Electrophosphorescent Organic LEDs

Introduction to OLEDs

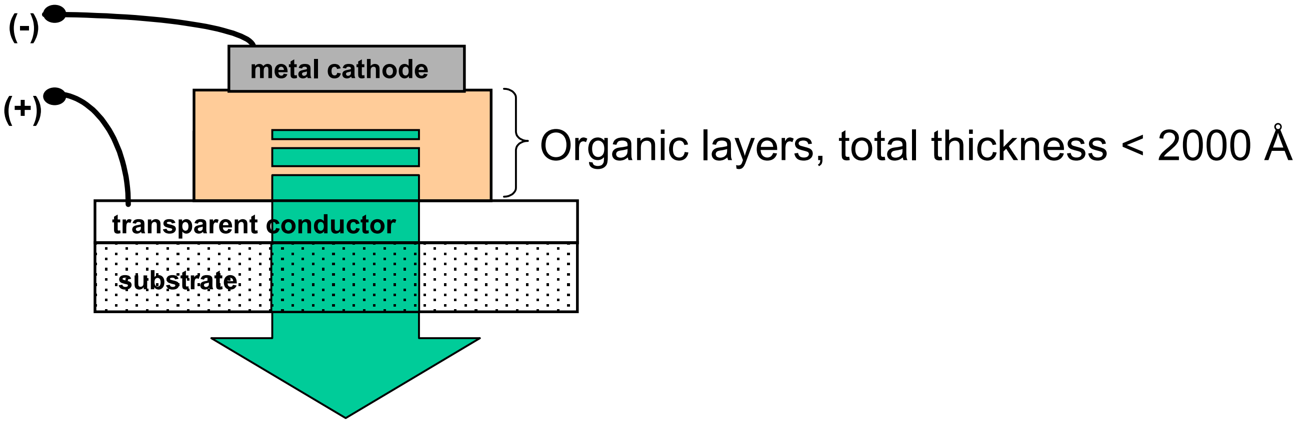
Designing Efficient OLEDs: toward 100% internal efficiency

- Utilizing triplets: phosphorescence and confinement
- Optimizing recombination and emission processes

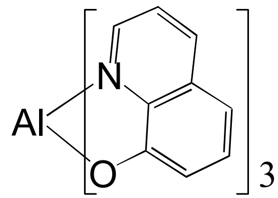
Color Tuning

- Ligand tuning of emission colors
- Efficient electroluminescence from Ir based phosphors, Green $\rightarrow$ Red
- Blue phosphorescence

First Efficient OLEDs

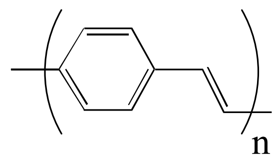


- First efficient LED with a molecular organic emissive layer reported by Tang and VanSlyke, *Apl. Phys. Let.*, **1987**, emitter = **Alq_3**.



= Alq_3

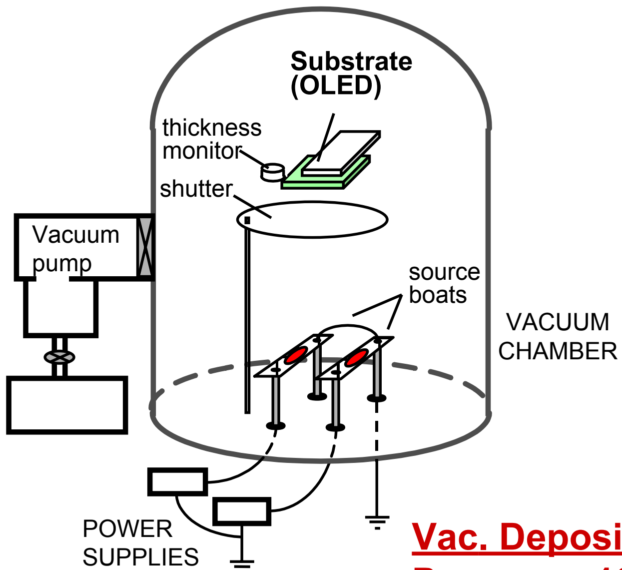
- First report of an LED fabricated with a polymeric emissive layer reported by Friend, *et. al.*, *Nature*, **1990,** emitter = **PPV**.



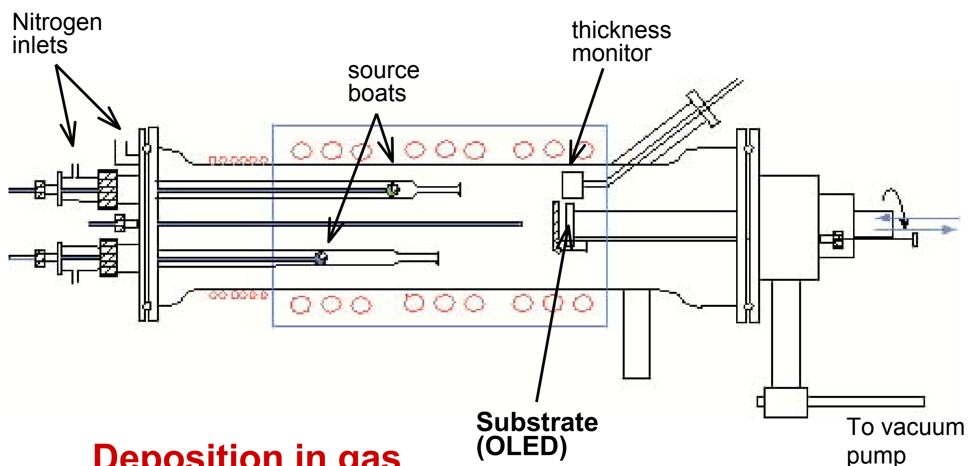
= PPV

Organic thin film deposition methods

- Methods are inexpensive and most can be scaled to reasonably large areas (1 ft^2)
- Small molecule layers
  - Vacuum deposition – used for both organic thin films and metal electrodes
  - Organic vapor phase deposition (OVPD) - good control over film thickness and composition
    see V. Adamovich, ORGN poster # 335
  - Solution processing – spin coating, simple but not readily scalable to large areas
- Polymeric thin films
  - Solution process (spin coating) is the most common
  - CVD – scalable, but the quality of polymer layers is typically very low
  - OVPD – useful for low molecular weight polymers (potentially up to 10,000 g/mol; 5,000 demonstrated)

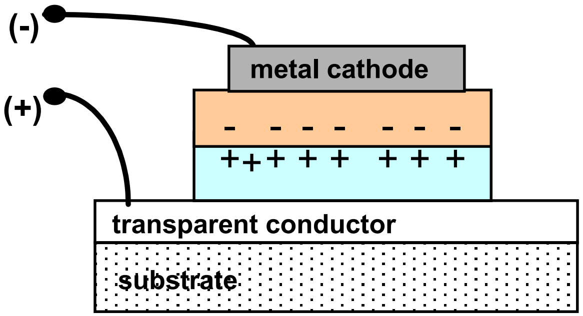


Vac. Deposition
Pressure: 10^{-6} Torr



Deposition in gas flow (OVPD)
Pressure: 1 Torr

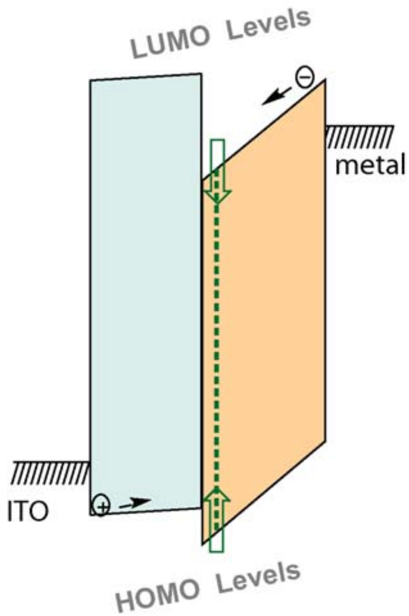
Carrier Balance (heterostructure)



- Tang and VanSlyke device had two organic layers
  - one hole transporting and other electron transporting

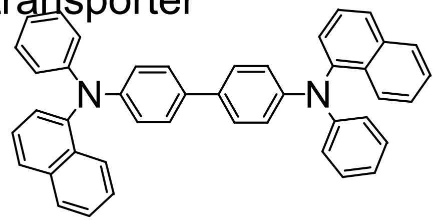
- Hole is typically more mobile than electron

$\mu(+) \approx 10^{-3}$ cm^2/V-sec, $\mu(-) \approx 10^{-(4\text{-}5)}$ cm^2/V-sec.



= hole transporter

e.g.

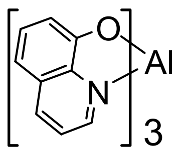


(NPD)

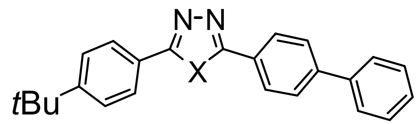
- readilly oxidized to give cation radical (hole state)
- **see Ren, Inorg. Poster # 495**

= electron transporter

e.g.



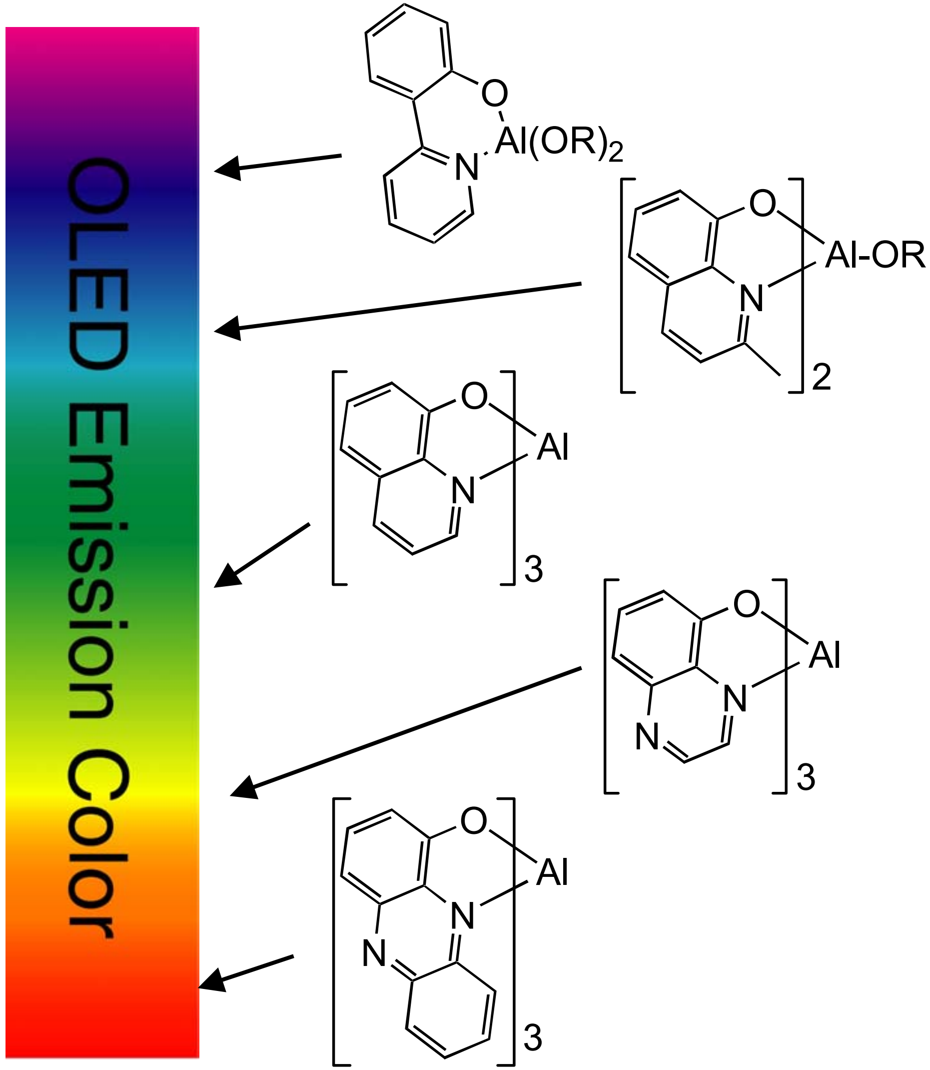
or

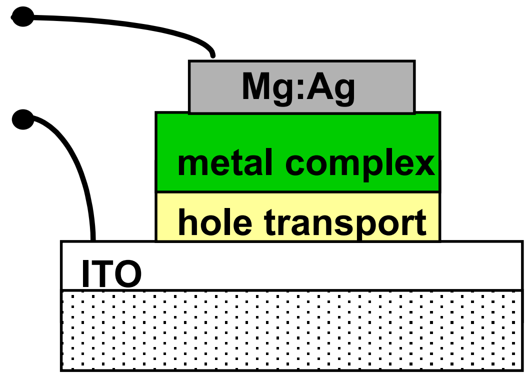


X = O, NR

- form stable anion radicals in the solid state

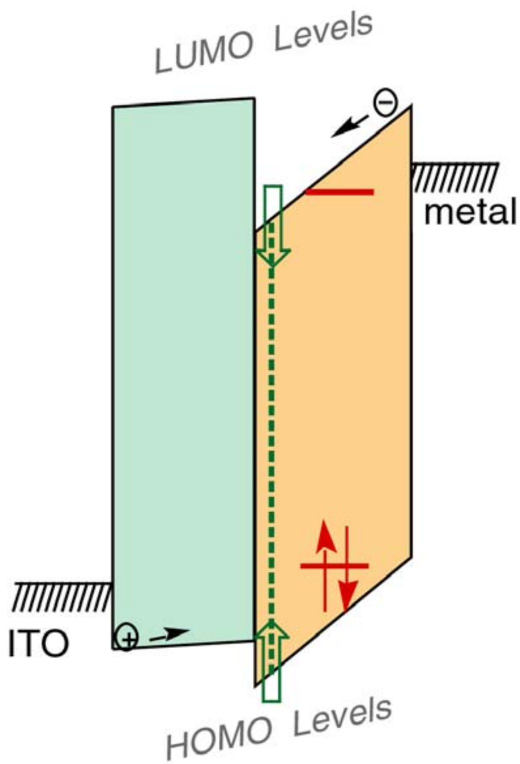
ITO/hole-transporter/metal complex/Mg-Ag OLED Emission





- Emission exclusively from metal complex, leading to efficient color tuning
- Emission lines are broad, typically > 100 nm FWHM
- OLED efficiency is only good for Alq_3 based device
  - poor I-V characteristics
  - poor luminescence eff.

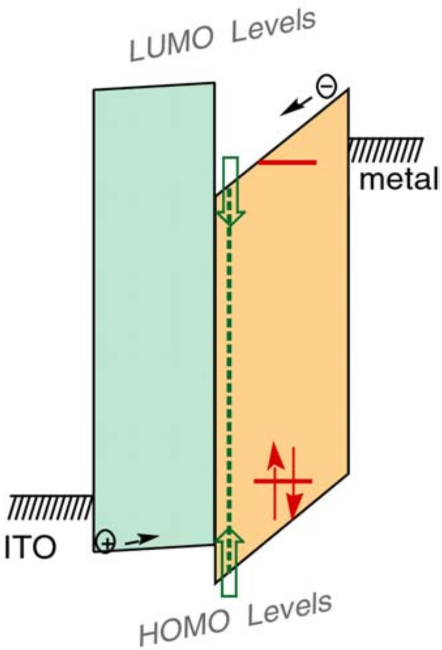
Dye doping to tune colors in OLEDs



- Color tuned by the dye
- Enhanced efficiency and narrower lines
- Efficient energy transfer to dye requires good overlap of ETL emission and dye absorption spectra
- Energy transfer typically by Förster mechanism
- First report: Tang & Van Slyke, *J. Appl. Phys.* (1989)

OLED Efficiency

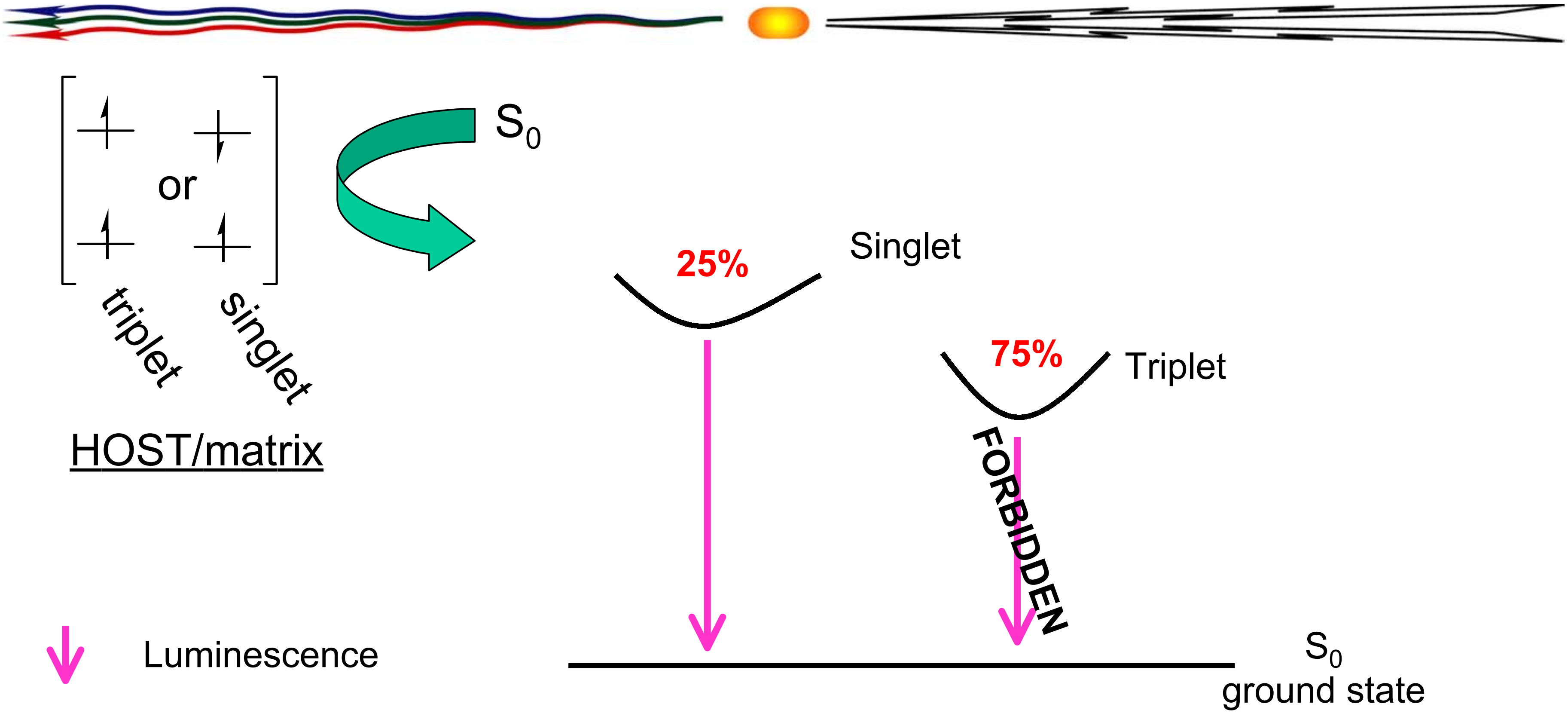
$$\Phi_{el} = \Phi_{pl}\chi\eta_r\eta_t\eta_e$$



