Organic LEDs – part 4

E L E C T R O P H O S P H O R E S C E N C E

1. OLED efficiency
2. Spin
3. Energy transfer
4. Organic phosphors
5. Singlet/triplet ratios
6. Phosphor sensitized fluorescence
7. Endothermic triplet energy transfer

Lecture by Prof. Marc Baldo

April 10, 2003 – Organic Optoelectronics - Lecture 17

POWER EFFICIENCY

The eye's response is wavelength dependent.

The unit of perceived optical power is defined as the lumen (lm).

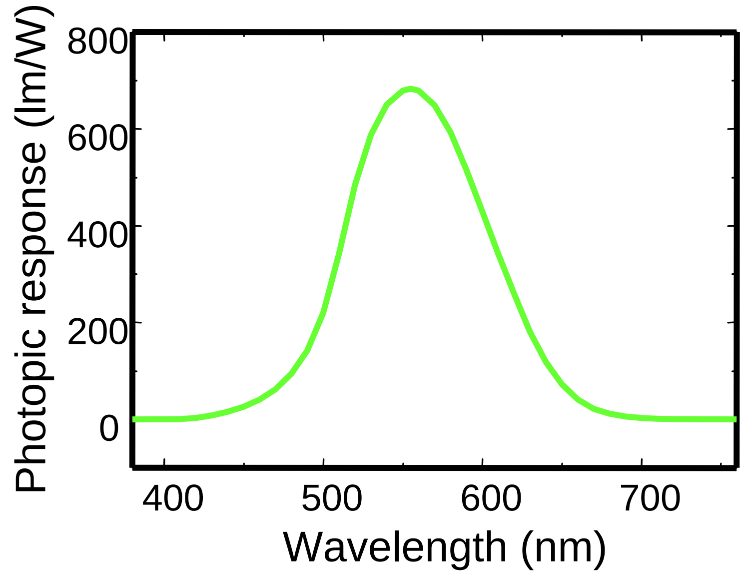
Power efficiency of LED's is therefore measured in lumens/Watt.

The maximum photopic response is:

Φ ~ 20 lm (blue)

Φ ~ 680 lm (green)

Φ ~ 100 lm (red)



For an OLED of given color, we must maximize:

- quantum efficiency (η_Q = photons out/electrons in)
- electrical efficiency (V_λ/V = photon energy/operating voltage)

$$\eta_P = \frac{L}{VI} = \Phi\,\eta_Q\,\frac{V_\lambda}{V}$$

Power efficiency = photopic response of eye ***x*** quantum efficiency ***x*** electrical efficiency

Quantum efficiency

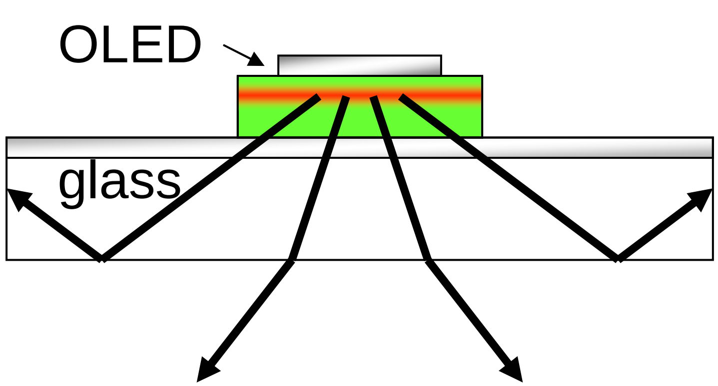
is the measure of a luminescent dye's performance.

η_Q= *the number of photons emitted per electron injected.*

$$\eta_Q = \chi \eta_{out} \phi_{PL}$$

ϕ_{PL} is fundamental luminescence efficiency of organic material.

η_{out} is output coupling fraction reduced by absorption losses and wave guiding within the device and its substrate.



χ is fraction of luminescent molecular excitations
(defined by spin selection rules)
typically ~ 25%

remaining energy is wasted

Imposes a fundamental limit to OLED efficiencies

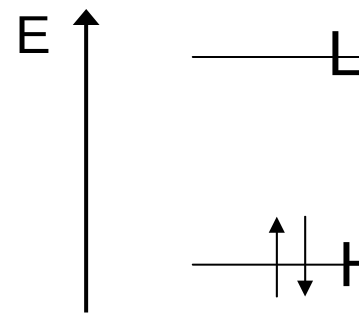
EXCITON SPIN AND SYMMETRY

Molecular excited states (or excitons) are typically mobile, with binding energy ~ 1eV, and spin S = 0,1

Molecular ground state

(spatially symmetric under exchange of electrons)

S=0, singlet

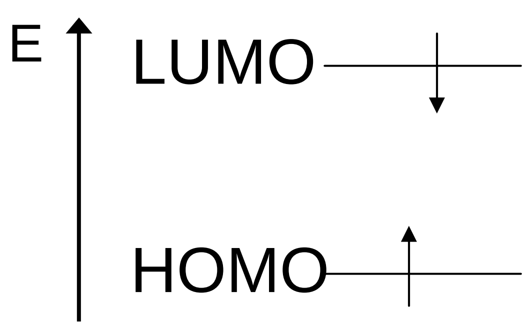


Lowest unoccupied (LUMO) molecular orbital

Highest occupied (HOMO) molecular orbital

1st excited state

(spatially anti-symmetric (triplet) or spatially symmetric (singlet))



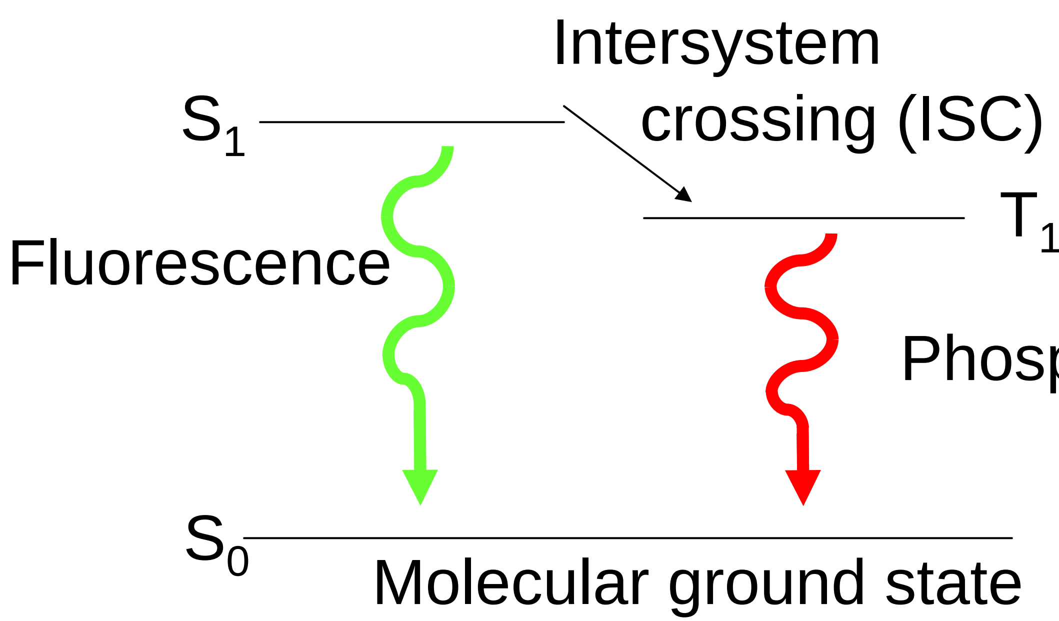
$$\psi = |\uparrow\uparrow\rangle$$
$$\psi = |\uparrow\downarrow\rangle + |\uparrow\downarrow\rangle$$
$$\psi = |\downarrow\downarrow\rangle$$

} S=1, triplet

$$\psi = |\uparrow\downarrow\rangle - |\uparrow\downarrow\rangle$$

S=0, singlet

Fluorescence and Phosphorescence



Triplet has lower energy because it is spatially antisymmetric under exchange of electrons. (e–e- repulsion lower).

