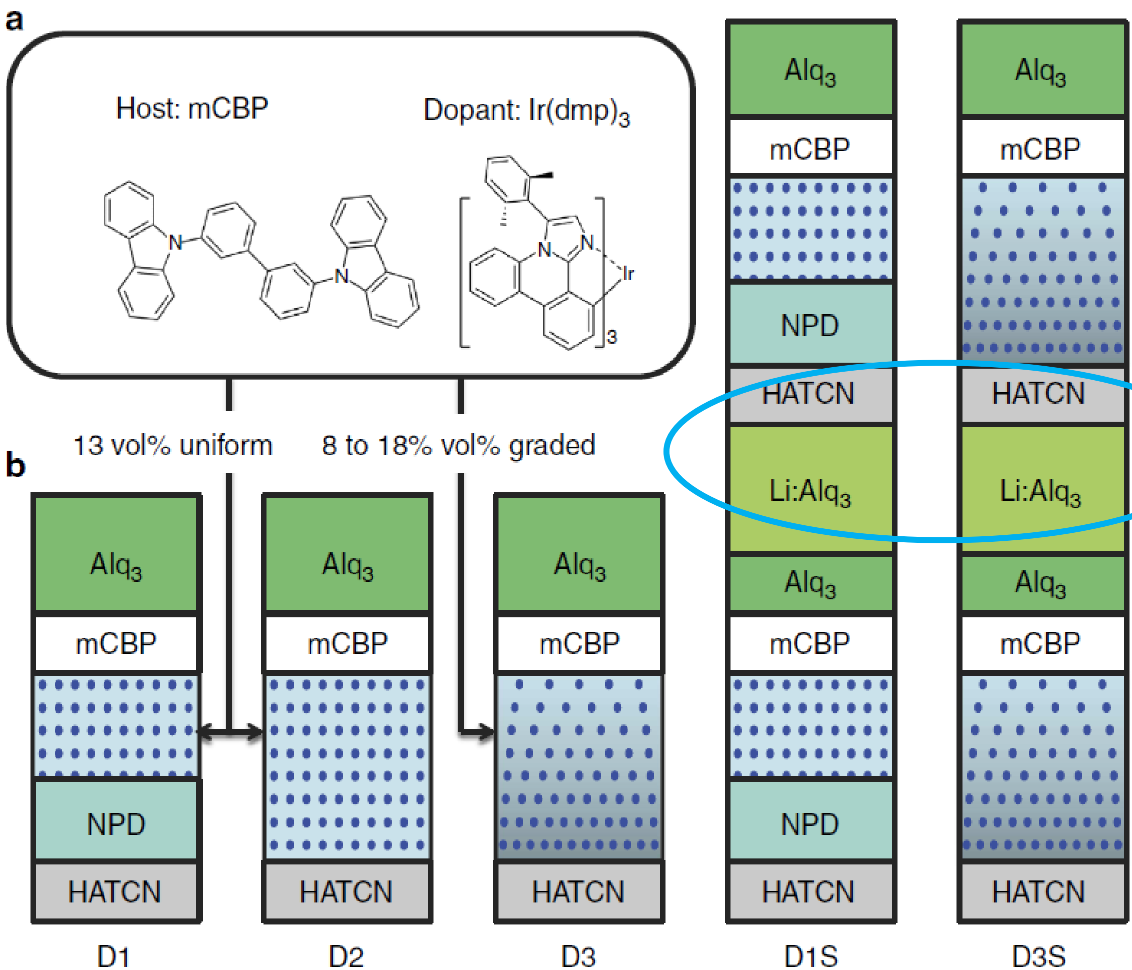

$T_1 + P^- \rightarrow S_0 + P_n^-$

Exciton-Polaron Annihilation

N.C. Giebink, *et. al, J. Appl. Phys.* (2008)