$\Phi_{el/pl}$	electroluminescent / photoluminescent quantum efficiencies
χ	fraction of excitons that contribute to emission
η_r	recombination efficiency (hole + electron ⇒ exciton)
η_t	exciton transfer (host → dopant) efficiency
η_e	emission coupling efficiency out of device (typically 0.2) ⇒ shaped substrates can improve η_e to 0.5 (Gong Gu *et al.*, **1997**)

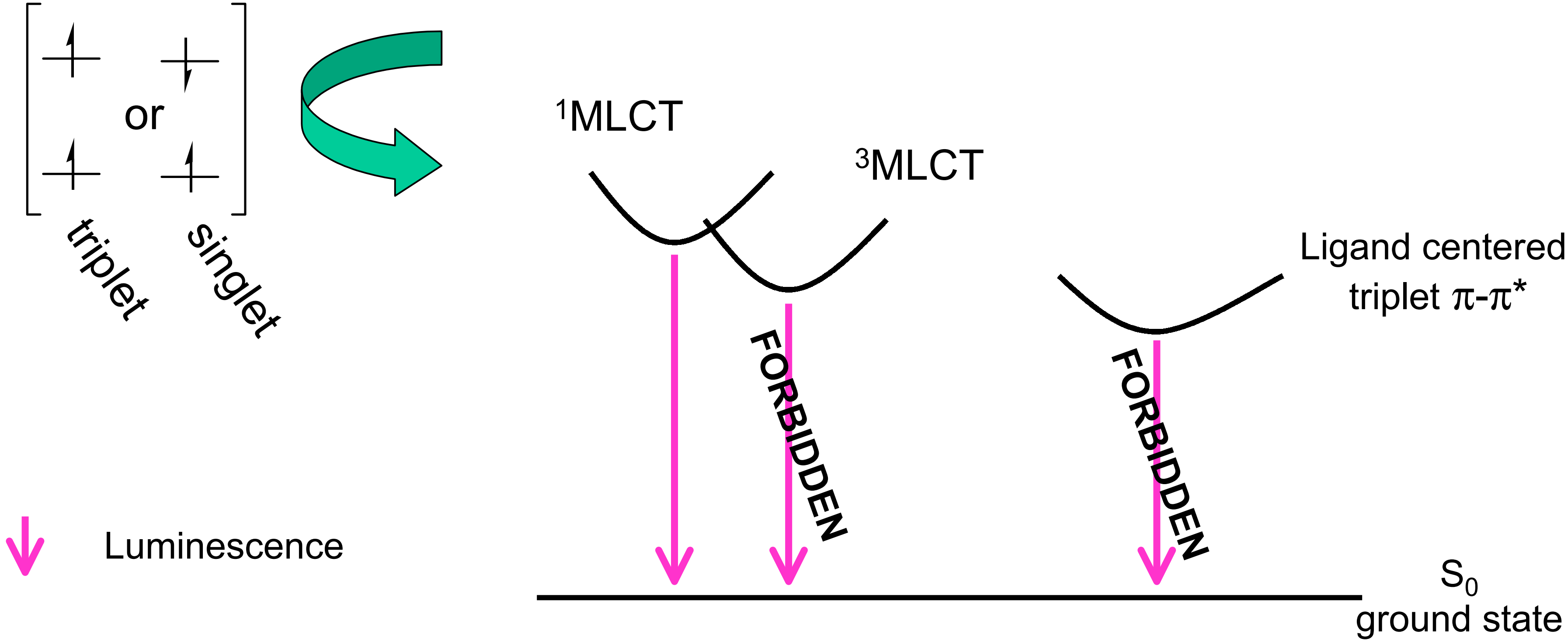
• Φ_{el} limited by $\chi \cdot \phi_{pl}$

Fluorescent dopant emission



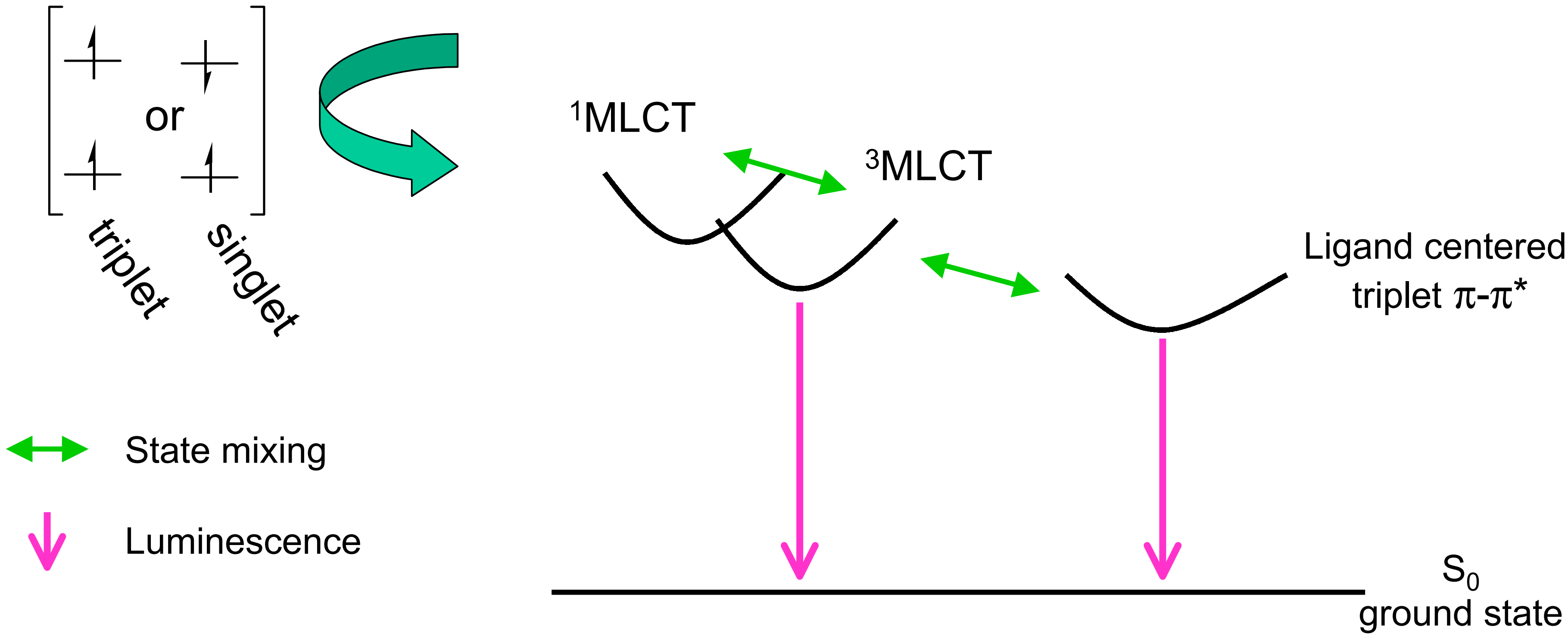
- Energy transfers from host/matrix excitonic states conserve spin.
- For typical fluorescent dopants, emission from triplet excited states is forbidden.
- Experimentally determined fraction = 22±3% singlets.
  M.A. Baldo, *et.al.*, *Phys. Rev. B* (1999)

MLCT emission



- MLCT = metal-to-ligand charge transfer
- Luminescence from ^{3}MLCT and $^3\pi$-π^* are formally forbidden transitions

Heavy metal facilitated triplet emission



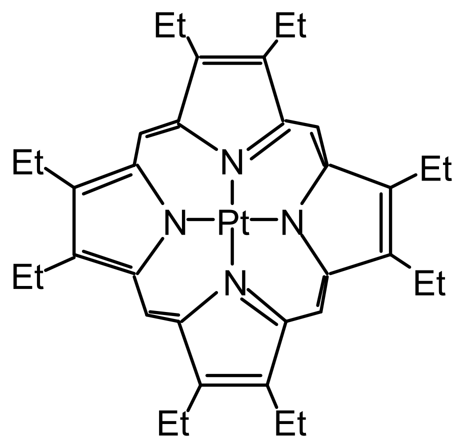
- Strong spin-orbit-coupling mixes singlet and triplet MLCT states, for M = Ir, Pt, Au, *etc.*
- Mixing of ligand centered and ^{3}MLCT states makes with ^{1}MLCT makes phosphorescence a largely allowed transition

Pt based phosphorescent dye/dopant

- Heavy atom (Pt) effects facilitate $S_1 \leftrightarrow T_1$ mixing, enhancing phosphorescence (radiative T_1 to S_0)

- Platinum octaethylporphine (PtOEP) is well suited to OLED doping
  - PL efficiency (phosphorescence) is **0.5** at 298 K (in polystyrene), t = 91 msec
  - PL efficiency **0.9** at 77K, t = 130 msec

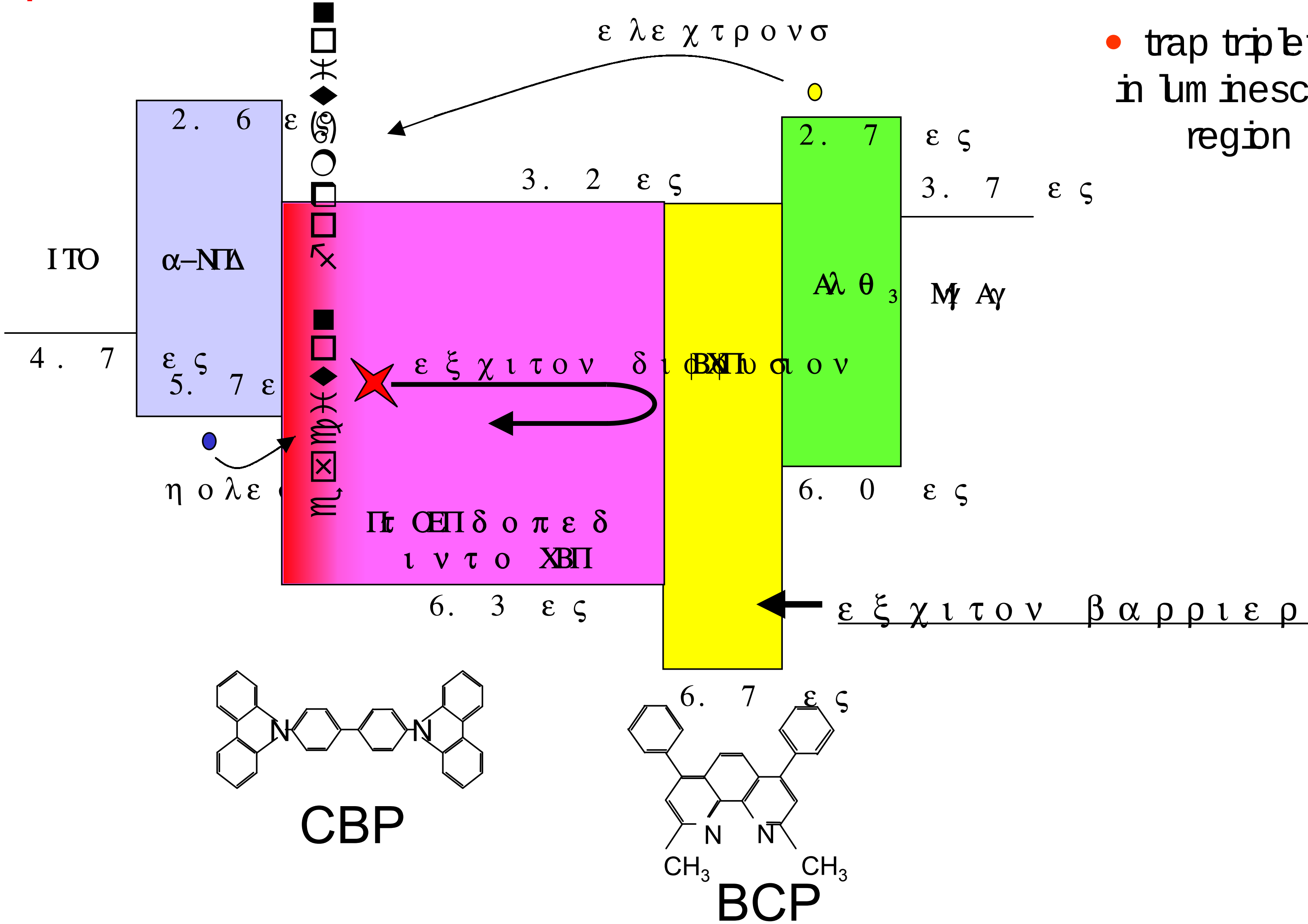
- Simple structure gives good efficiency (4 % external at low brightness), exclusive PtOEP <u>triplet</u> emission.
  - λ_{max} = 635 nm, FWHM = 35 nm



PtOEP

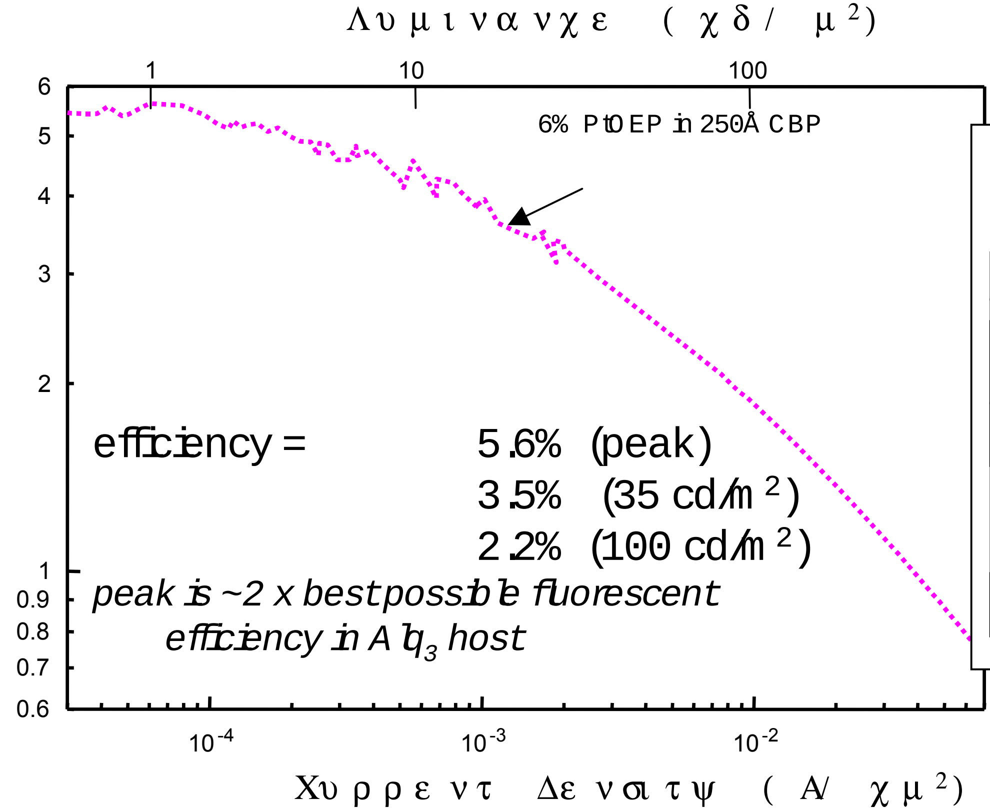
Electrophosphorescent device structure

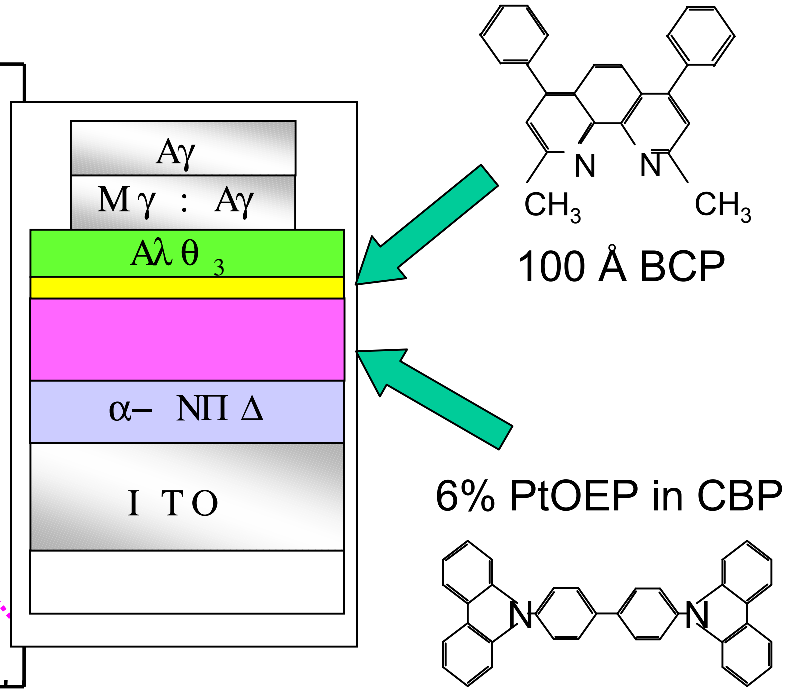
Triplet excitons can diffuse > 1500 Å



- trap triplets in luminescent region

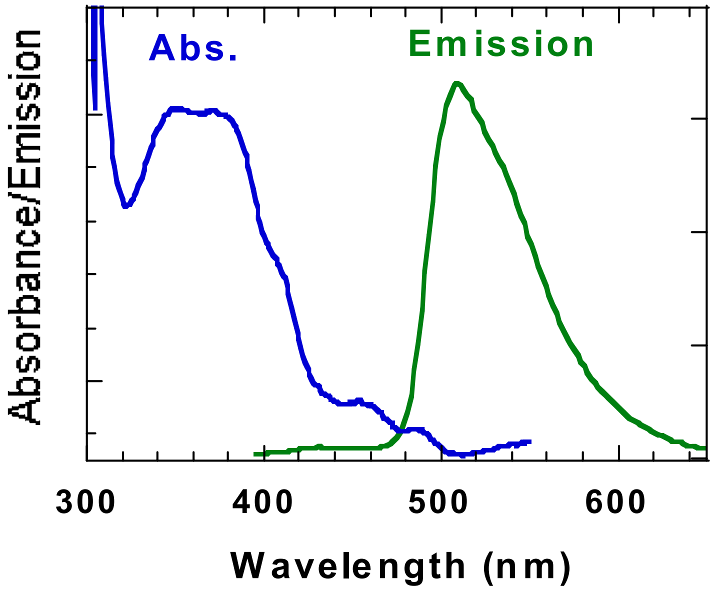
Quantum Efficiencies of PtOEP OLEDs with an Exciton Blocking Layer