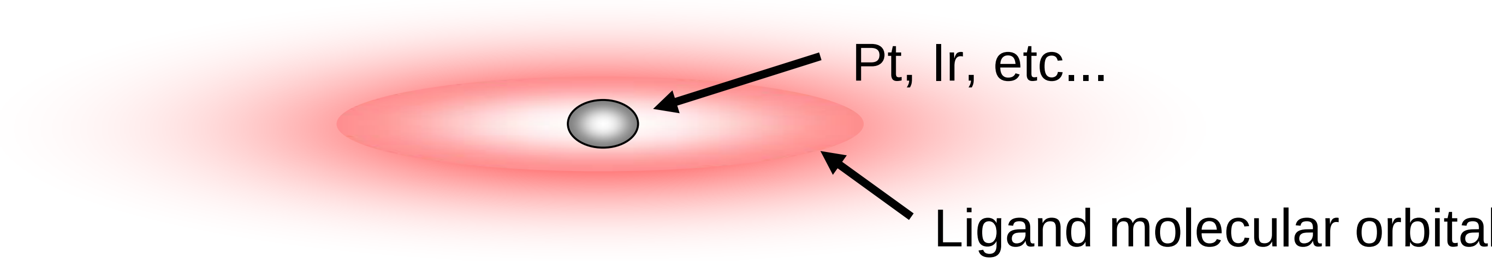
Fluorescence:
Decay from singlet allowed by symmetry: fast ($10^9\ s^{-1}$) and often efficient.

Phosphorescence:
Decay from triplet disallowed by symmetry: slow (> 1 s^{-1}) and inefficient.

Efficient phosphorescence

Need to mix singlet and triplet states:
- make both singlet and triplet decay allowed.

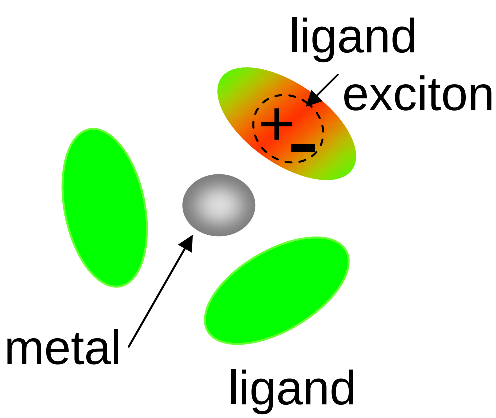
Use metal-organic complexes with heavy transition metals:

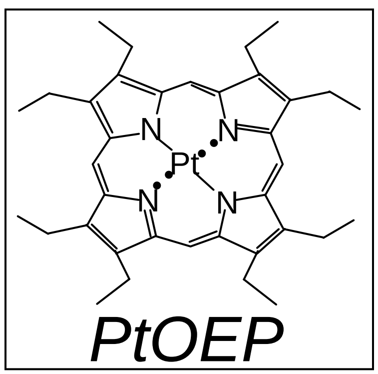


Spin orbit coupling mixes states: proportional to atomic number Z^4

Type I phosphor

Exciton localized on organic

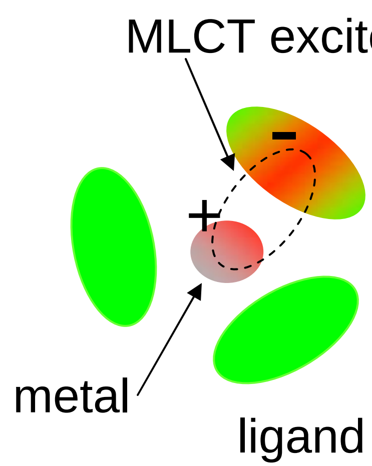


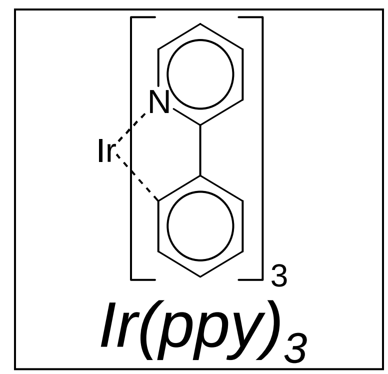


less mixing ~ 100μs triplet lifetime

Type II phosphor

Metal-ligand charge transfer exciton



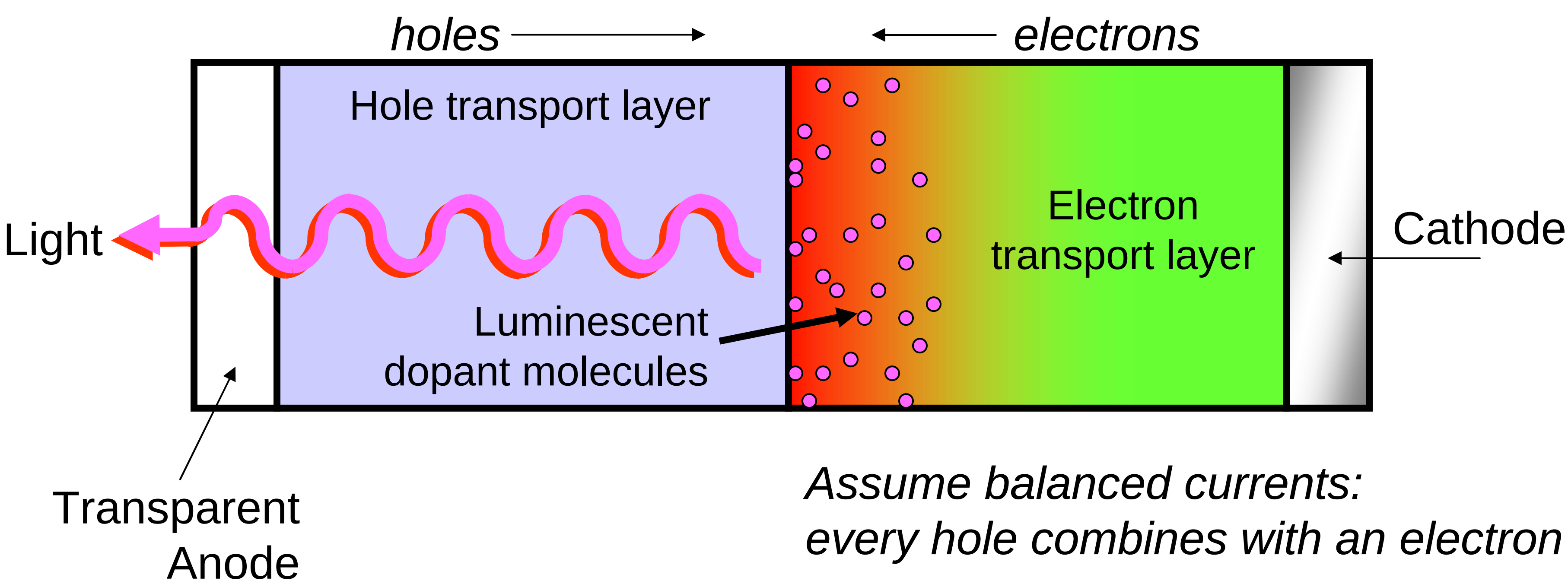


most mixing ~ 1μs triplet lifetime

Structure and operation of OLEDs

- must transfer energy from host material to luminescent dopant. This determines the quantum efficiency of luminescence.