# Spreading the recombination zone: Dopant/Host Grading

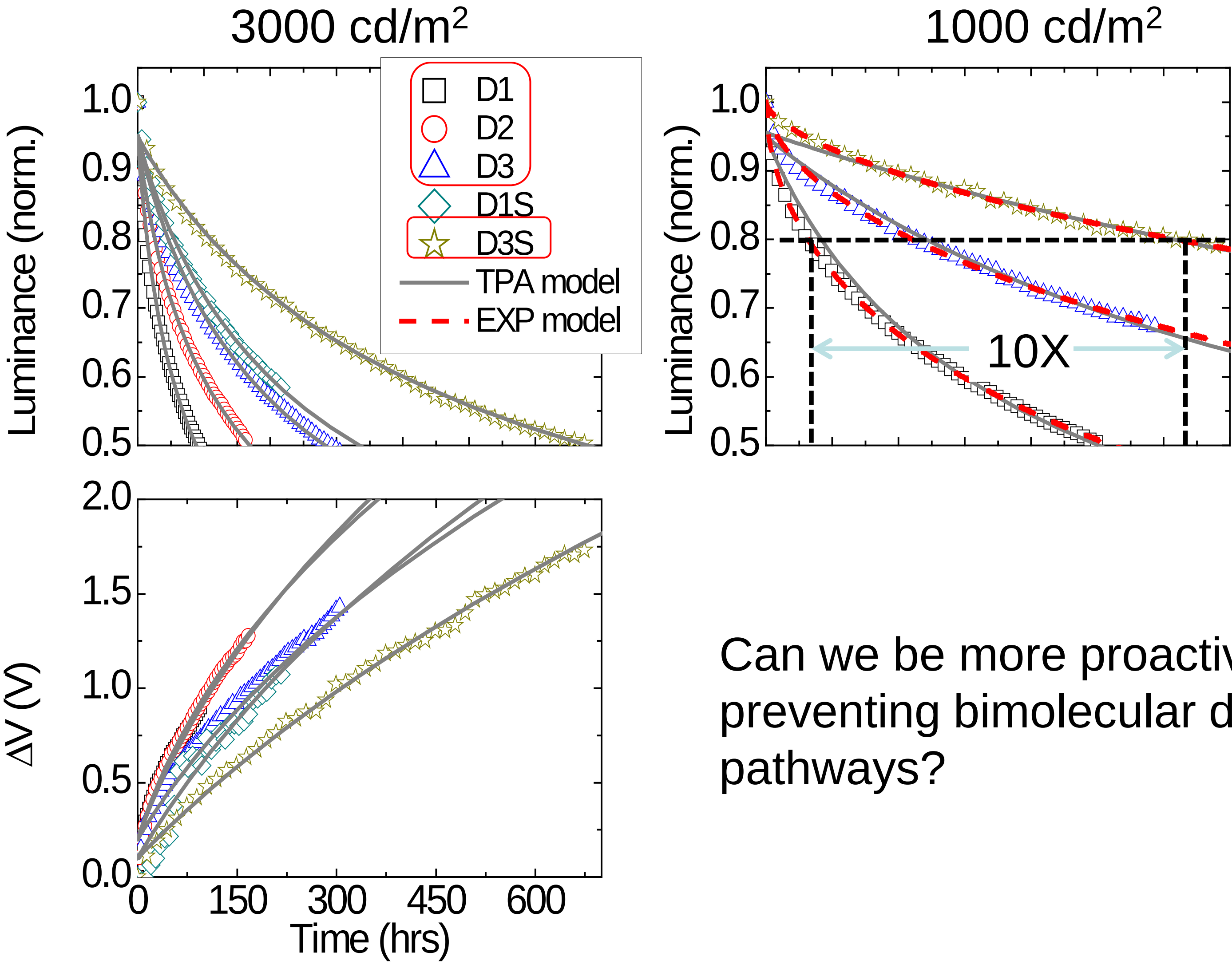
$$Rate_{annhilation} = k[T_1][T_1,P^-]$$