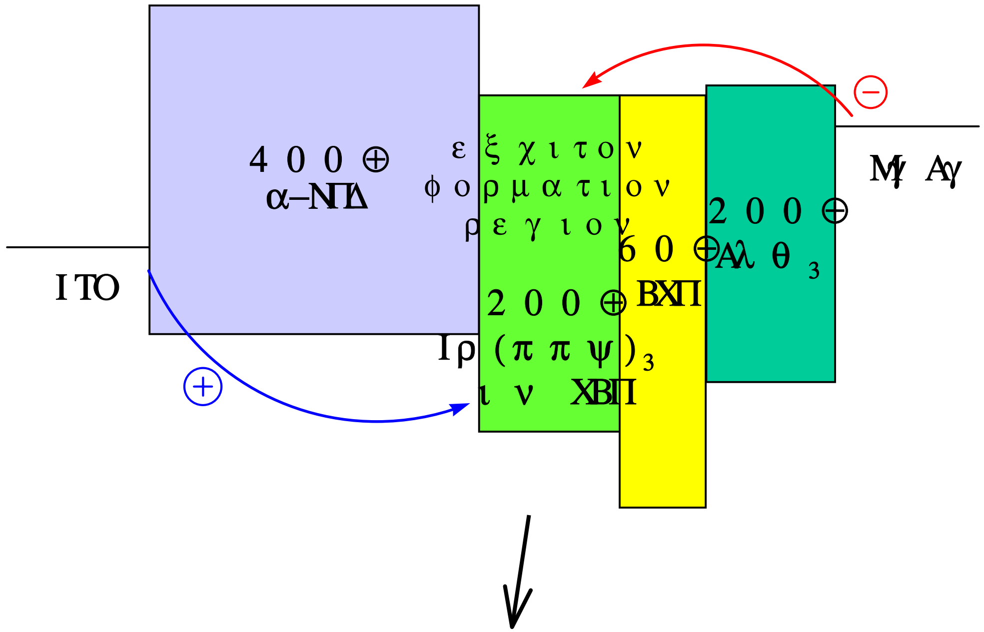


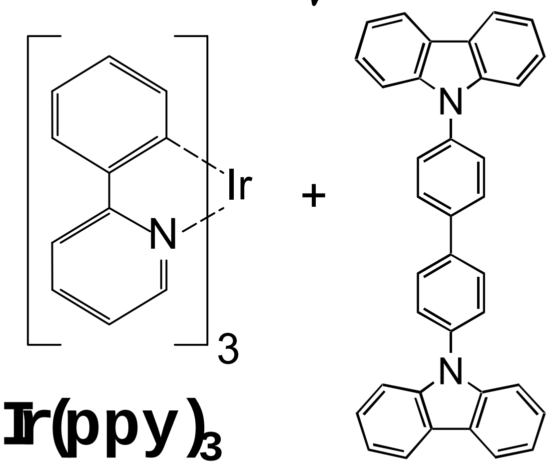


- Q.E. decay as current is increased is due to T-T annihilation
  - $T_1 + T_1 \rightarrow S_0 + S_1$, second order quenching process !!
  - decrease the effects of T-T annihilation by:
    - $\Rightarrow$ decrease [triplets], lower the doping level: phosphor saturation a problem
    - $\Rightarrow$ short triplet lifetime will decrease T-T annihilation

Organometallic Ir Phosphor





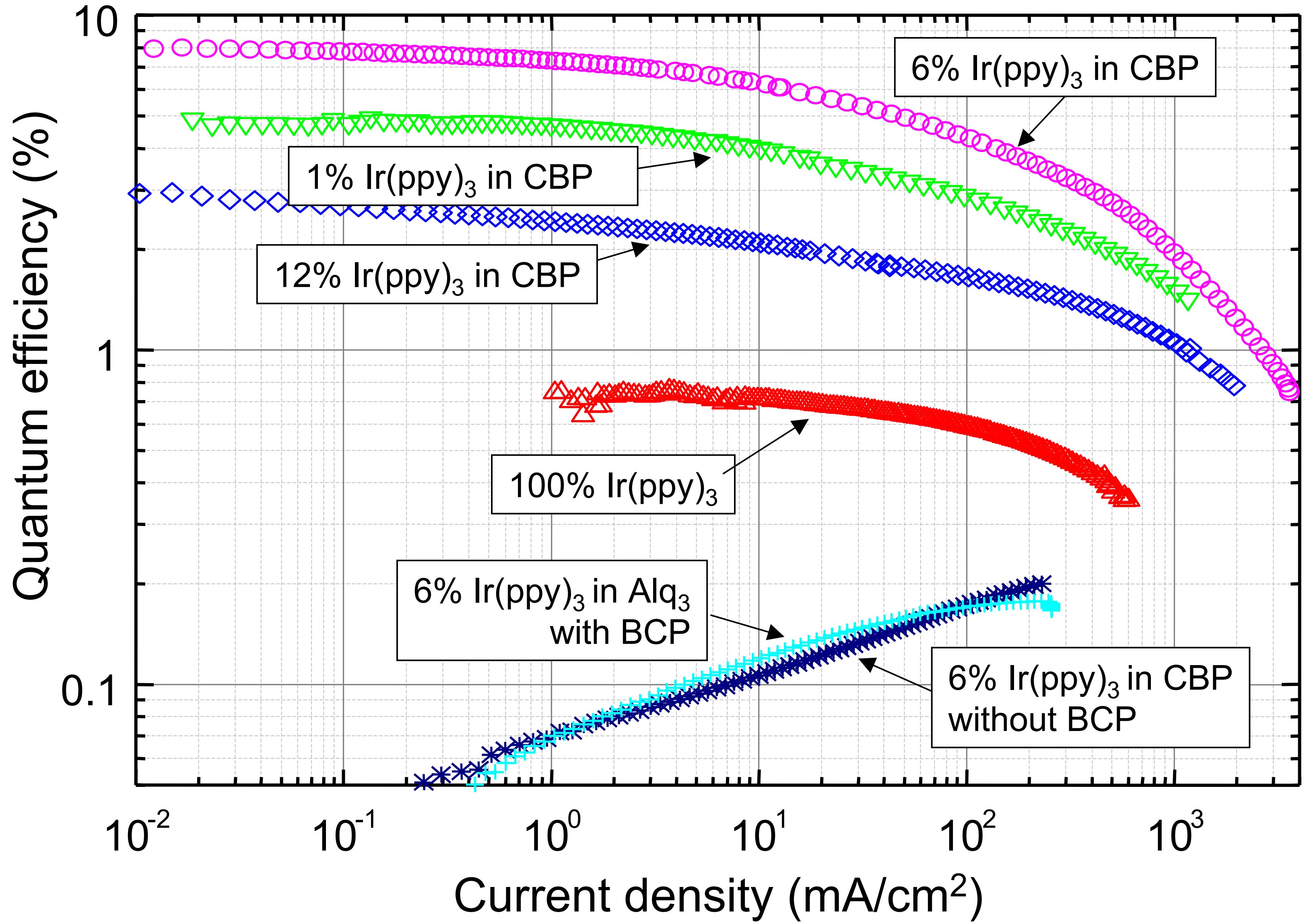


Ir(ppy)$_3$

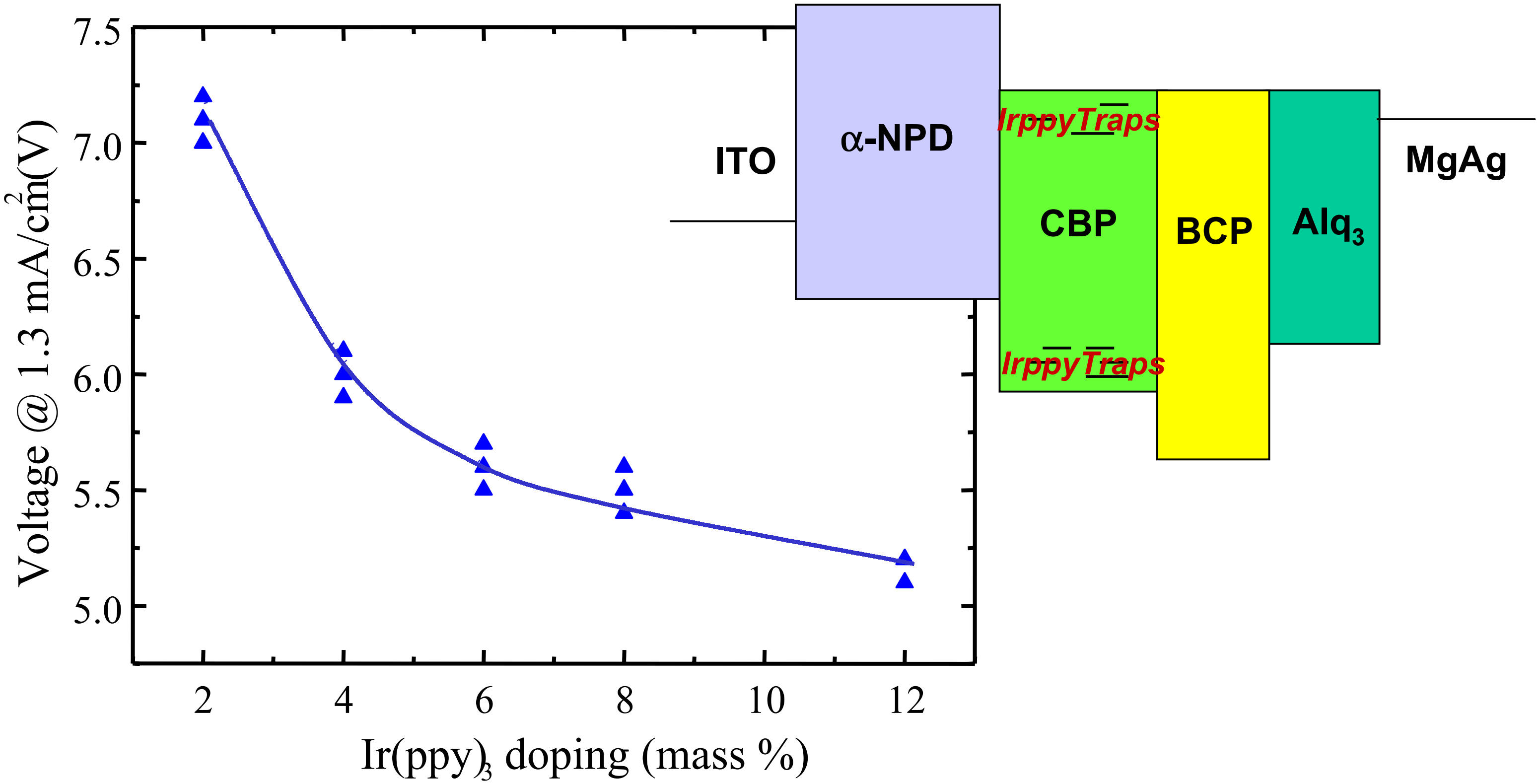
- **short lifetime: 500ns in CBP**
- no fluorescence observed, only phosphorescence
  Iridium ⇒ strong intersystem crossing
- R.J. Watts, *et. al*, *Inorg. Chem.* (1991)

See: M.A. Baldo, *et. al.*, *Apl. Phys. Lett.*, **1999**

External quantum efficiency of $Ir(ppy)_3$ in CBP



Conduction through $Ir(ppy)_3$ trap states



- Holes are efficiently carried by the $Ir(ppy)_3$ dopant at doping levels > 5%
- HOMO level for $Ir(ppy)_3$ is 300 mV above the CBP HOMO
- Hole-electron recombination at the $Ir(ppy)_3$ dopant occurs

Recombination at Dopants

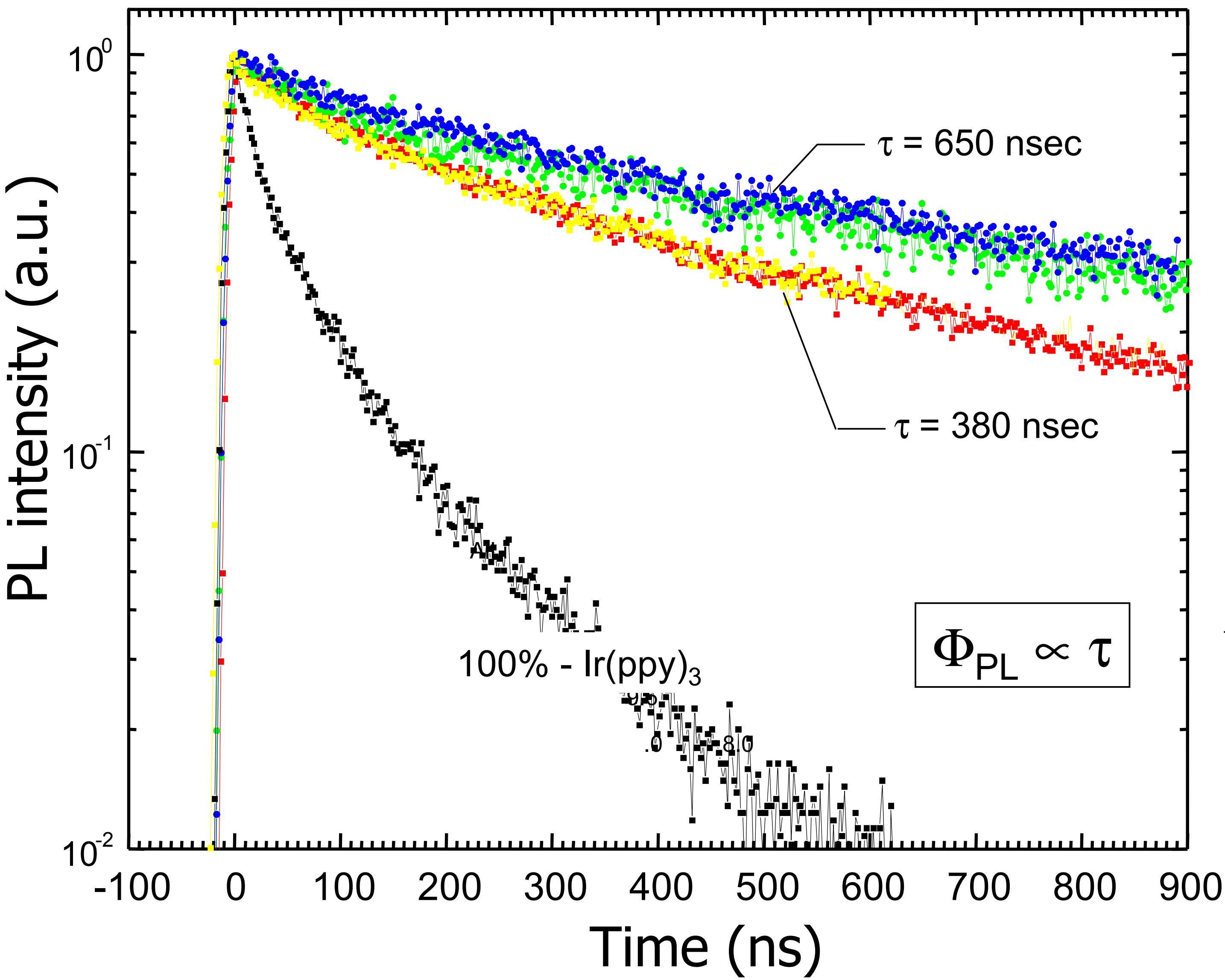
$$\Phi_{el} = \Phi_{pl}\chi\eta_r\eta_t\eta_e$$