A heterostructure OLED

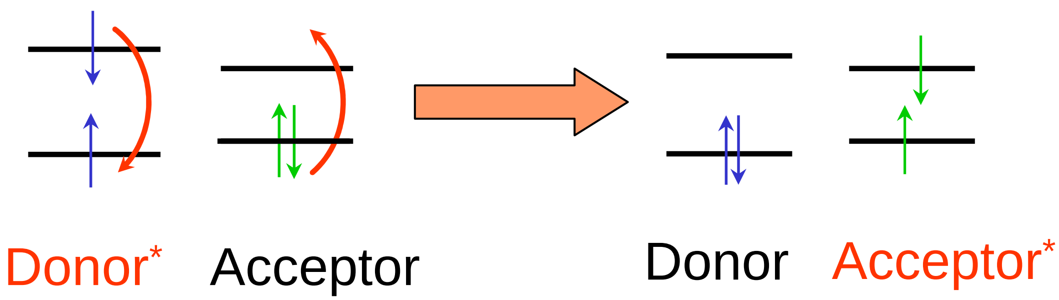


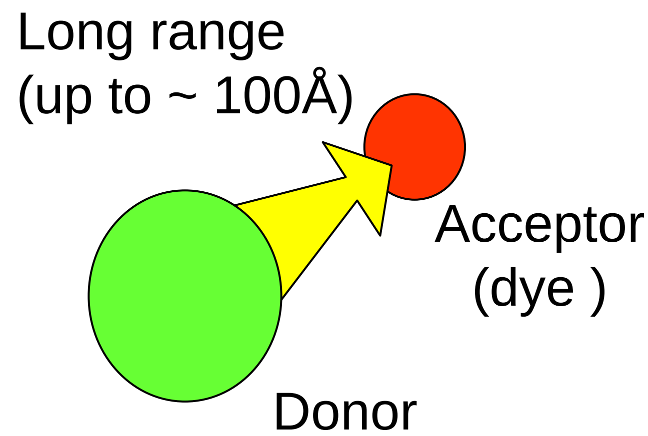
Assume balanced currents:
every hole combines with an electron

Excitons form in host at interface.
Ideally energy is transferred to luminescent molecules

Energy transfer

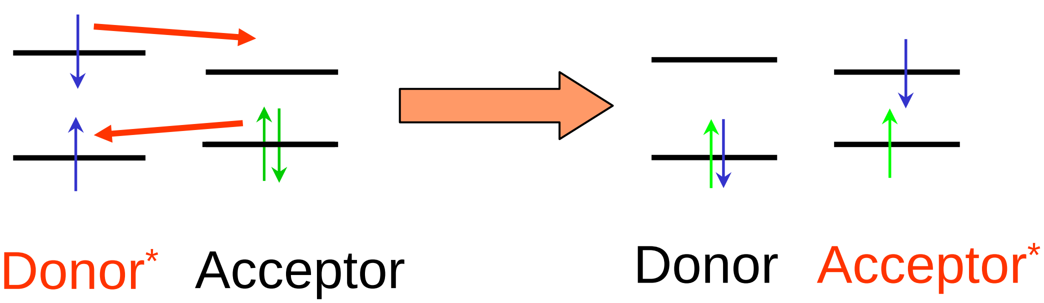
(a) Förster energy transfer

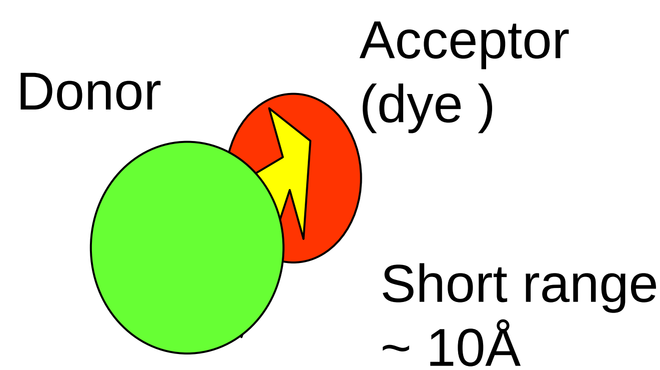




Exciton non-radiatively transferred by dipole-dipole coupling if transitions are allowed (usually singlet-singlet).

(b) Dexter energy transfer



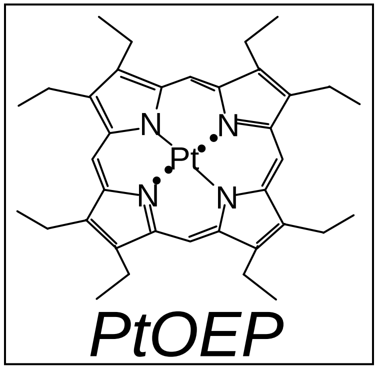


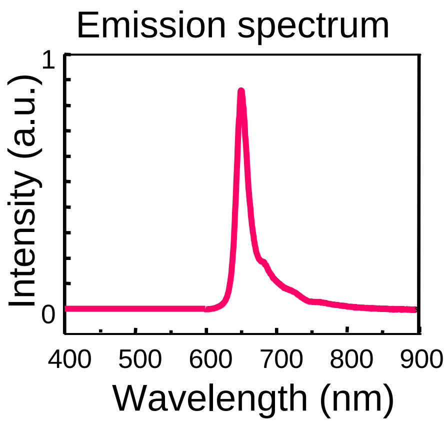
Exciton hops from donor to acceptor.

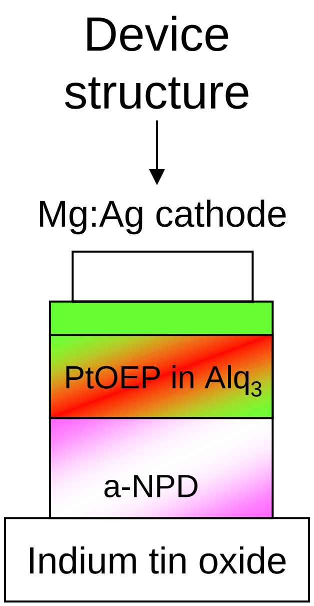
A red phosphor:

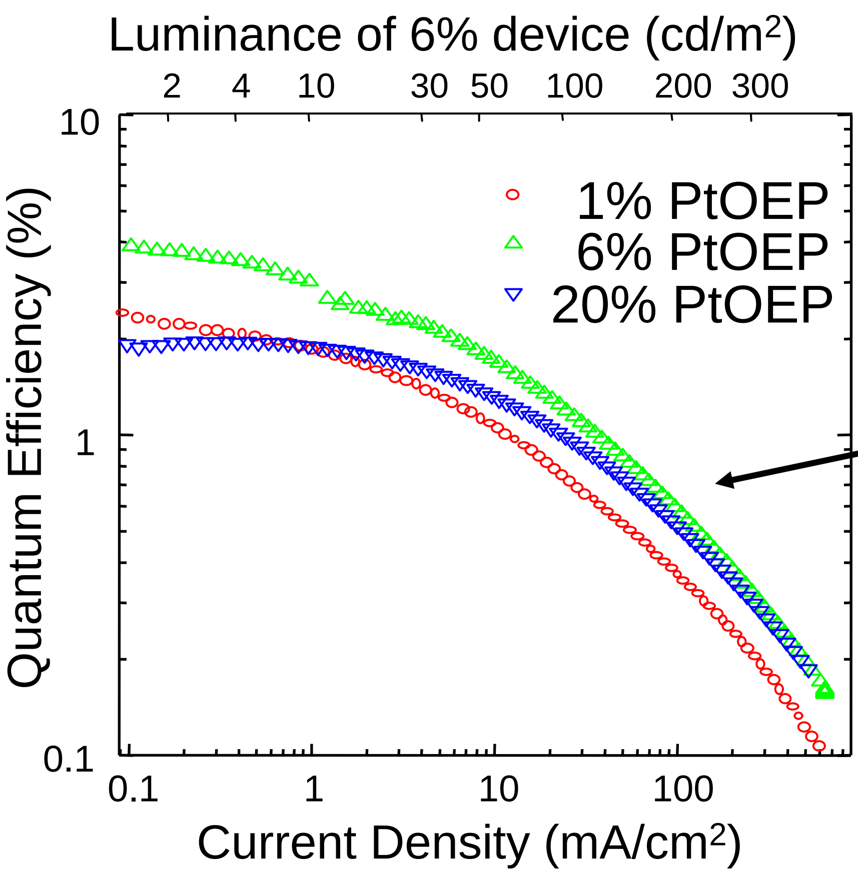
Platinum octaethylporphyrin

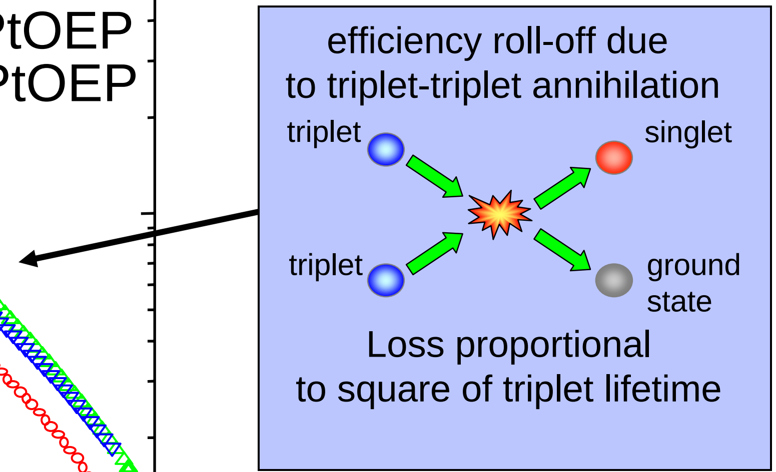
- Triplet lifetime ~100ms
- Peak external quantum efficiency in Alq_3 ~ 4%





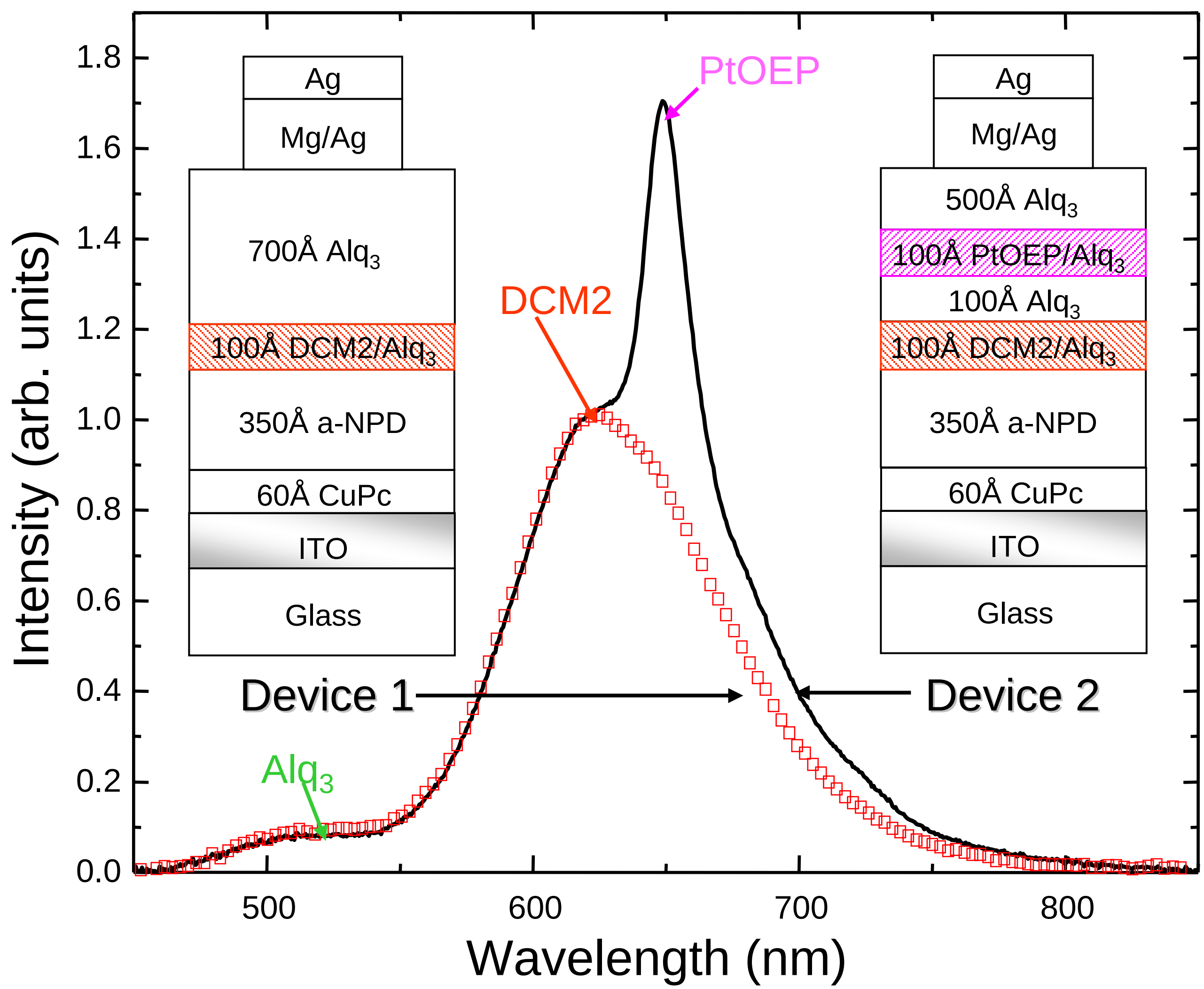






DOES PTOEP CAPTURE ALQ_3 TRIPLETS?