Stacked devices reduce the current in each PHOLED by 2X

Y. Zhang, et al., *Nature Comm.* (2014), DOI: 10.1038/ncomms6008

# Grading: 10 X Lifetime Improvement Over Standard

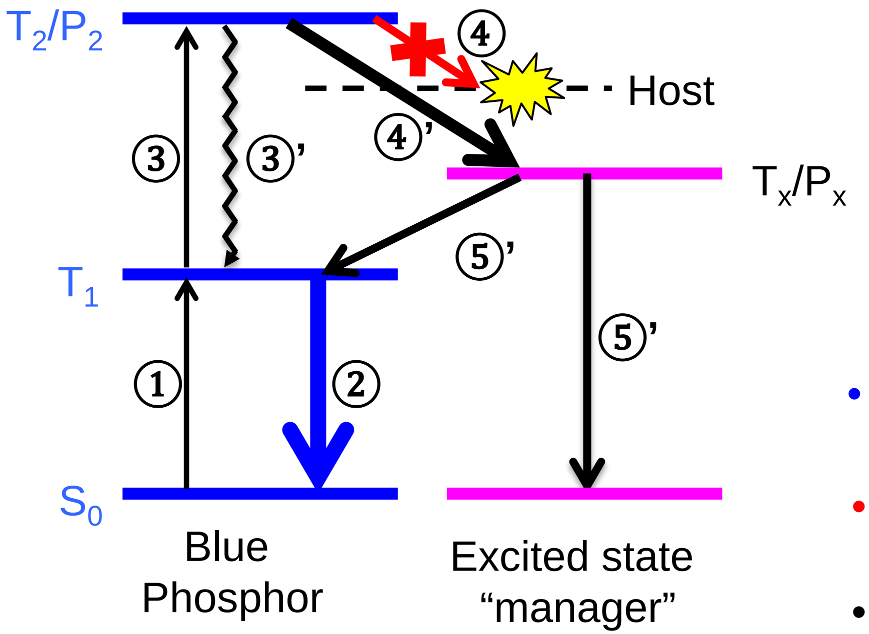



Can we be more proactive about preventing bimolecular decay pathways?

USC

Y. Zhang, et al., *Nature Comm.* (2014), DOI: 10.1038/ncomms6008

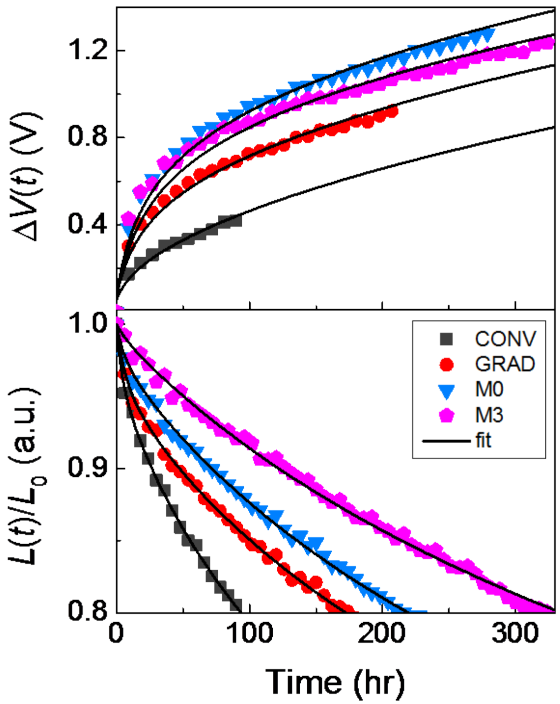
# The Problem of TTA or TPA

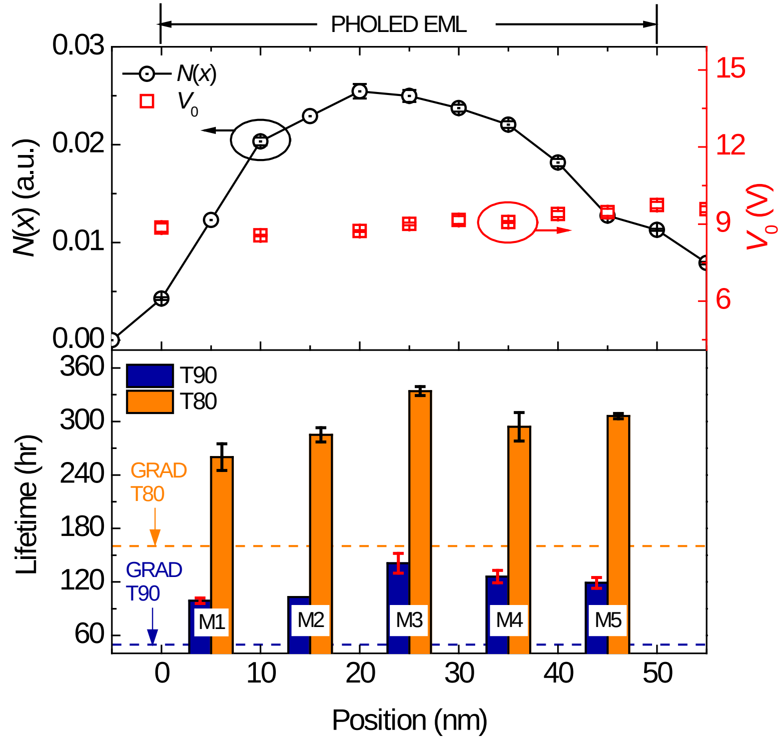



① Electrical excitation
② Blue Emission
③ TTA / TPA
③' Vibronic relaxation
④ Dissociative reaction (Bond cleavage)
④' High energy particle management
⑤' Non-radiative/radiative decay