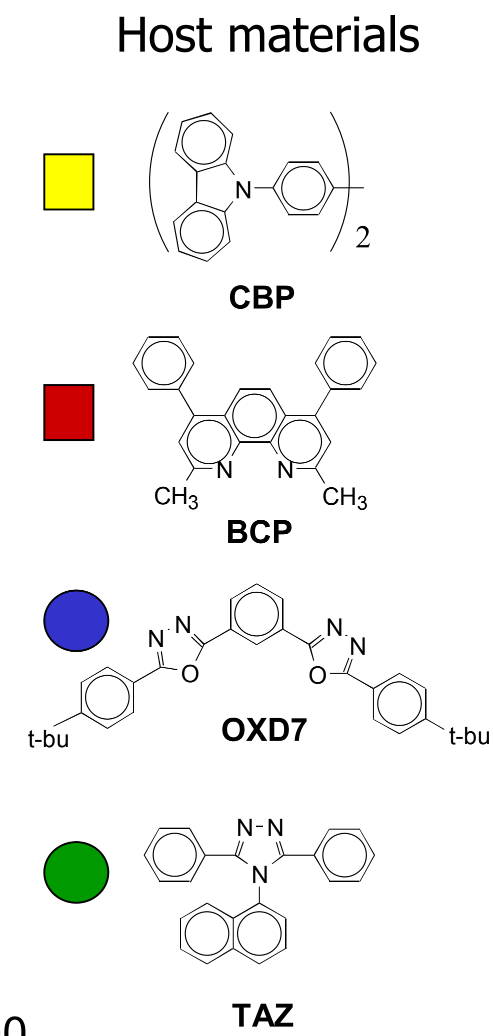
$\Phi_{el/ph}$	electroluminescent / phosphorescent quantum efficiencies
χ	fraction of excitons that contribute to emission, for phosphorescence $\chi = 1$
η_r	**recombination efficiency (hole + electron $\Rightarrow$ exciton)**
η_t	**exciton transfer (host $\rightarrow$ dopant) efficiency**
η_e	emission coupling efficiency out of device

η_r and η_t are combined into a single process: $\eta_r \bullet \eta_t \Rightarrow 1$

Φ_{el} is still limited by Φ_{pl}

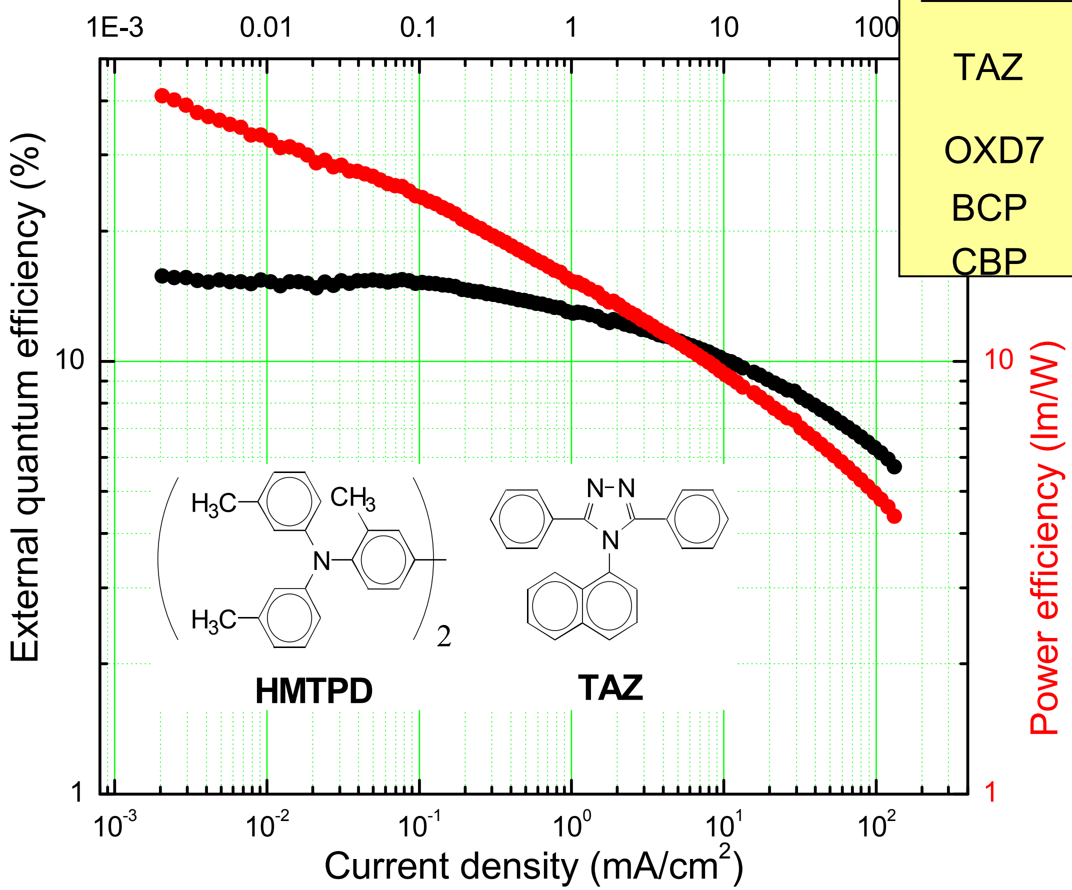
PL decay time of 7%-Ir(ppy)$_3$ doped hosts





ITO/HMTPD/7%-Ir(ppy)$_3$:TAZ/BCP/Alq/AlLi

Host	cathode	η_{ext} (%) at J (mA/cm^2) 0.1	1	10	100	τ (ns)
TAZ	AlLi	**15.4**	12.9	10.0	6.3	650± 35
	MgAg	**12.3**	11.9	9.7	5.8	
OXD7	MgAg	11.6	11.9	8.9	4.4	650± 35
BCP	MgAg	9.6	8.3	6.3	3.8	380± 20
CBP	MgAg	**9.0**	8.0	6.3	4.3	380± 20



ϕ_{PL} Irppy:TAZ > Irppy:CBP

η(internal) > 80%

Proper choice of both dopant and matrix/host are important for the best eff.

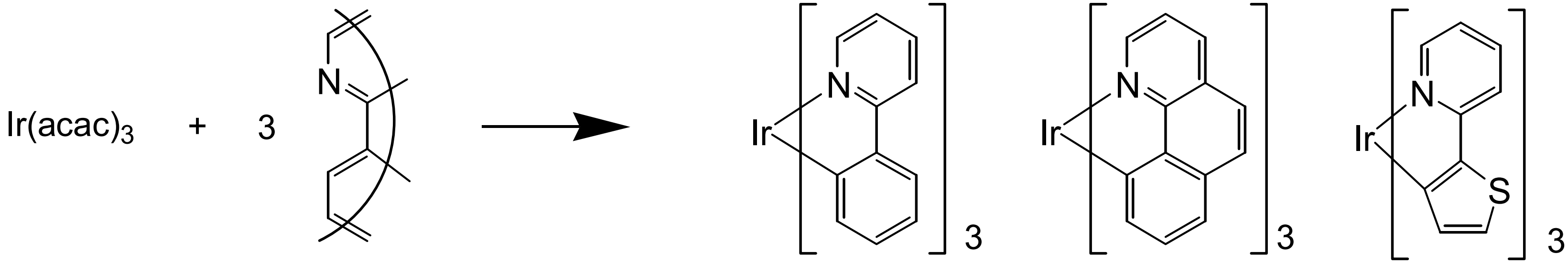
C. Adachi, *et. al.*, *Apl. Phys. Let.*, **2000**

Maximizing OLED efficiency

Parameters important in achieving high OLED external efficiency:

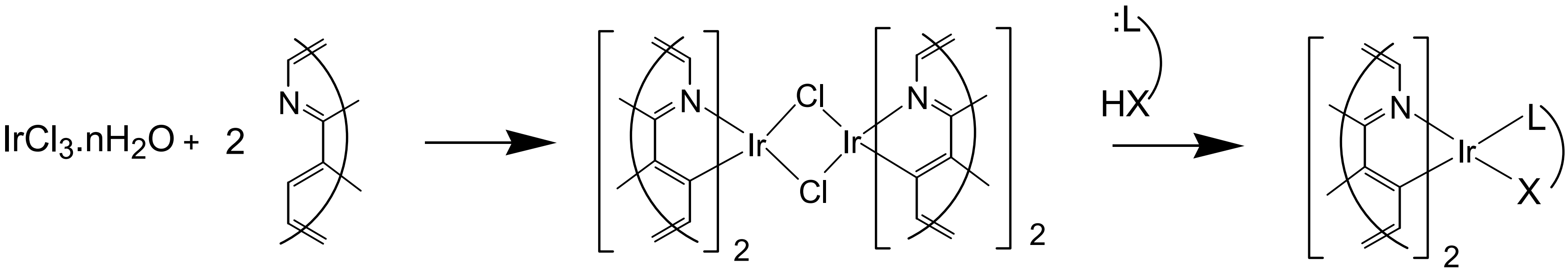
- Exciton Creation
  - Balanced carrier injection
  - Carrier trapping followed by +/- recombination is good, $\eta_r \eta_t \rightarrow 1$
- Exciton Relaxation
  - Confine excitons and carriers within the organic multilayer structure
  - Efficiently utilize excitons
    - Phosphorescence – collect and emit from triplets
    - Phosphor sensitized fluorescence
      triplet $\rightarrow$ singlet $\rightarrow$ emission
      M.A. Baldo, *et. al., Nature (2000)*
  - Design host/dopant to eliminate back energy transfer quenching

Synthesis of Cyclometallated Ir Complexes



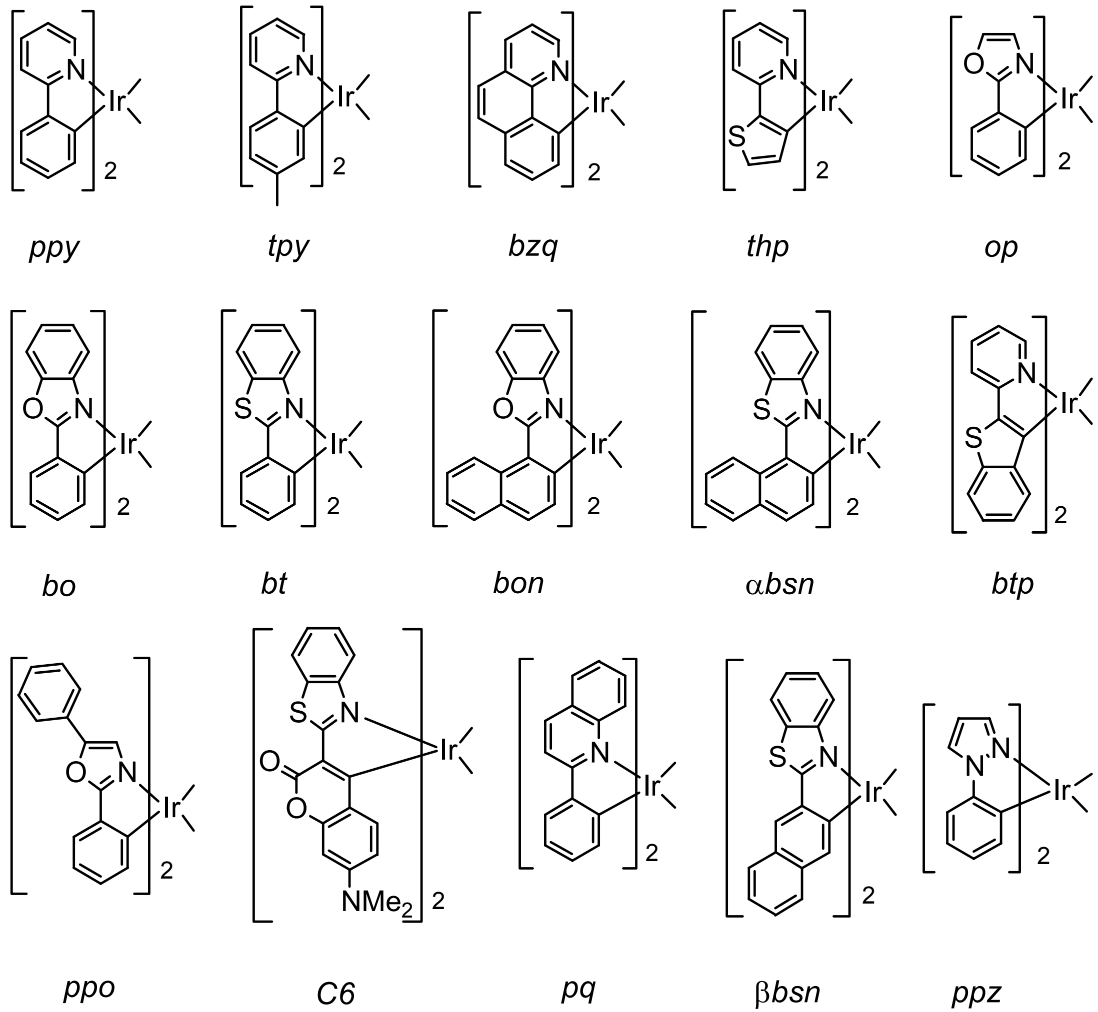
Ir(ppy)$_3$ **Ir(bq)$_3$** **Ir(thpy)3**

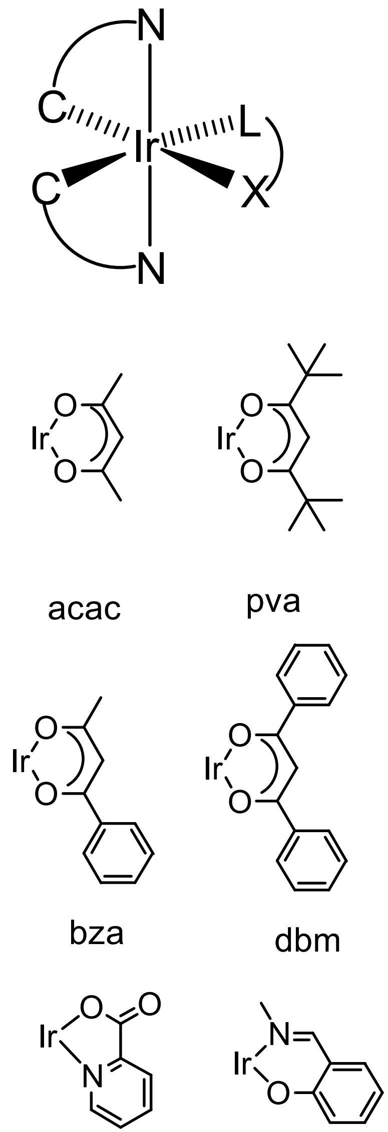
typical yield = 30%, reaction only works for ppy, bq and thpy ligands



typical yield > 90%, similar yields for a wide variety of ligands

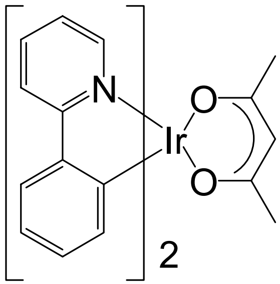
Phosphorescent $(C—N)_2Ir(LX)$ Complexes