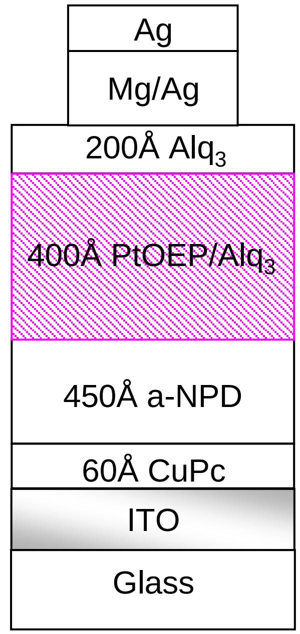
Put fluorescent dye DCM2 in exciton formation zone.



The singlet/triplet ratio in Alq_3

Device 1
emits from
singlets only

Device 2
emits from
singlets and triplets

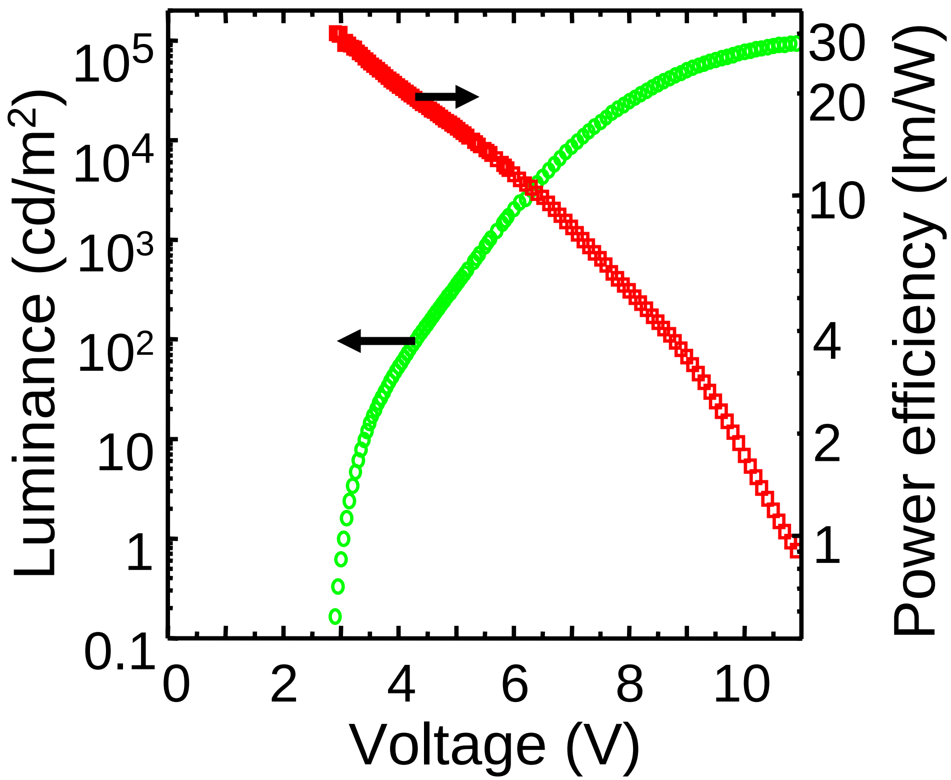


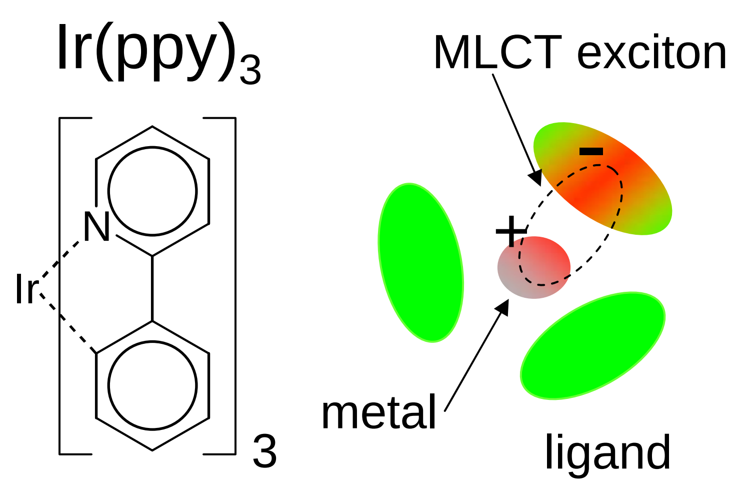
Compare ratio of EL emission from devices to get singlet fraction.
After correction for PL efficiency of DCM2 and PtOEP, get:
χ=(22±3)%

IMPROVED PHOSPHORS

Must reduce triplet lifetime to minimize T-T annihilation.
Increase MLCT component of excited state.

The first high efficiency green phosphor was iridium tris(2-phenylpyridine)

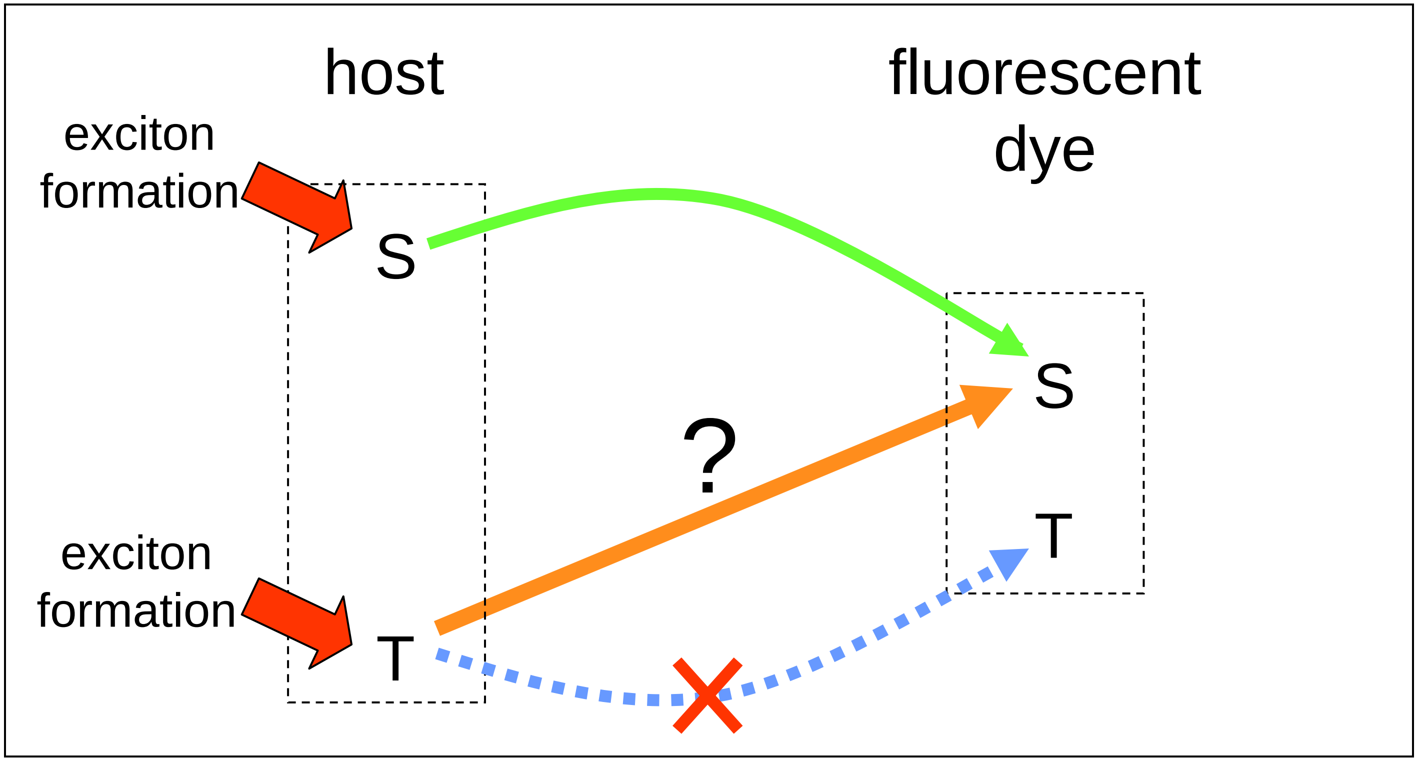




Broad green emission at λ ~ 515 nm.
Phosphorescent lifetime, τ ~ 1 ms.