- Desirable blue emission
  ① → ②
- Dissociative reaction (degradation)
  ① → ③ → ④
- **High-energy states management**
  ① → ③ → ④' → ⑤'

- To increase lifetime: decrease bimolecular collisions/processes
  - Lower [exciton] and [polaron], but this increases voltage
- Grading is good, but how do we improve on it?
  - New, more stable blue phosphors and host materials (on going)
  - Relax the hot-polaron before it decays (managers)

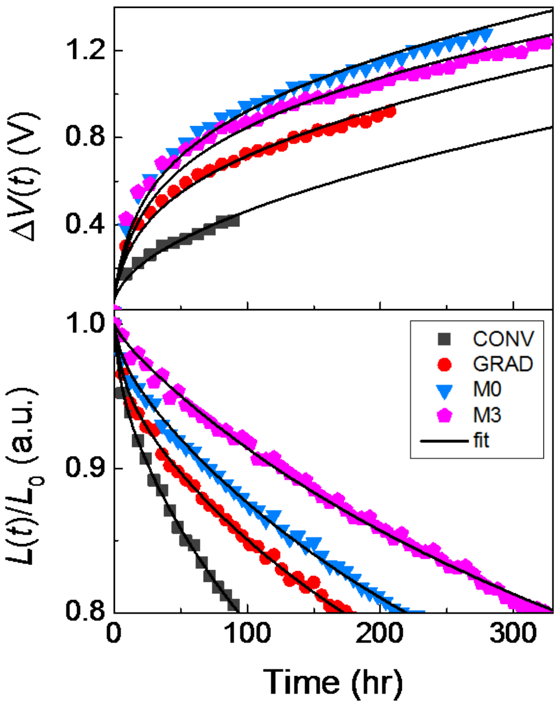


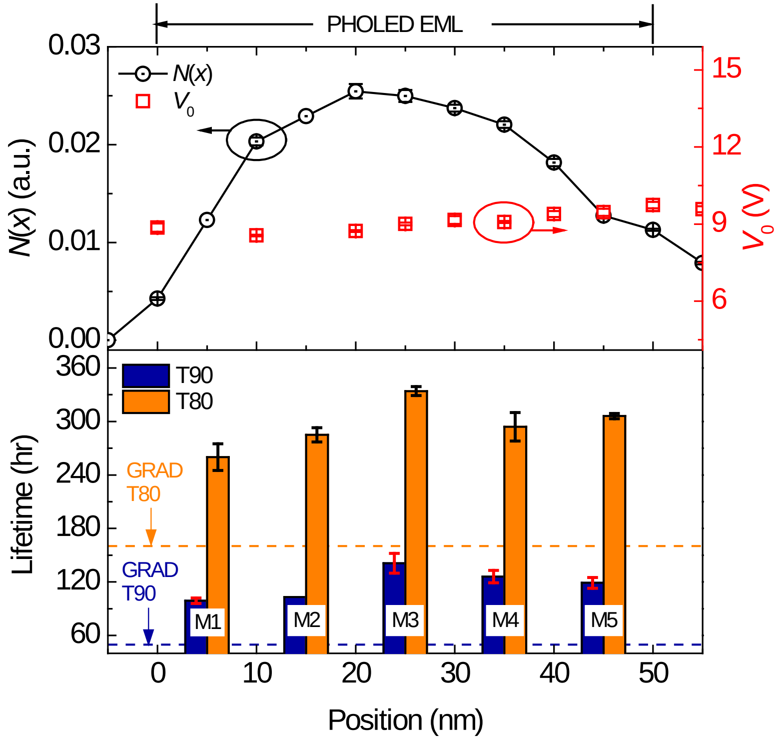




## Blue PHOLED measured at initial luminance of 1,000 cd/m²

| Device | Driving J [mA/cm²] | EQE [%] | LT80 [hr] | ΔV [V] | CIE @5 mA/cm² |
|---|---|---|---|---|---|
| CONV | 6.7±0.1 | 8.0 | 93±9 | 0.4±0.1 | [0.15,0.28] |
| GRAD | 5.7±0.1 | 8.9 | 173±3 (+86%) | 0.9±0.1 | [0.16,0.30] |
| M3 | 5.3±0.1 | 9.0 | 334±5 (+260%) | 1.5±0.2 | [0.16,0.30] |