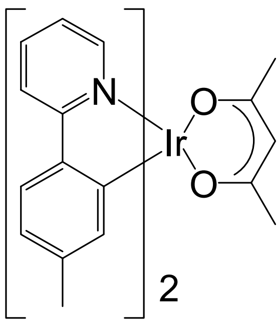


PL spectra of PPIr and PTIr

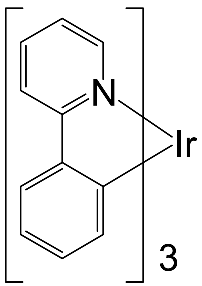
PPIr

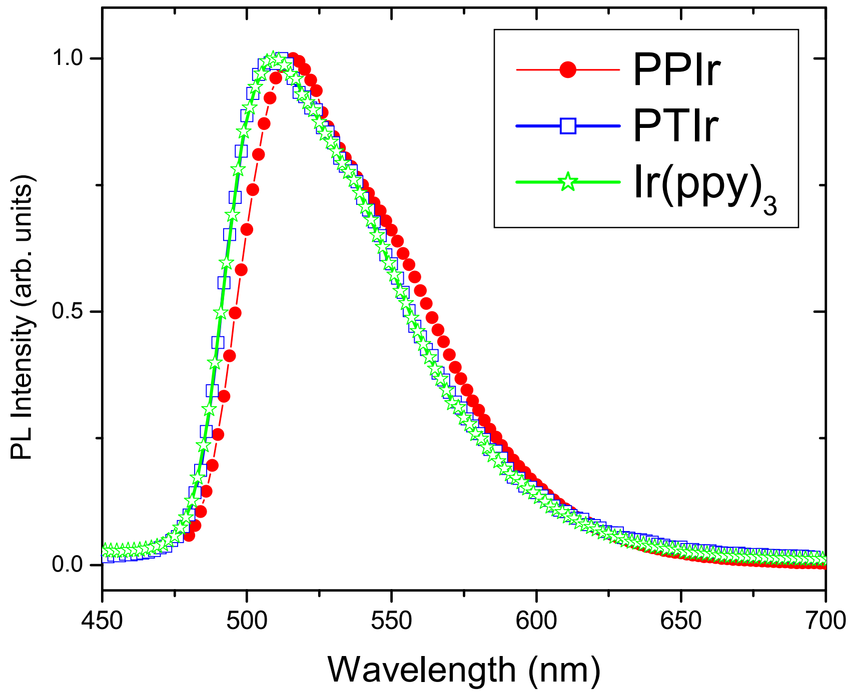


PTIr



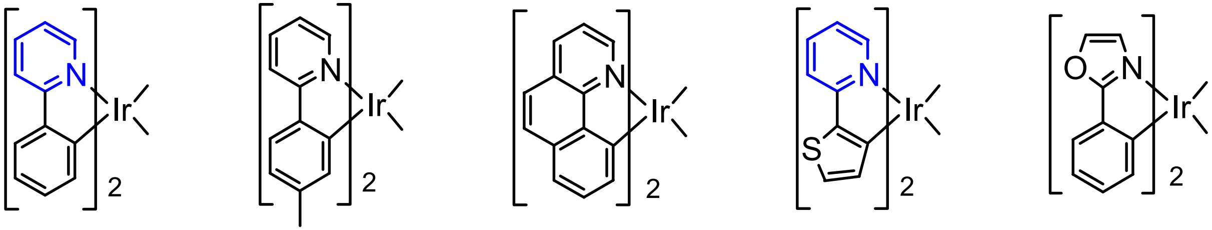
Ir(ppy)$_3$



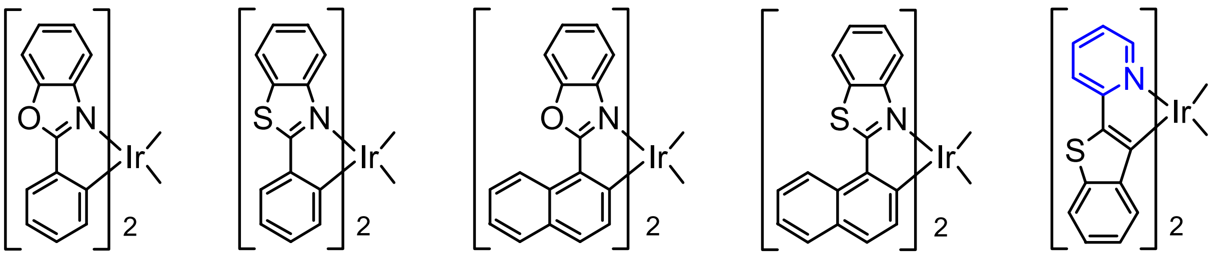


- PPIr and PTIr give solution PL identical to Ir(ppy)$_3$
- Similar volatility (sublimation temps.) for all three complexes
- Same lifetime (2 μsec) and Φ_{PL} (0.4) for all three complexes

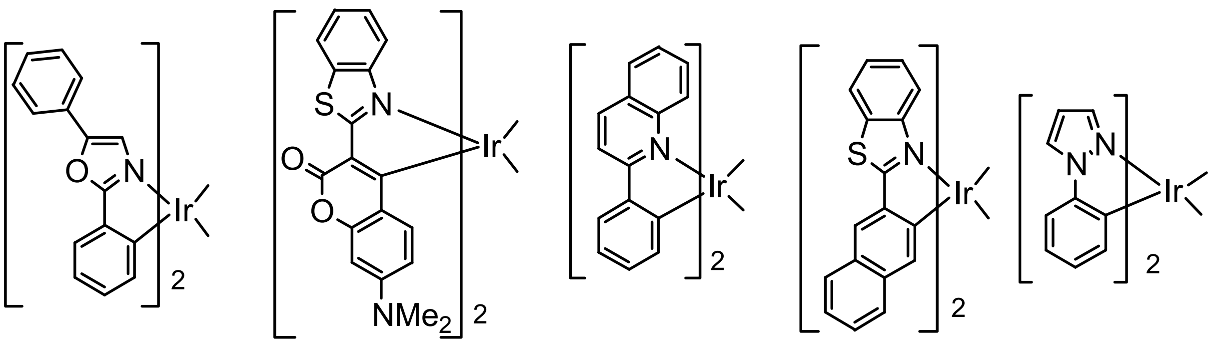
$(C^\wedge N)_2Ir(LX)$ Complexes



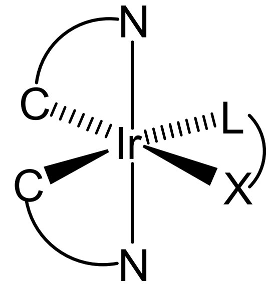
ppy | tpy | bzq | thp | op

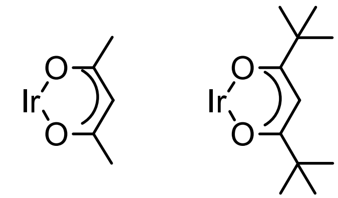


bo | bt | bon | αbsn | btp

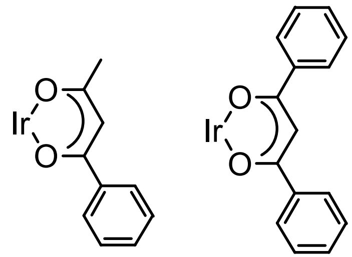


ppo | C6 | pq | βbsn | ppz

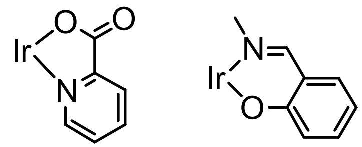




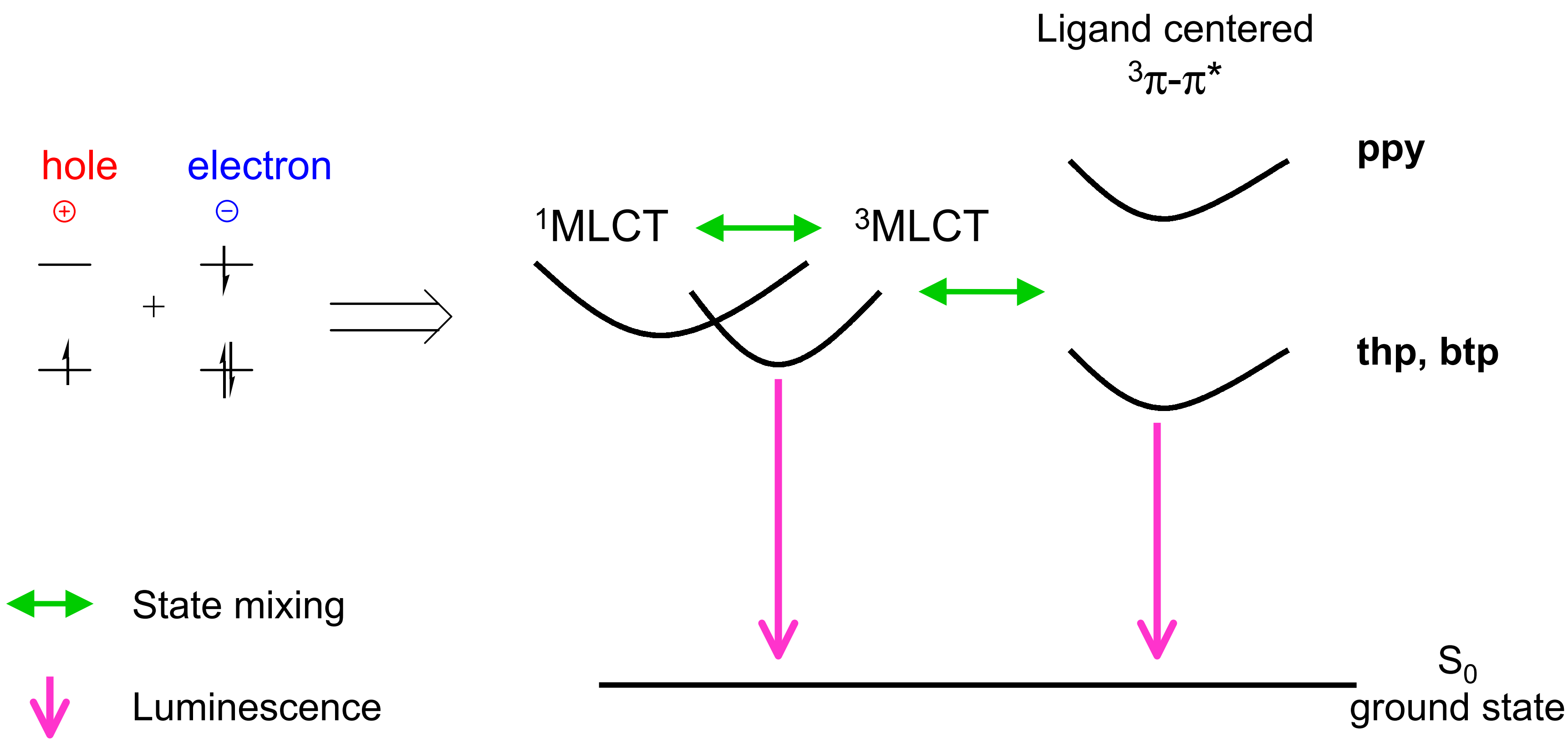
acac | pva



bza | dbm



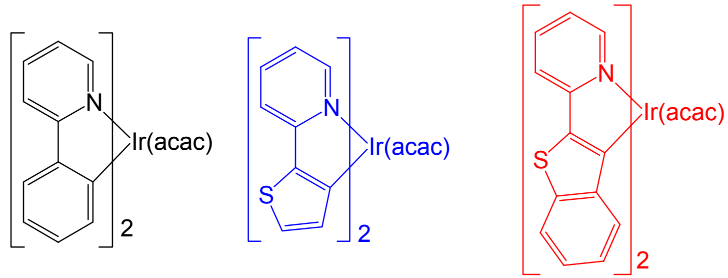
MLCT facilitated triplet emission

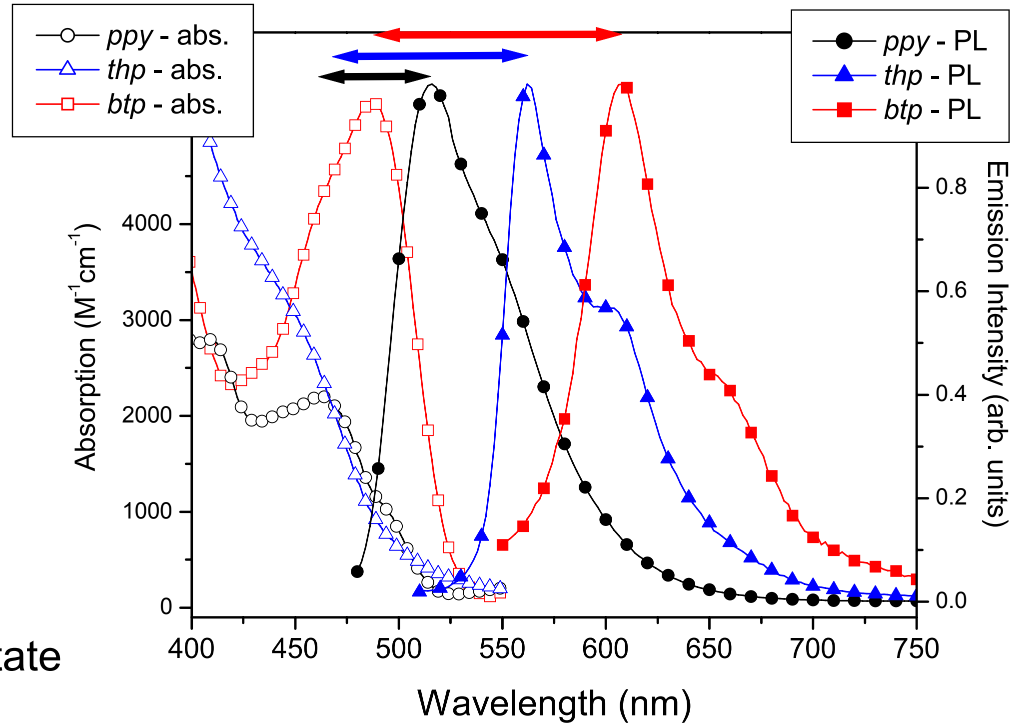


- MLCT energy similar for all three compounds (ppy, thp, btp)
- The choice of ^{3}MLCT or $^3\pi$-π^* emitting state depends on which is lower in energy
- MLCT excited state lowest energy, expect a small Stokes shift

L_2IrX Excited State is a Mixture of MLCT and $^3\pi$- π*

- Lowest energy abs. band is metal-to-ligand-charge transfer (^{3}MLCT).
- All have $\phi_{PL} > 0.3$
- Large Stokes shift ⇒ ligand centered excited state, $^3(\pi$-$\pi^*)$,MLCT absorption band *e.g. thp, btp.*
- Vibronic fine structure consistent with ligand based excited states.
- Small amount of MLCT character in the excited state leads to efficient phosphorescence for $^3(\pi$- $\pi^*)$.

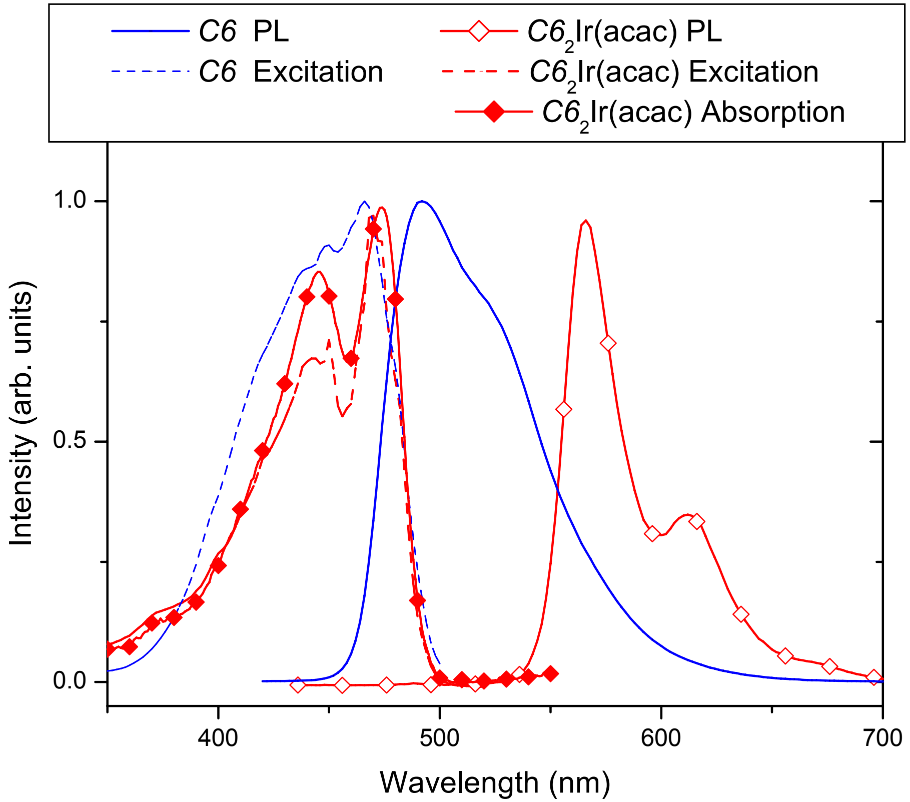


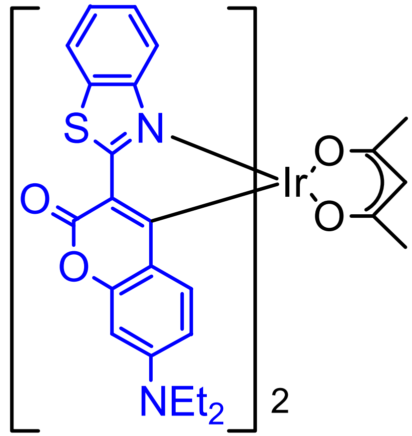


$E_{abs} - E_{PL}$ (*ppy*) = 2,300 cm^{-1} : MLCT excited state

$E_{abs} - E_{PL}$ (*thp, btp*) = 4,100 cm^{-1} : $^3\pi$- π^* excited state

$C6_2$Ir(acac) Excitation and Emission

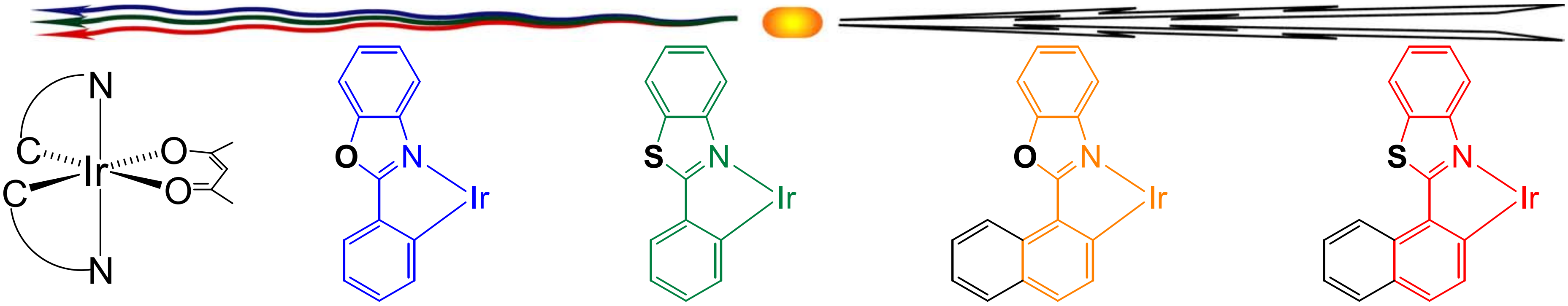




C6$_2$Ir(acac)
C6 is shown in blue

- Coumarin 6 (*C6*) is a common green laser dye, used in green fluorescent OLEDs
- When this complex is cyclometallated to Ir the emission shifts to orange
  - Ir shifts dominant emission process to C6 based phosphorescence
  - Excitation spectra of *C6*$_2$Ir(acac) show lines for *C6* as well as MLCT transitions for "L_2IrX"
  - η (PL) for *C6*$_2$Ir(acac) = 0.6 and τ = 14 μsec