TRIPLET-SINGLET ENERGY TRANSFER

There are many more fluorescent than phosphorescent materials.
Can we get high efficiency from a fluorescent dye?



Need to prevent exciting triplet state in fluorescent dye.
Want mechanism for triplet-singlet energy transfer.

Phosphor sensitized fluorescence

1. Triplet-singlet hopping transfer is disallowed
2. Triplet-singlet Förster transfer permitted if triplet relaxation on donor is allowed

i.e. triplet-singlet transfer is possible from a phosphorescent donor

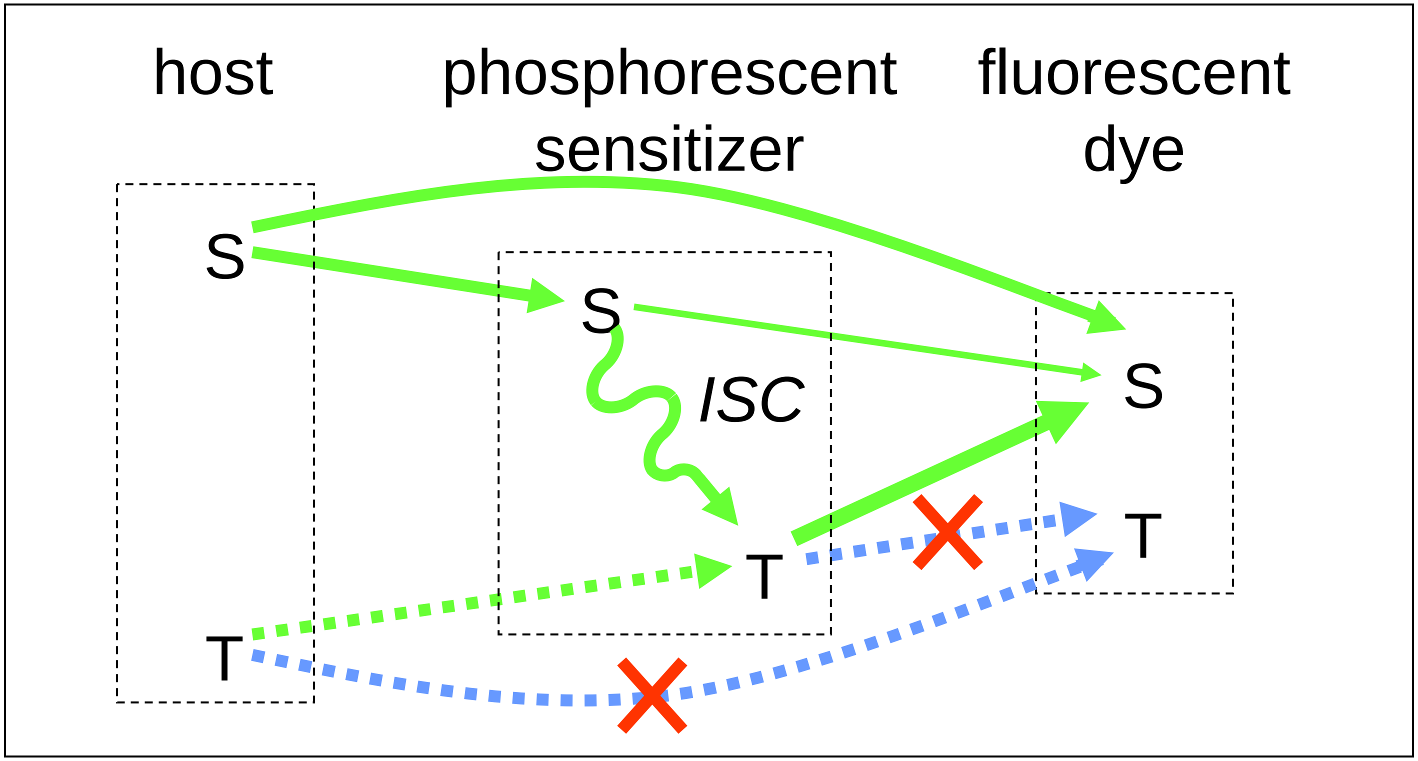
Predicted by Förster in 1959 (†)
Observed by Ermolaev and Sveshnikova in 1963 (§)

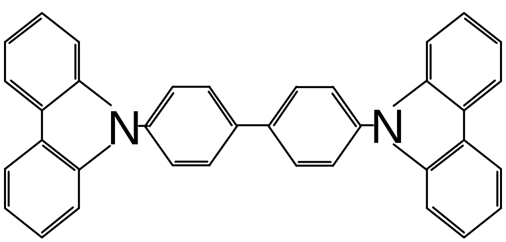
e.g. for triphenylamine as the donor and chrysoidine as the acceptor, in rigid media at 77K or 90K the interaction length is 52Å

(†) Förster, Th. *Dicussions of the Faraday Society* **27**, 7-17 (1959).

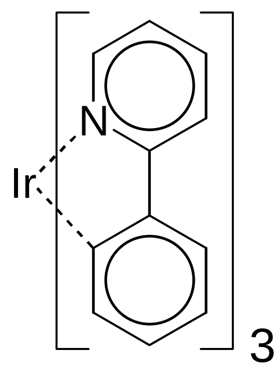
(§) Ermolaev, V.L. & Sveshnikova, E.B. *Doklady Akademii Nauk SSSR* **149**, 1295-1298 (1963).