USC




Need lots of new stuff to extend lifetime:

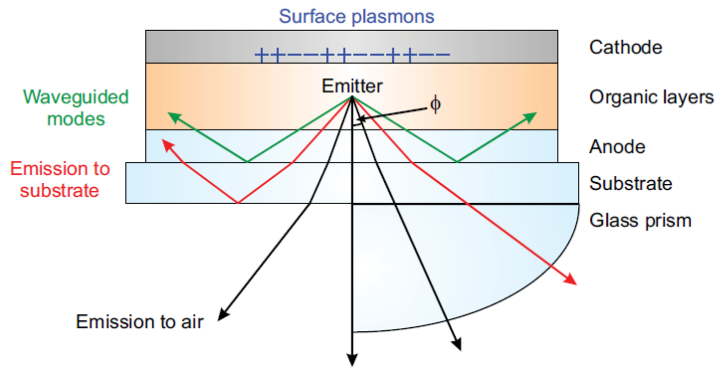
- Stable emitters, hosts, blockers, transporters
- Managers to help protect the hosts and emitters
- New device structure ideas to maximize external efficiency

# Phosphorescent OLED Efficiency:

$$\Phi_{EL} = \Phi_{PL}\chi\eta_r\eta_e$$

| | |
|---|---|
| $\Phi_{EL/PL}$ | luminescent quantum efficiencies |
| $\chi$ | fraction of usable excitons |
| $\eta_r$ | carrier recombination efficiency |
| $\eta_e$ | out coupling efficiency |

- Good devices: $\Phi_{PL}$, $\chi$, $\eta_r \rightarrow 1$
– **$\Phi_{EL}$ limited by $\eta_e$:**
– $\eta_e \uparrow$ $mA/cm^2 \downarrow$ lifetime $\uparrow$