Ligand Effects on Emission energy



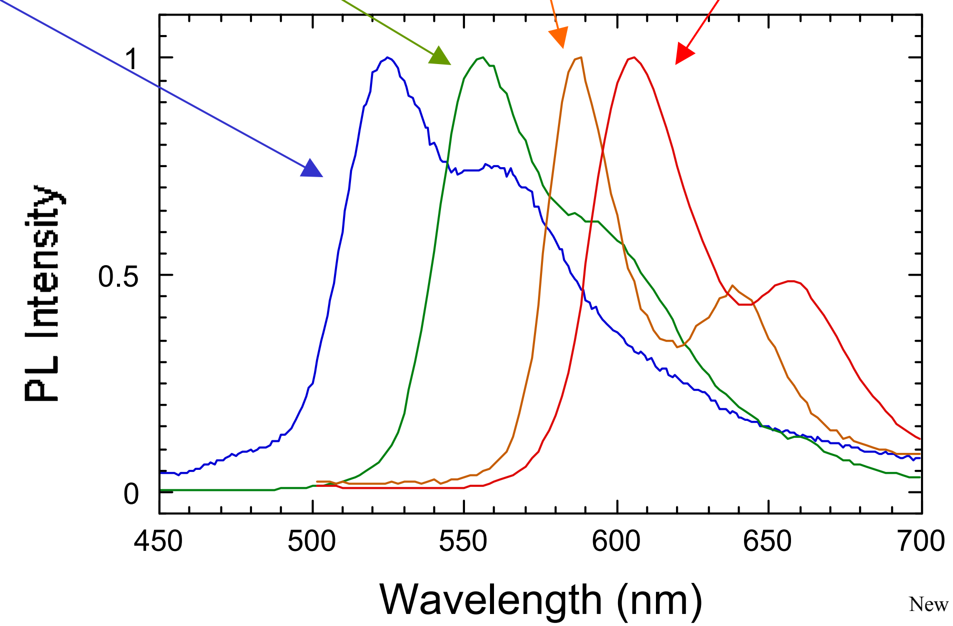
PL eff. = 0.35
τ = 4 μsec (77K)
λ_{max} = 525 nm

PL eff. = 0.4
τ = 2 μsec
λ_{max} = 555 nm

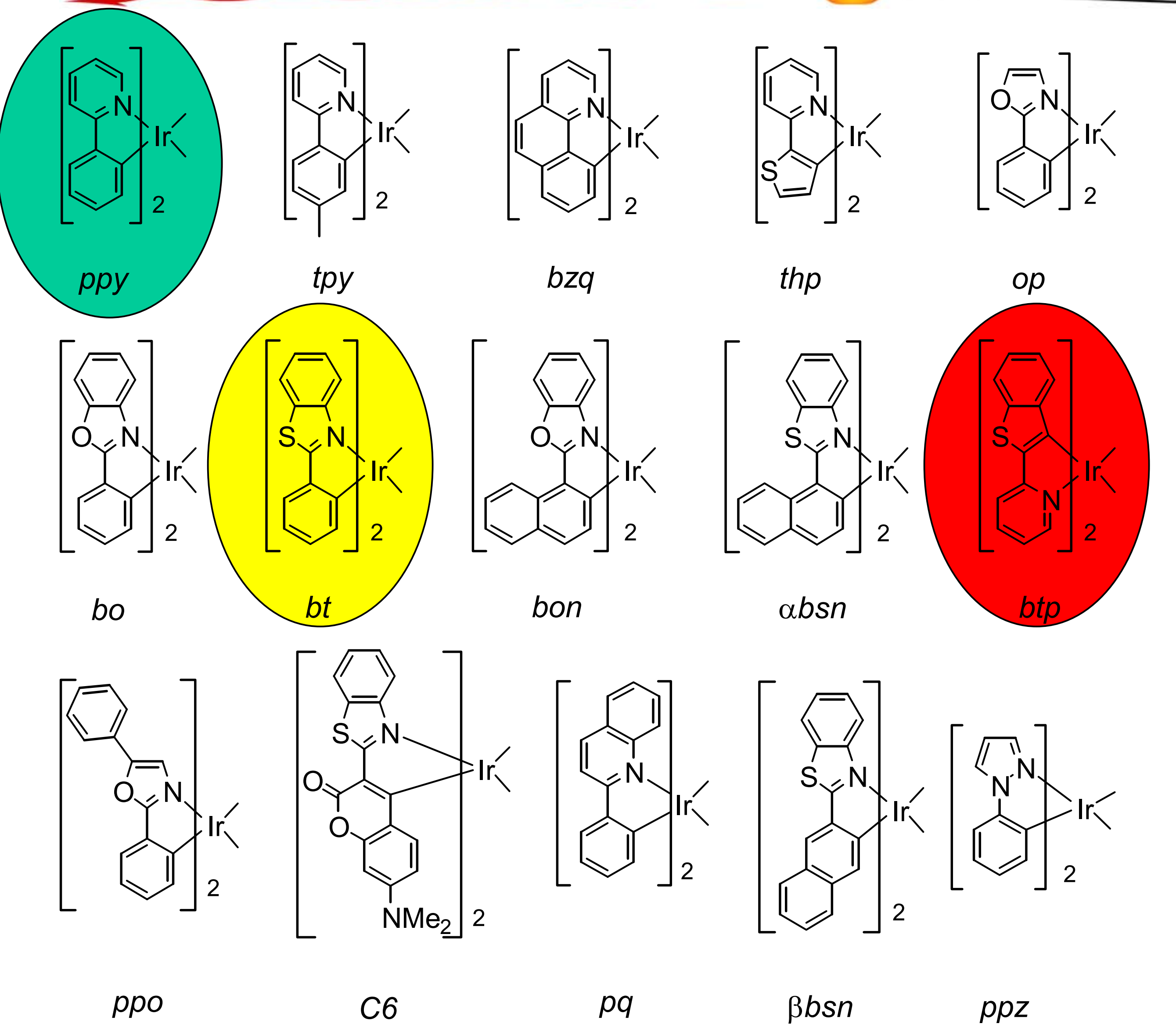
PL eff. = 0.05
τ = 2 μsec
λ_{max} = 590 nm

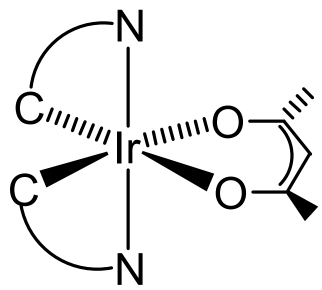
PL eff. = 0.2
τ = 2 μsec
λ_{max} = 605 nm

- Photoluminescence in solution
- Lifetime in polystyrene at R.T.
- Bathochromic shifts for:
  - O ⇒ S
  - phenyl ⇒ napthyl
  - Effect is additive

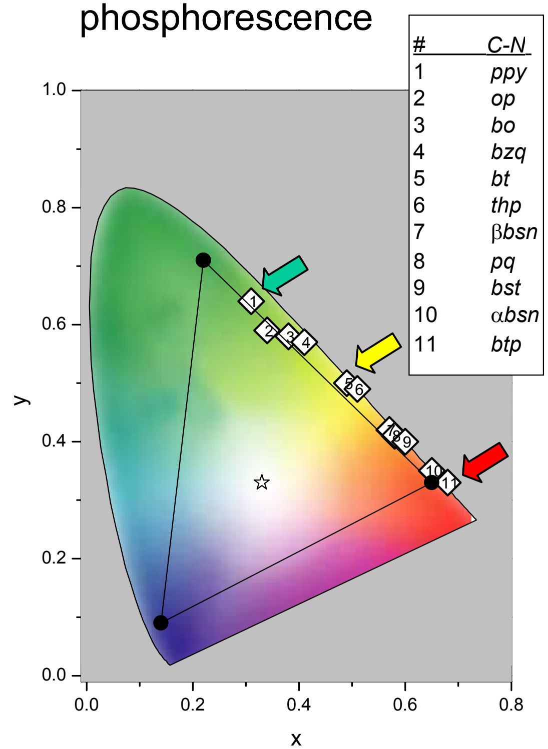


Green, yellow and red phosphors for OLED study $[L_2Ir(acac)]$

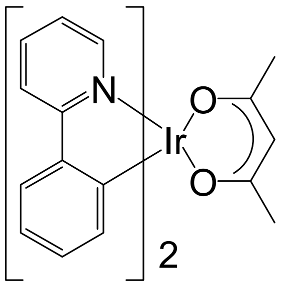




CIE coords. based on phosphorescence



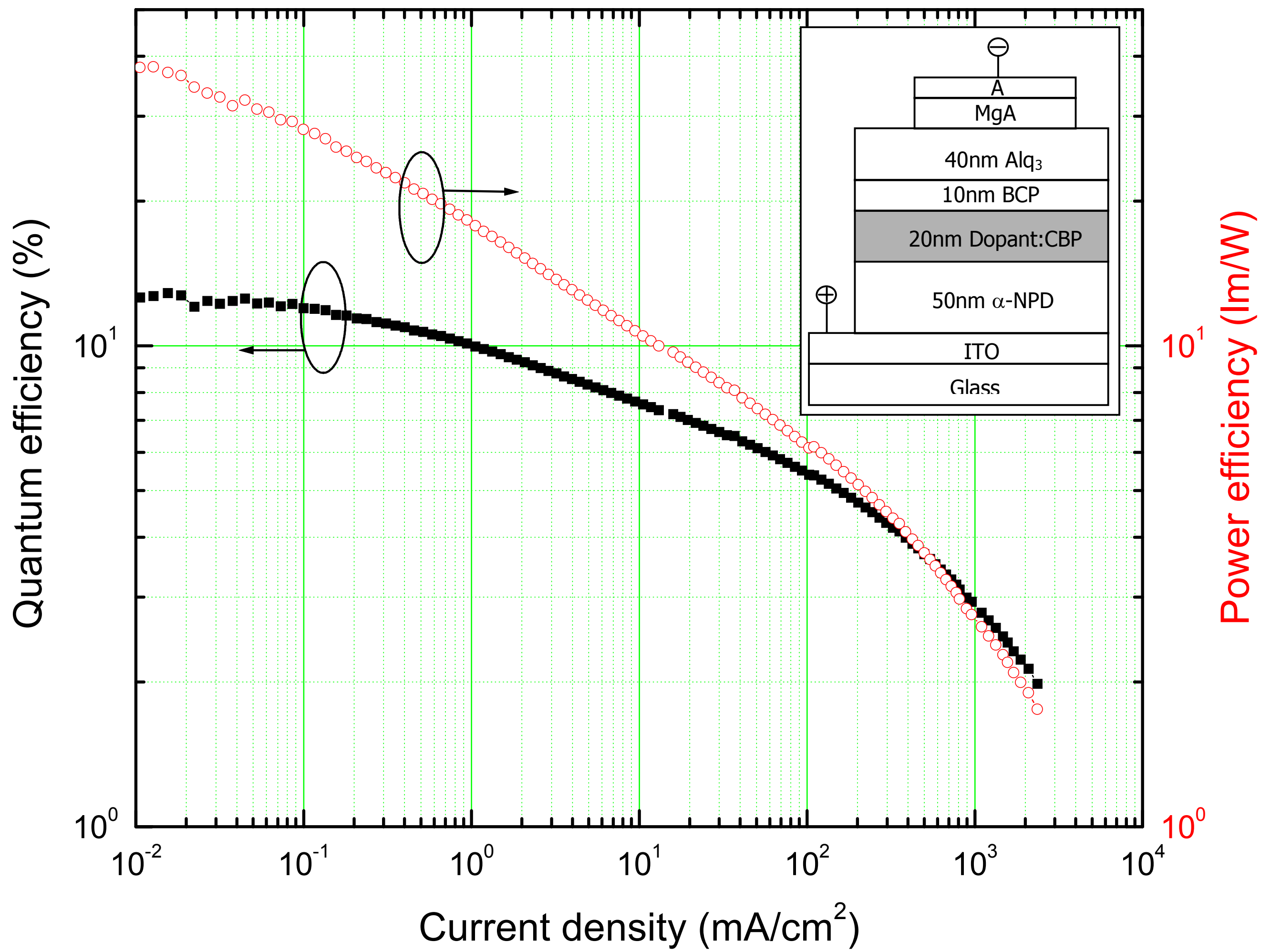
Performance of PPIr doped OLED



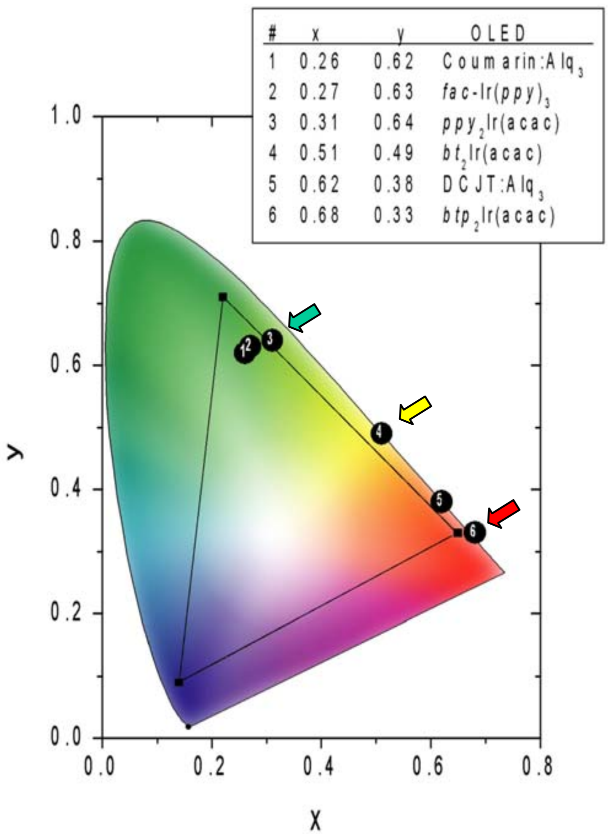
PPIr

Peak external quantum Efficiency = 12.5%, 40 lm/W

Device structure and doping concentration have not been optimized.

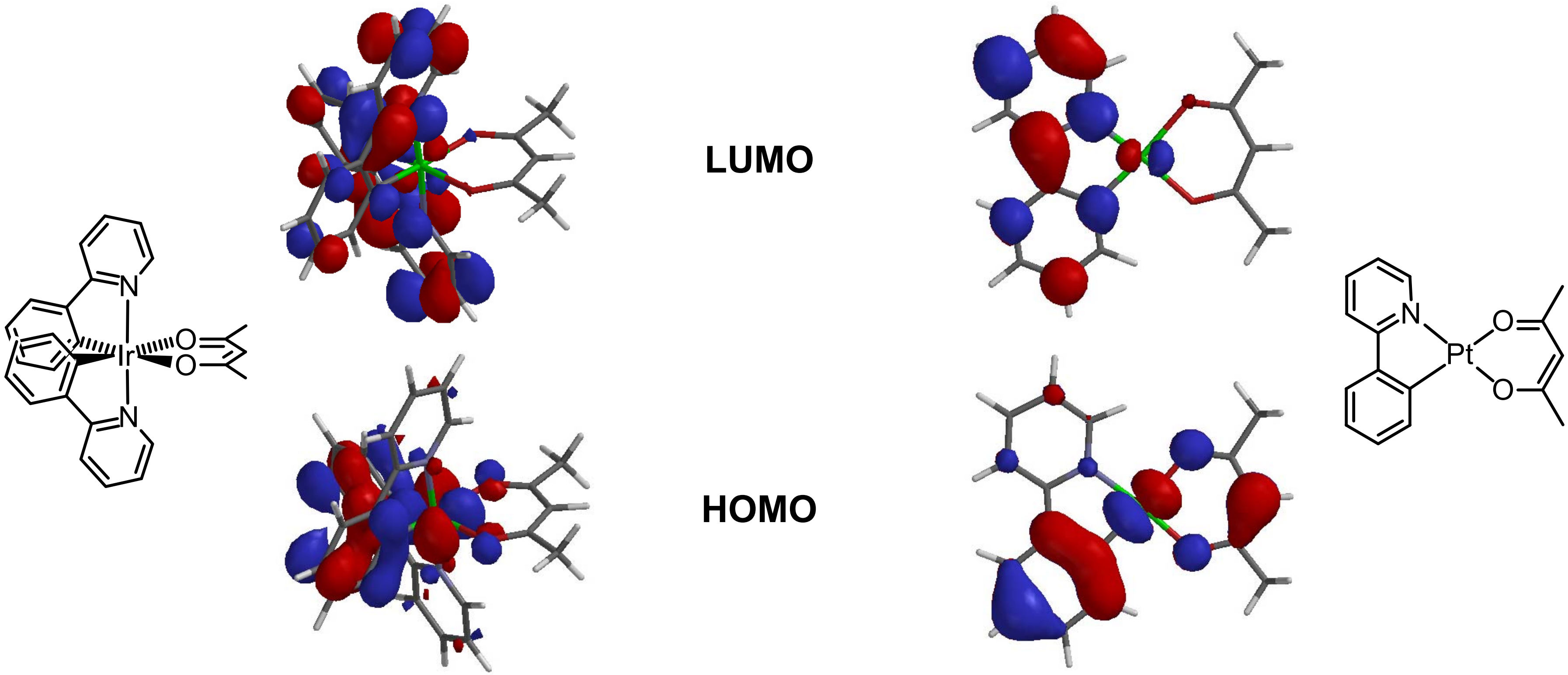


PPIr, BTIr and BTPIr doped (7%) OLED performance



Dopant phosphor	PPIr	BTIr	BTPIr
EL color	Green	Yellow	Red
Peak wavelength (nm)	525	565	617
CIE-x	0.31	0.51	0.68
CIE-y	0.64	0.49	0.33
Luminance @1 mA/cm^2(cd/m^2)	441	300	62
Drive voltage (V) @ 1 mA/cm^2	7.2	7.3	8.5
Ext. quantum efficiency (%) @ 1 mA/cm^2	10.0	9.7	6.6
" @ 10 mA/cm^2	7.6	8.3	6.0
" @ 100 mA/cm^2	5.4	5.5	4.6
Power efficiency (lm/W) @ 1 mA/cm^2	18	11	2.2