IMPLEMENTATION OF TRIPLET-SINGLET ENERGY TRANSFER

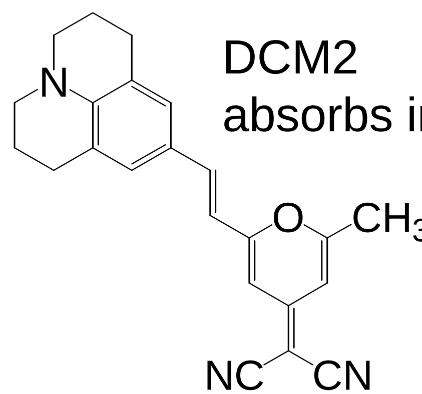




CBP

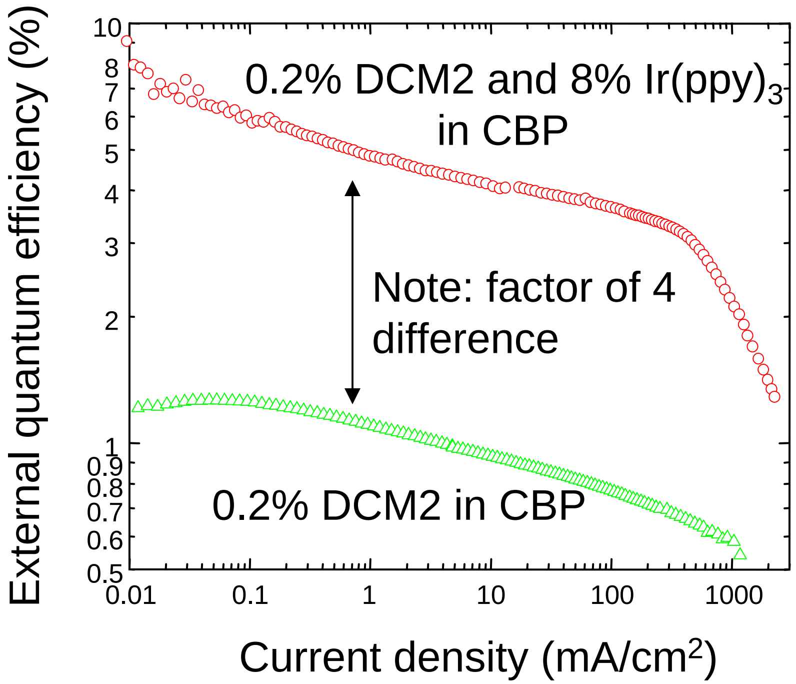


$Ir(ppy)_3$

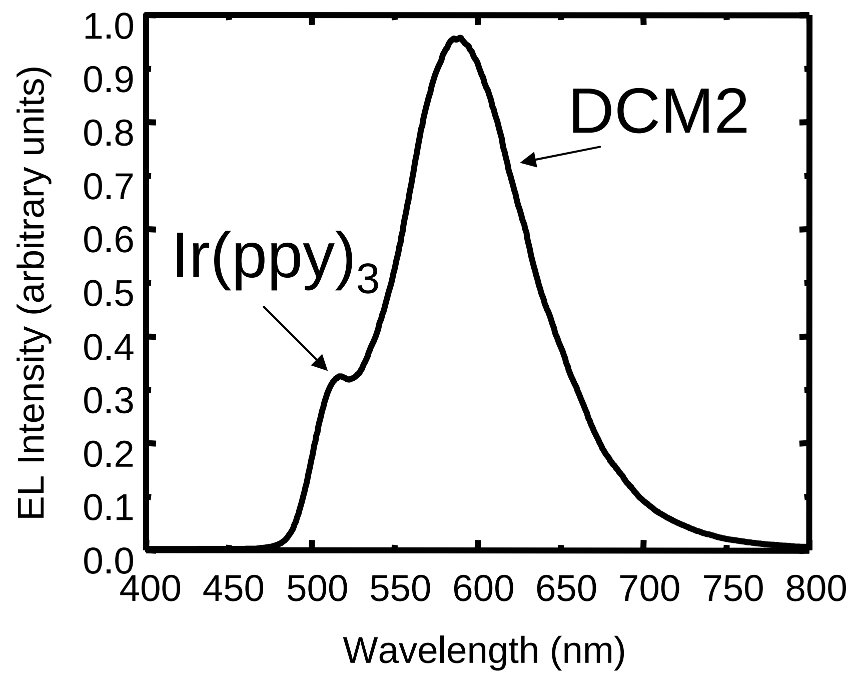


DCM2
absorbs in the green

DCM2 fluorescence sensitized by Ir(ppy)$_3$

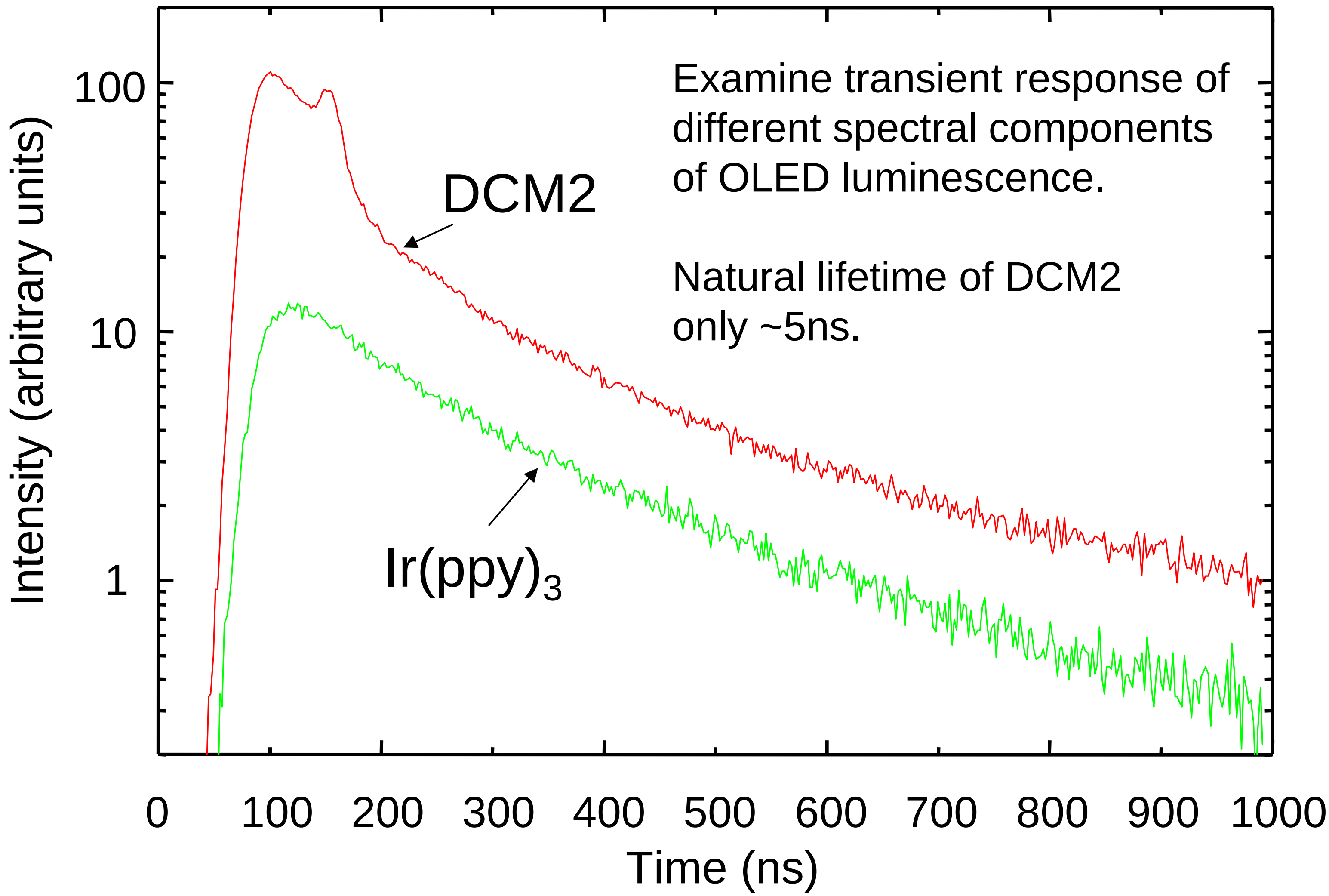


Roll-off in efficiency is due to charge trapping on DCM2 molecules



Nearly complete energy transfer from Ir(ppy)$_3$ to DCM2

OLED TRANSIENT RESPONSE

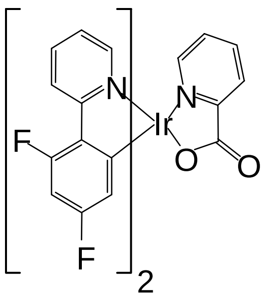


Delayed DCM2 fluorescence confirms sensitizing action of $Ir(ppy)_3$

B L U E

Problem: the most energetic charge transport hosts currently available have blue-green triplets.