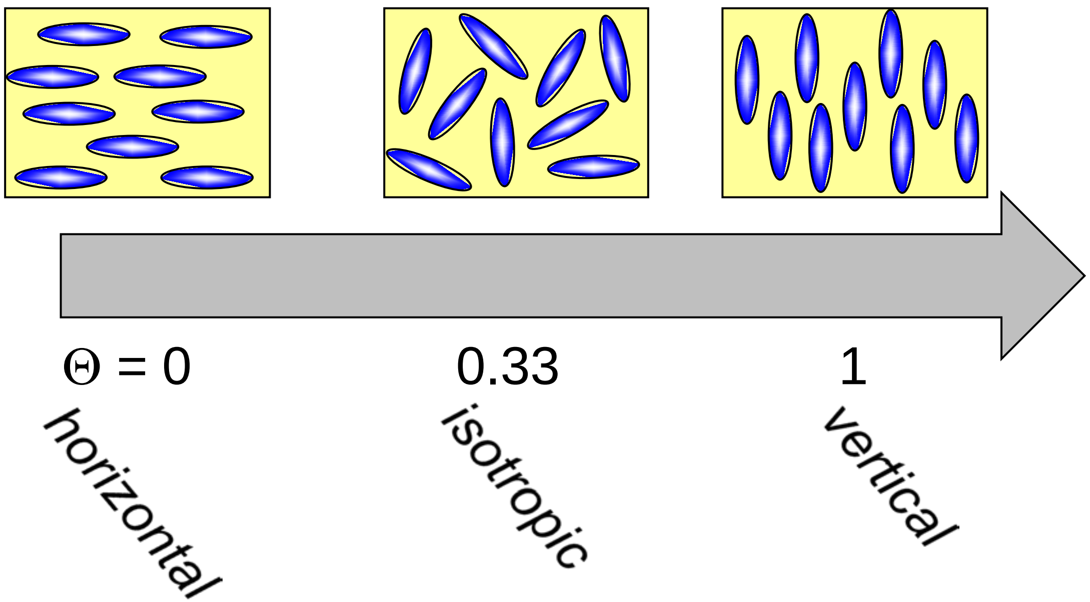


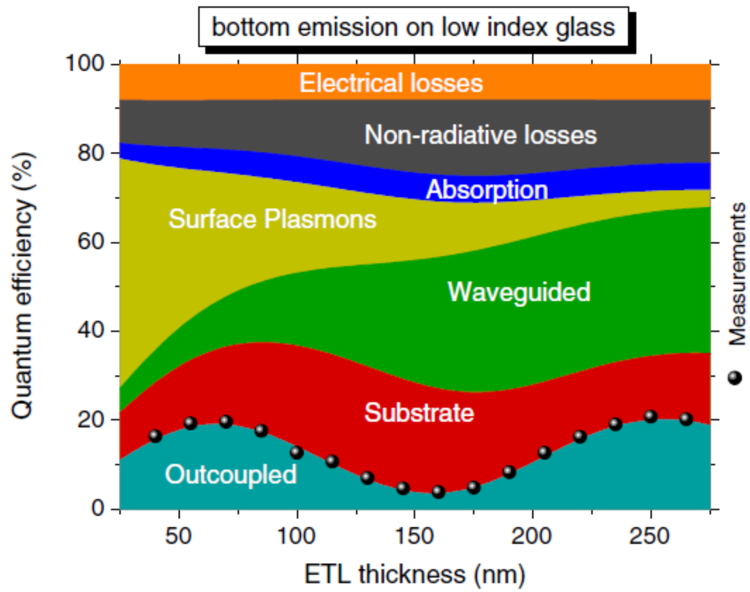
# Non-Isotropic Emitter Orientation

Consider the orientation of the transition dipole relative to the substrate.

- Anisotropy factor:

$$\Theta = \frac{p_z}{p_x + p_y + p_z} = \frac{p_\perp}{p_{||} + p_\perp}$$



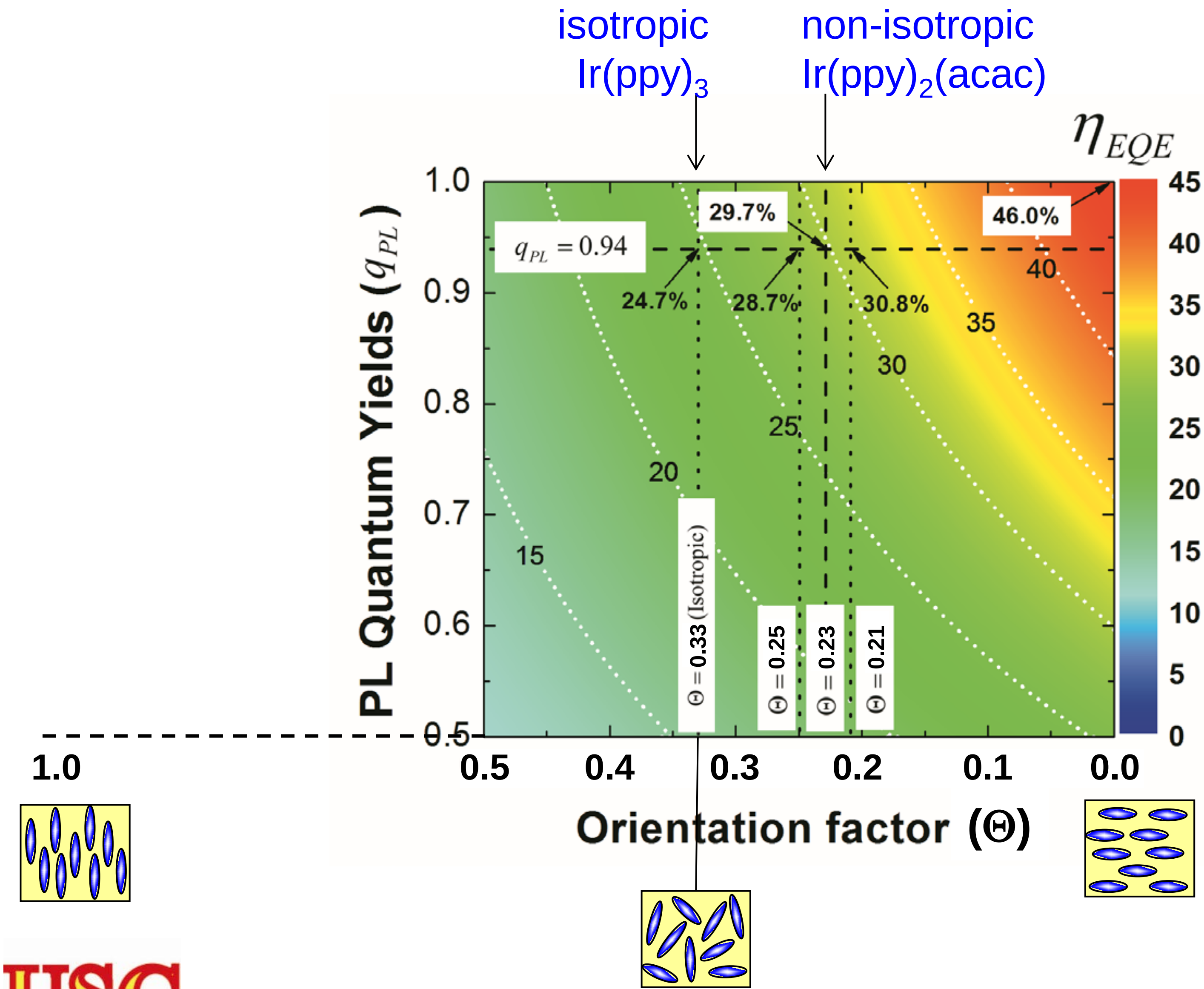




$p_z$ strongly couples to plasmon modes, $p_X$ and $p_Y$ do not couple to plasmon modes

USC

T.D. Schmidt *et al.*, Appl. Phys. Lett. **99**, 163302 (2011)

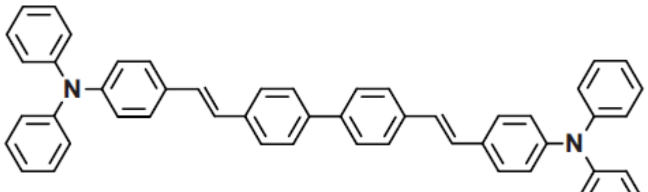
# Orientation and EQE




S.-Y. Kim *et al.*, Adv. Funct. Mater. **2013**, *23* 3896

# Alignment of emitters in doped films

- Linear fluorescent molecules

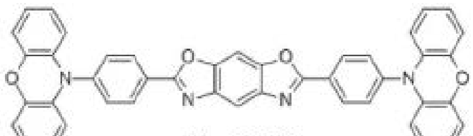



BDASBi

in CBP, Θ = 0.09

W. Bruetting, *et. al, APL* (2010)

- TADF emitters

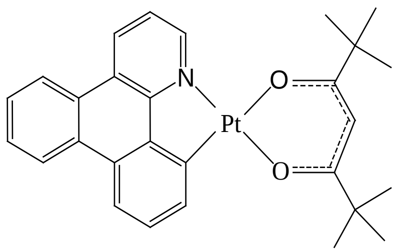



*Cis*-BOX2

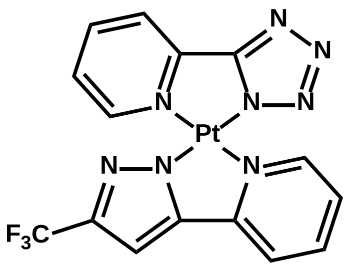
in CBP, Θ < 0.05, $\eta_{EXT}$ = 33%

C. Adachi, *et. al, APL* (2016)

- Square planar platinum complexes

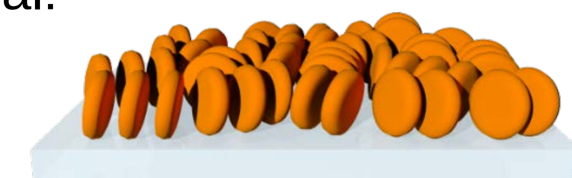



Θ = 0.59




Θ = 0.67

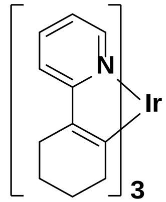
Vertical!