(*ppy*)Pt(acac) vs. (*ppy*)$_2$Ir(acac)



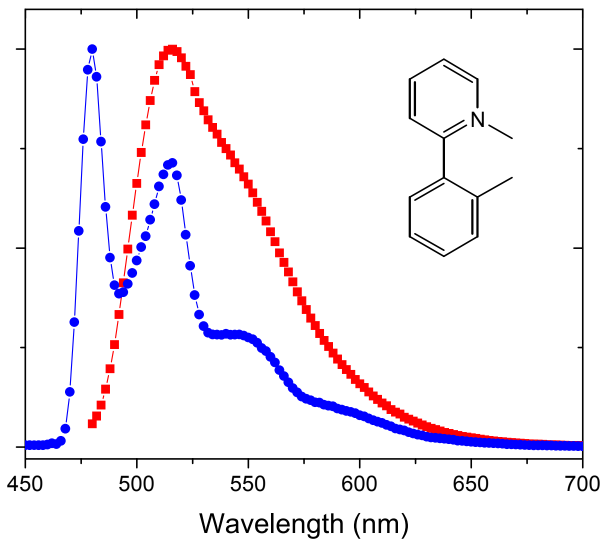
(*ppy*)$_2$Ir(acac) (*ppy*)Pt(acac)

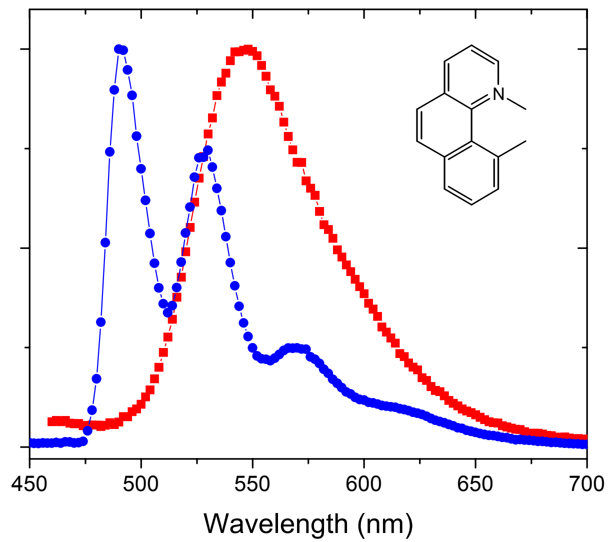
- MO pictures from DFT calculations, Spartan calc. package
- Strong metal character in both HOMOs
- acac character only in Pt complex, lowering/stabilizing HOMO
  - M d orbitals are orthogonal to acac π in Ir and conjugated for Pt
  - Blue shifted Pt MLCT $\Rightarrow$ blue shifted emission

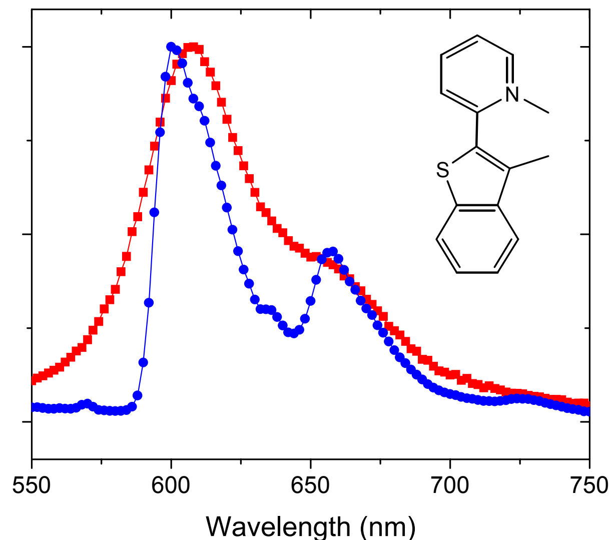
See Brooks Inorg. Poster #490

LPt(acac) Compared to L_2Ir(acac) Phosphors

- Emission spectra LPt(acac) complexes are shown in **blue** and L_2Ir(acac) complexes in **red**.
- Both spectra in a given graph are for the same L ligand, shown in the graph.
- All LPt(acac) complexes have lifetimes of 5-10 μsec: phosphorescence!
- Complexes with strong MLCT for Ir show significant blue shift, L = *ppy, bzq*.
- Complexes with very little MLCT show very little blue shift for Pt complex, L = *btp*

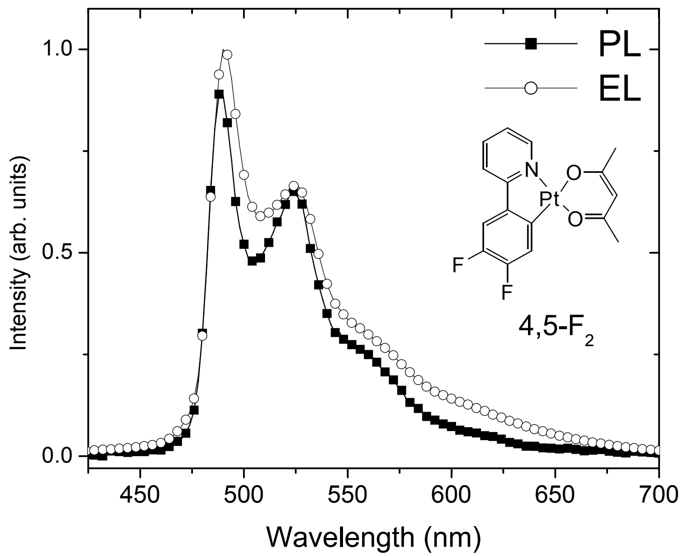


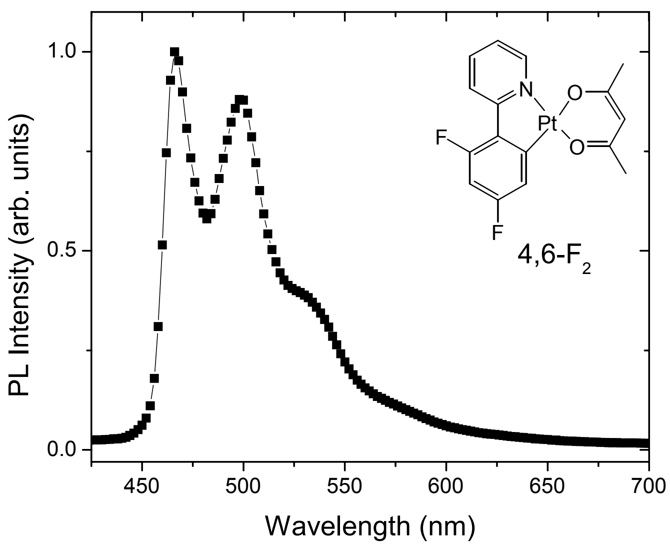




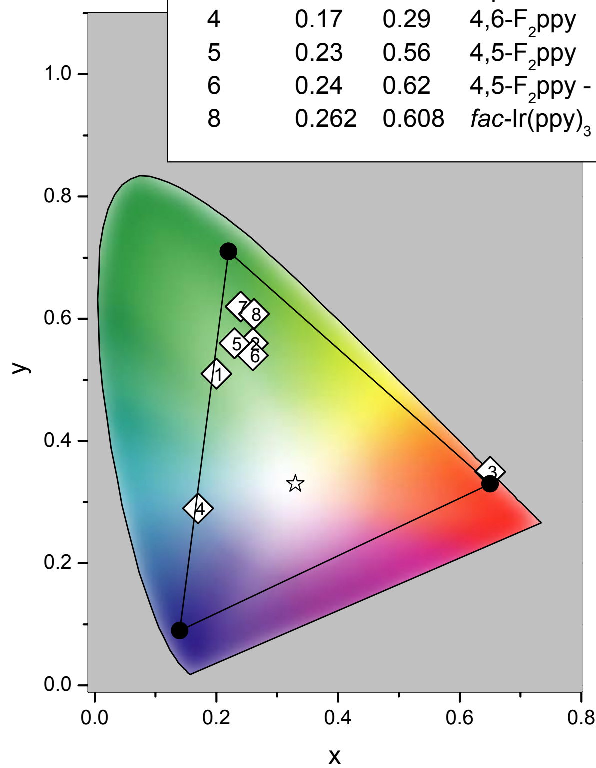
F_2-*ppy*Pt(acac) PL and EL

- Both difluoro derivatives give blue shifted emission
- PL and EL spectra nearly identical for 4,5-F_2-*ppy*



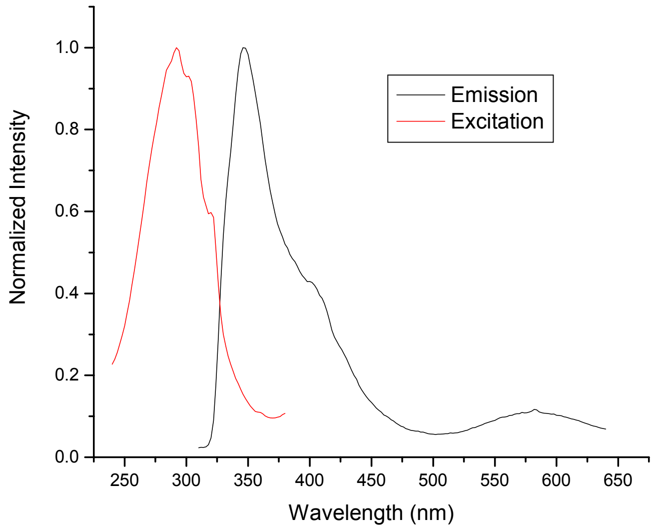


#	x	y	**L**Pt(acac)
1	0.2	0.51	ppy
2	0.26	0.56	bzq
3	0.65	0.35	btp
4	0.17	0.29	4,6-F_2ppy
5	0.23	0.56	4,5-F_2ppy
6	0.24	0.62	4,5-F_2ppy - **EL**
8	0.262	0.608	*fac*-Ir(ppy)$_3$

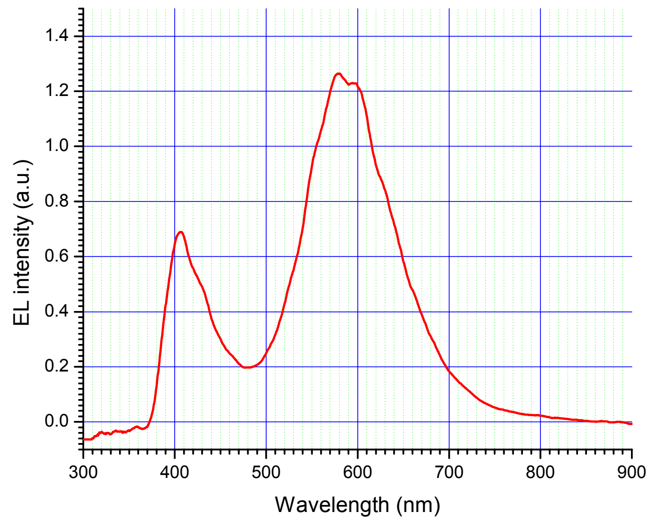


OLEDs with 4,6-F_2ppyPt(acac) doped TAZ

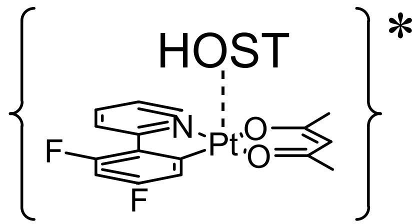
PL of TAZ / (4,6-dF_2-ppy)Pt(acac) (1%)



EL of ITO/M14/TAZ+4,6-F_2-ppyPt/Alq/MgAg

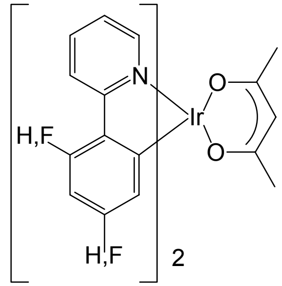


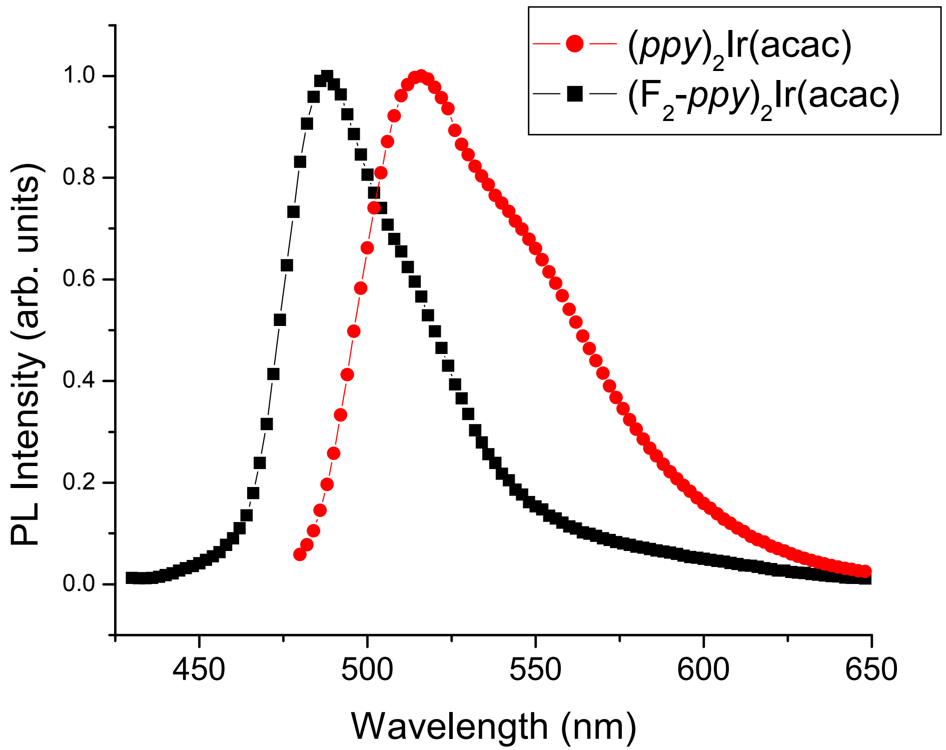
- TAZ is a common wide gap ETL, triplet energy = blue
- Only TAZ (350-400 nm) and exciplex (600 nm) emission observed in PL and EL
- Blue phosphors may require new carrier and host materials

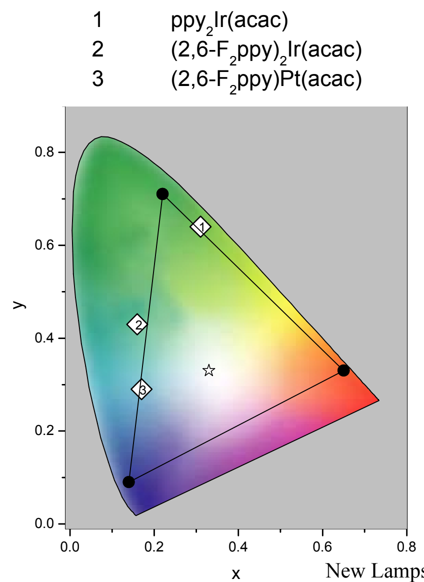


exciplex

(4,6-F$_2$-*ppy*)$_2$Ir(LX) solution PL

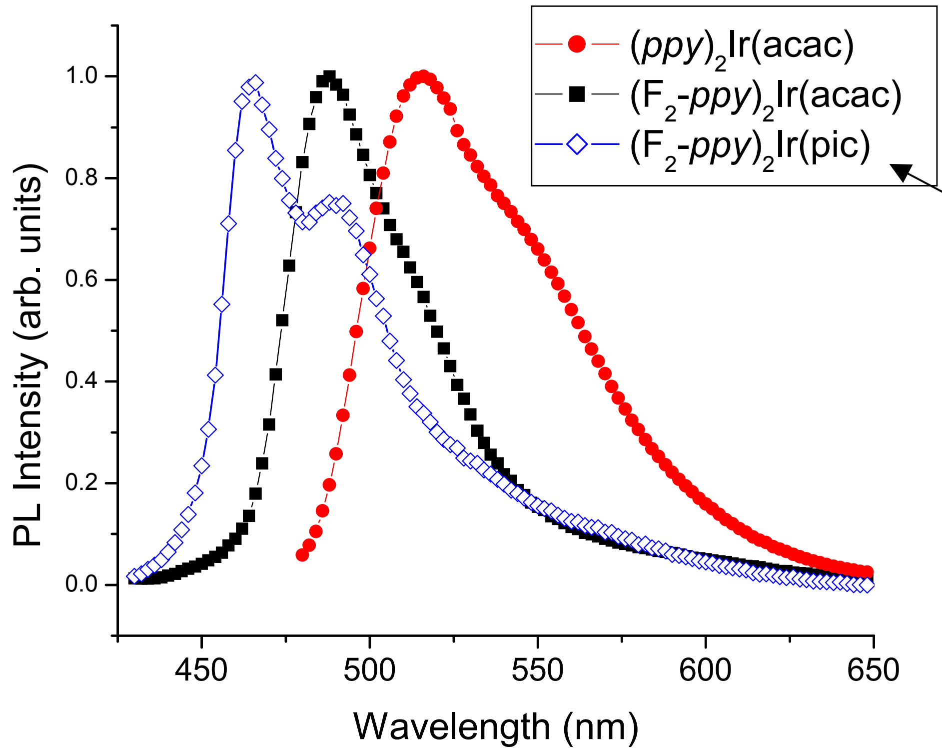


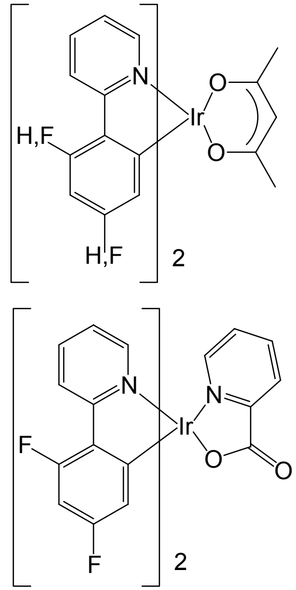




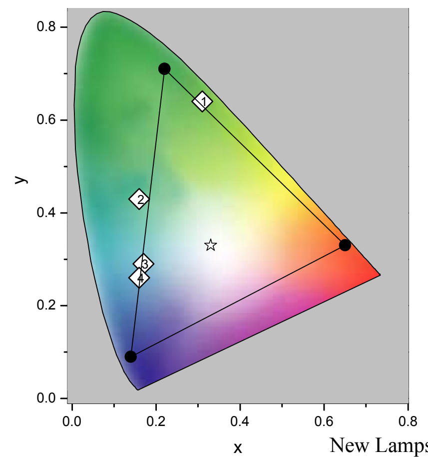
- All spectra recorded in CH_2Cl_2 solution
- Octahedral center should decrease exciplex formation