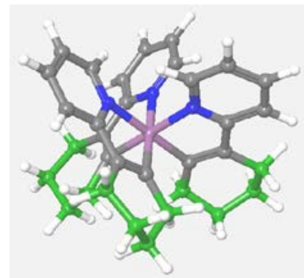


S.R Forrest and J. Kim, Univ. Mich. (2016)

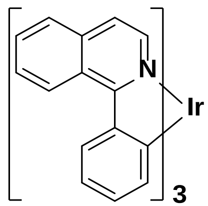
# Oriented Emitters: tris-ligand Ir based emitters

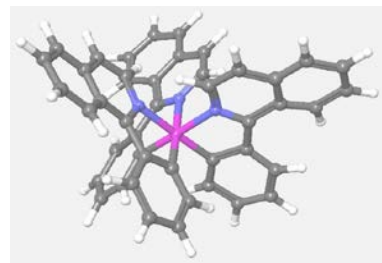
| Emitter | Host | Orientation (% vertical) |
|---|---|---|
| $Ir(dhfpy)_2(acac)$ | NPD | 25% |
| $Ir(ppy)_2(acac)$ | CBP | 23% |
| | CBP | 23% |
| | TCTA/ B3PYMPM | 24% |
| | TCTA/ B3PYMPM | 23% |
| $Ir(ppy)_2(tmd)$ | TCTA/ B3PYMPM | 22% |
| $Ir(MDQ)_2(acac)$ | NPD | 24% |
| | NPD/ B3PYMPM | 20% |
| | NPD | 24% |
| $Ir(bt)_2(acac)$ | BPhen | 22% |
| $Ir(chpy)_3$ | NPD | 23% |
| $Ir(mphmq)_2(tmd)$ | NPD/ B3PYMPM | 18% |
| $Ir(mphq)_2(acac)$ | NPD/ B3PYMPM | 23% |
| $Ir(phq)_3$ | NPD/ B3PYMPM | 30% |
| *$Ir(piq)_3$* | *NPD* | *22%* |
| $Ir(bppo)_2(acac)$ | CBP | 22% |
| $Ir(ppy)_3$ | CBP | 31% |
| | CBP | 33% |



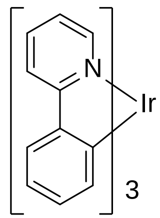


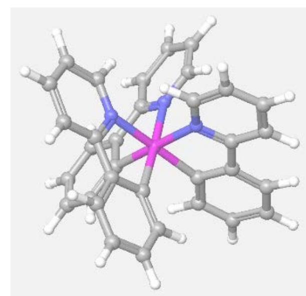
$Ir(chpy)_3$





$Ir(piq)_3$



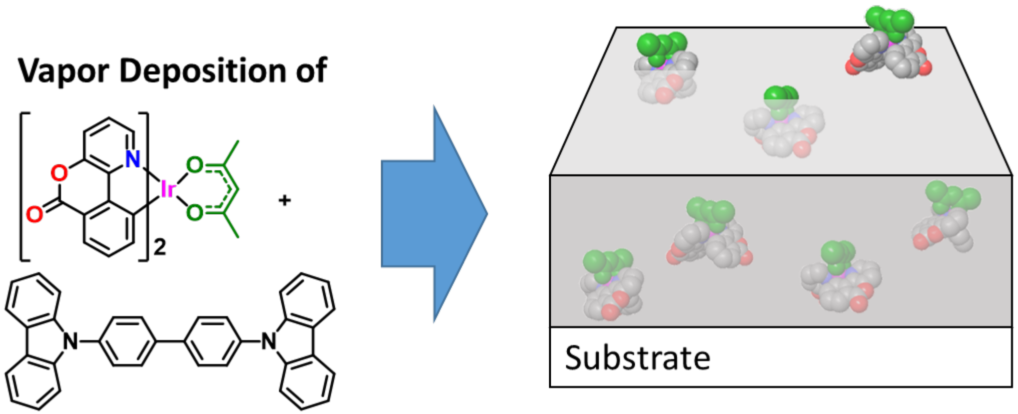


$Ir(ppy)_3$

Graf, A. *et al.*, *J. Mater. Chem. C*, **2014,** *2*, 10298-10304

# Why do dopant align in an isotropic matrix?

- ~~Electrostatic interactions between host and guest~~
- ~~Dopant aggregations induced by high dopant dipole moment~~
- Vacuum/Organic boundary induces molecular orientation with aliphatic (acac) groups directed toward vacuum.




- Chemical anisotropy can drive alignment
- Near horizontal alignment is possible for linear molecules
- Can we achieve the same high degree of alignment for high performance Ir based phosphors?

USC

M.J. Jurow, *et al.*, *Nat. Mater.*, **2015**, doi:10.1038/nmat4428