(4,6-F$_2$-*ppy*)$_2$Ir(LX) solution PL



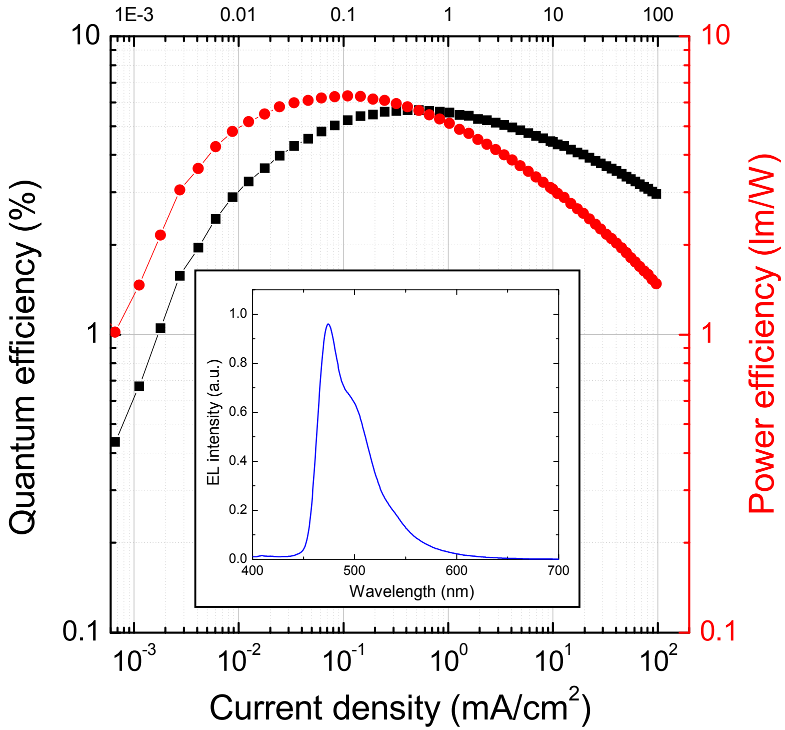


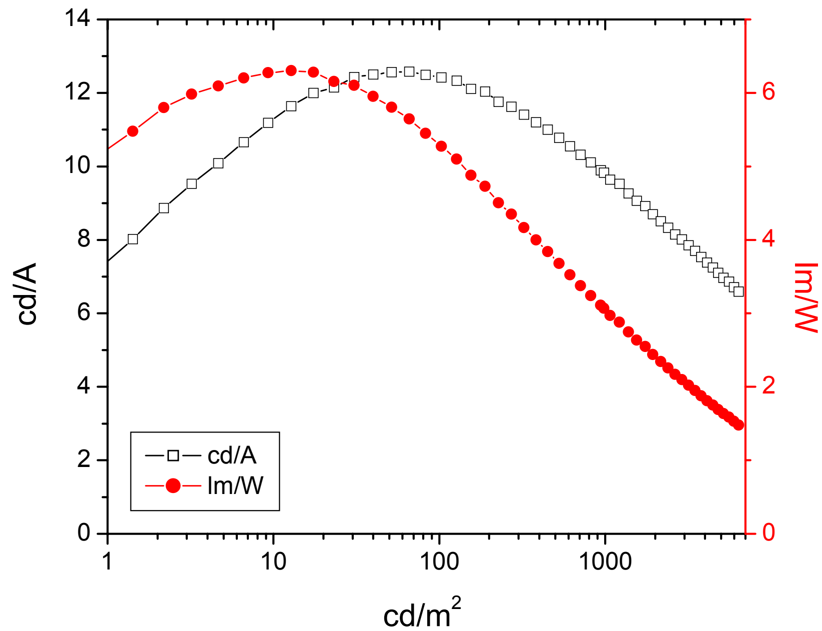
1	ppy$_2$Ir(acac)
2	(2,6-F$_2$-ppy)$_2$Ir(acac)
3	(2,6-F$_2$-ppy)Pt(acac)
4	(2,6-F$_2$-ppy)2Ir(pic)

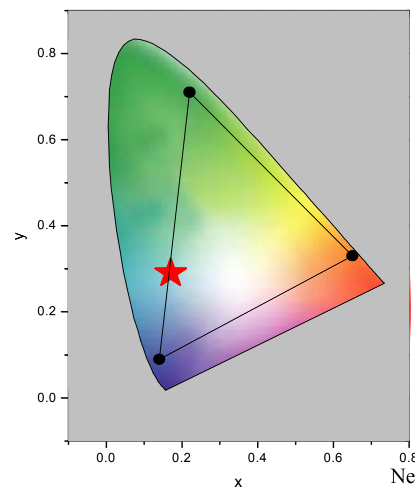


- (4,6-F$_2$*ppy*)$_2$Ir(pic) ⇒ > 200 lumin/optical Watt
- Very similar CIE coords for Pt(acac) and Ir(pic) cpds.
- Octahedral center should decrease exciplex formation

Blue phosphorescent OLEDs

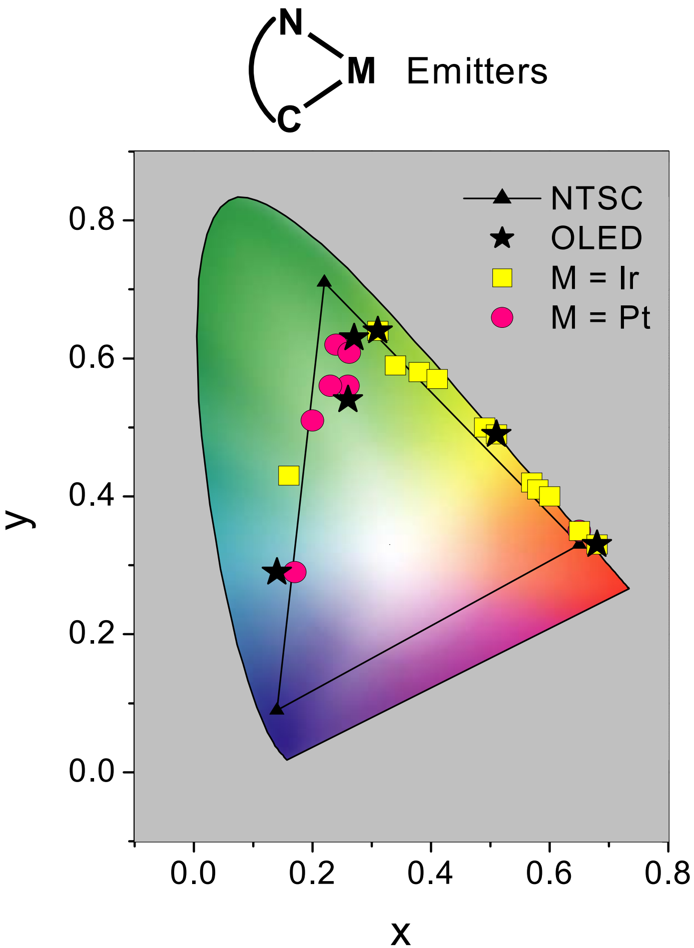






- Emission due solely to the phosphorescent dopant
  - No excimer or exciplex
- Efficiency = 5.5%, > 6 lum/W at 100 cd/m^2

Summary



- Careful control of the formation, confinement and relaxation of excitons can lead to highly efficient OLEDs
  - Heavy metals are important to utilize triplet excitons
  - Demonstrated η_{int} > 80 % for green, > 60% for red and yellow, > 10% for blue
  - Demonstrated $\tau > 10^5$ hours for red and > 20,000 hours for green
- Careful design of ligands in Ir and Pt complexes leads to efficient, highly tunable phosphors for OLEDs
  - High efficiency regardless of color (green, yellow, red)
  - Blue → Red

Acknowledgments

Sergey Lamansky, Peter Djurovich, Drew Murphy, Feras Abdel-Razzaq, Jason Brooks, Vadim Adamovich
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Princeton University

Raymond Kwong, Julie J. Brown
Universal Display Corporation

$$ Funding $$: Universal Display Corporation, NSF, DARPA

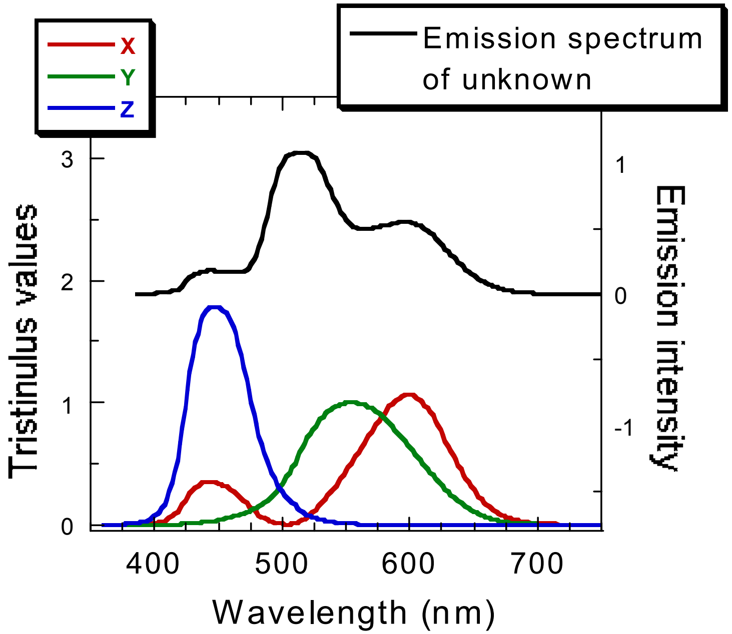
CIE Color Coordinates

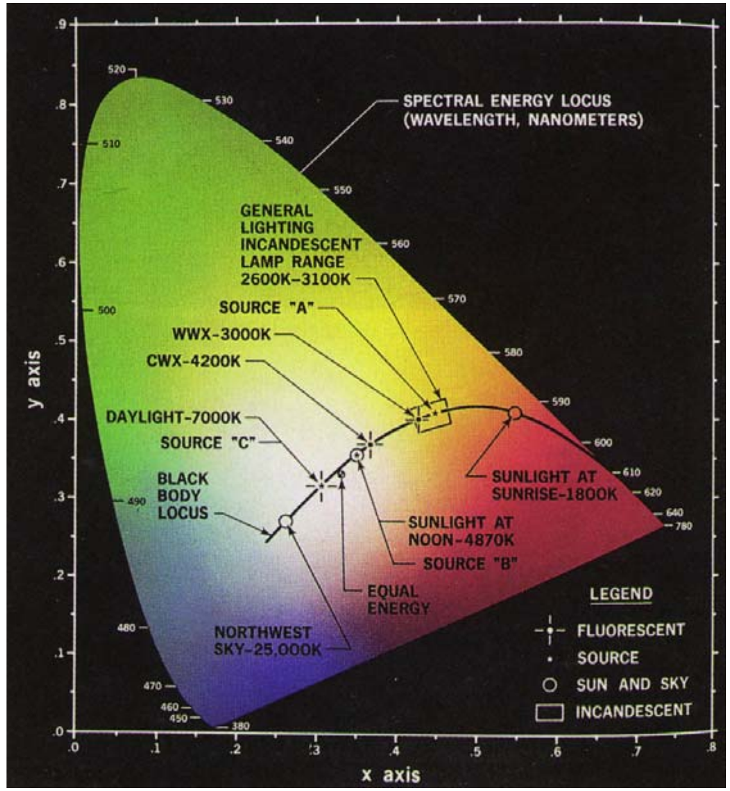
$$\bar{X} = \sum_{\lambda} \mathbf{X} \bullet \text{EL spectrum}$$

$$\bar{Y} = \sum_{\lambda} \mathbf{Y} \bullet \text{EL spectrum}$$

$$\bar{Z} = \sum_{\lambda} \mathbf{Z} \bullet \text{EL spectrum}$$

$$x = \frac{\bar{X}}{\bar{X} + \bar{Y} + \bar{Z}} \qquad y = \frac{\bar{Y}}{\bar{X} + \bar{Y} + \bar{Z}}$$





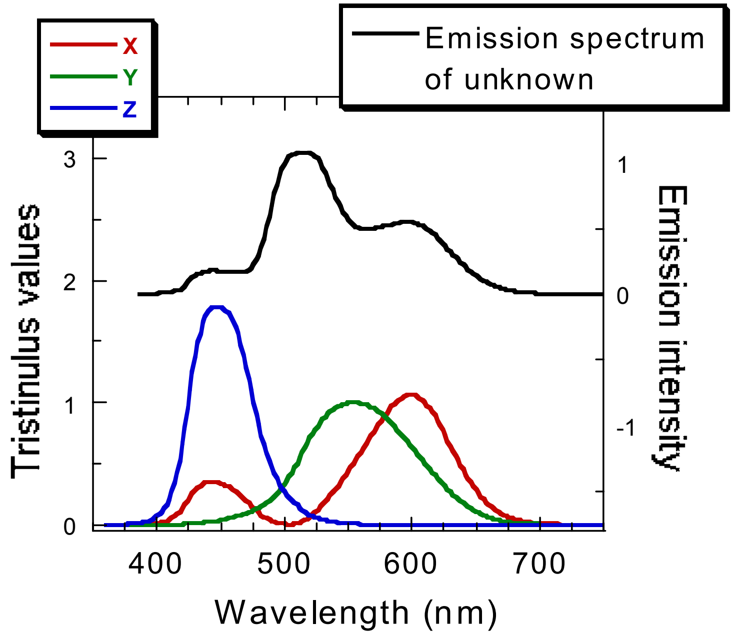
CIE Color Coordinates

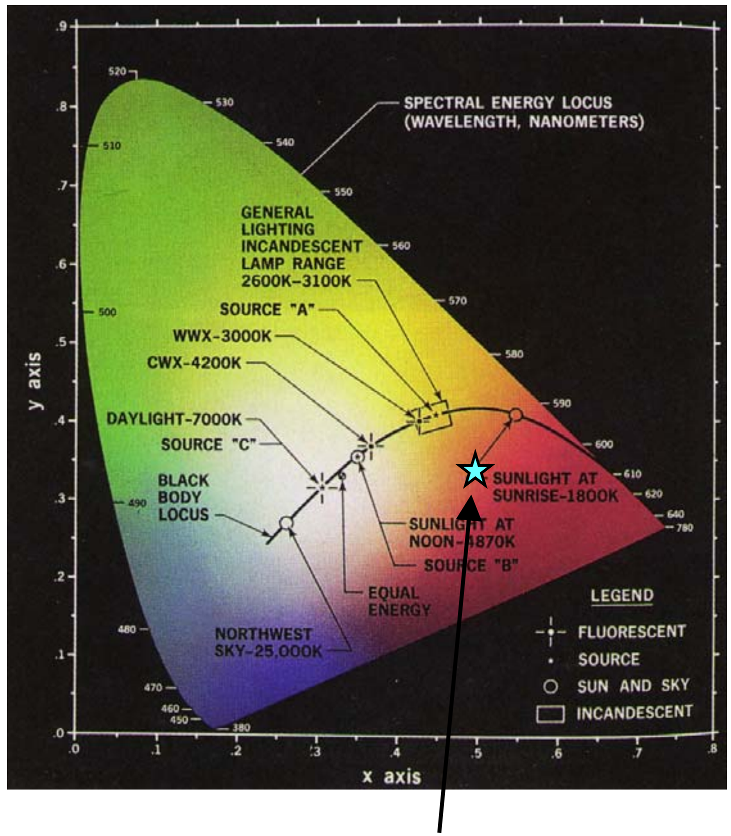
$$\bar{X} = \sum_{\lambda} \mathbf{X} \bullet \text{EL spectrum}$$

$$\bar{Y} = \sum_{\lambda} \mathbf{Y} \bullet \text{EL spectrum}$$

$$\bar{Z} = \sum_{\lambda} \mathbf{Z} \bullet \text{EL spectrum}$$

$$x = \frac{\bar{X}}{\bar{X} + \bar{Y} + \bar{Z}} \qquad y = \frac{\bar{Y}}{\bar{X} + \bar{Y} + \bar{Z}}$$





unknown = 0.33, 0.49