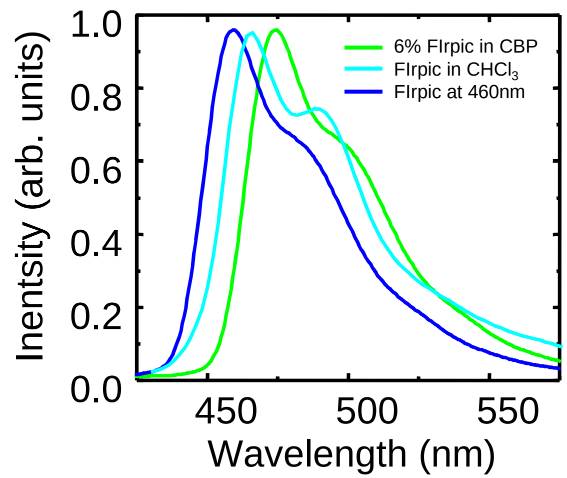
So to transfer energy to a blue phosphor, exciton transfer must be endothermic.

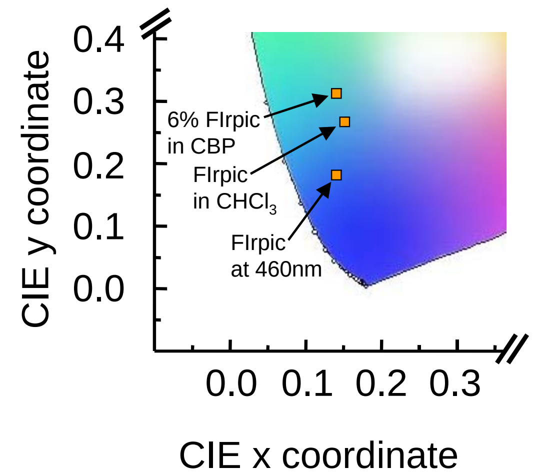


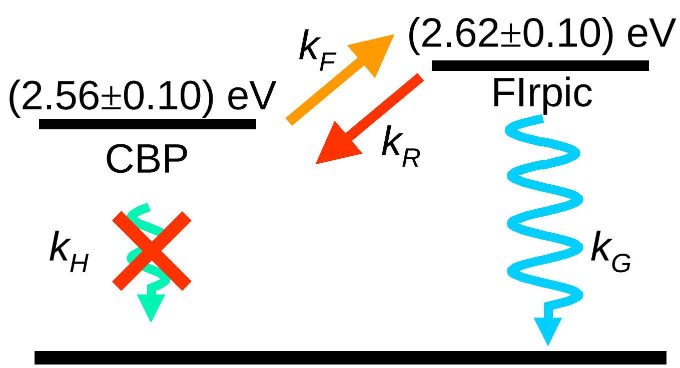
FIrpic (blue phosphor)

Peak wavelength 470nm

Triplet lifetime 10 μs



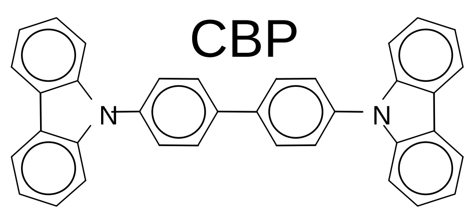




Possible to get efficient endothermic transfer

if decay of host triplet disallowed.

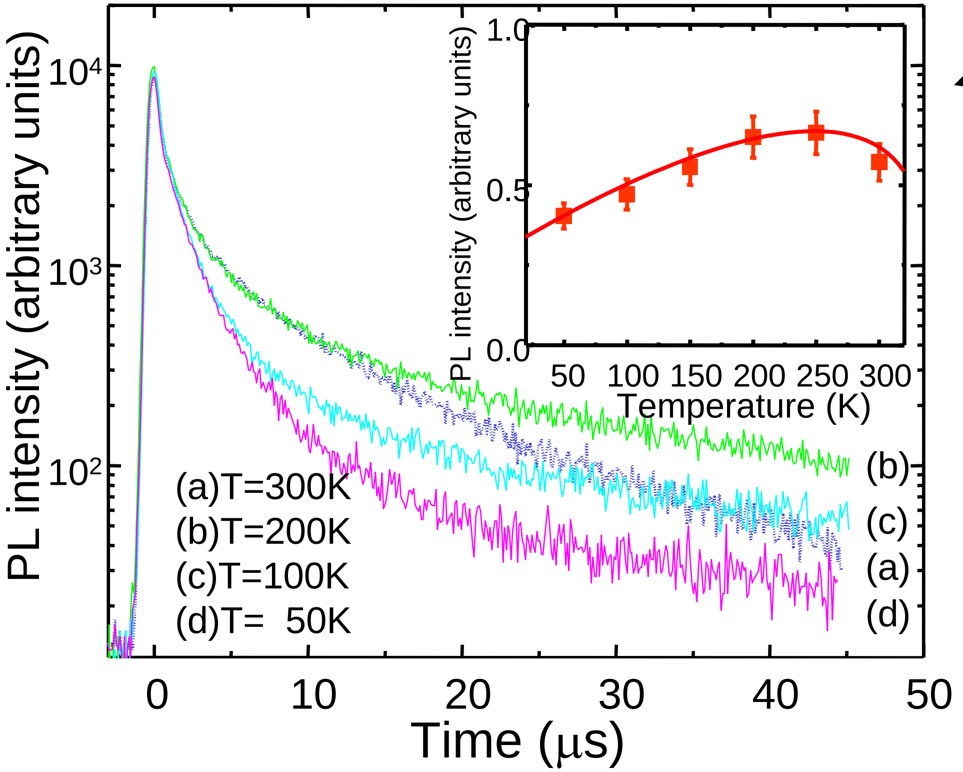
CBP



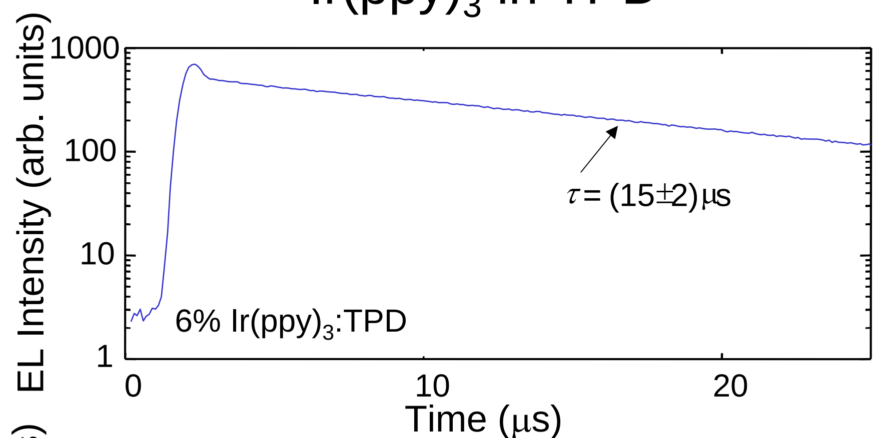
Host CBP triplet lifetime ~ 1s.

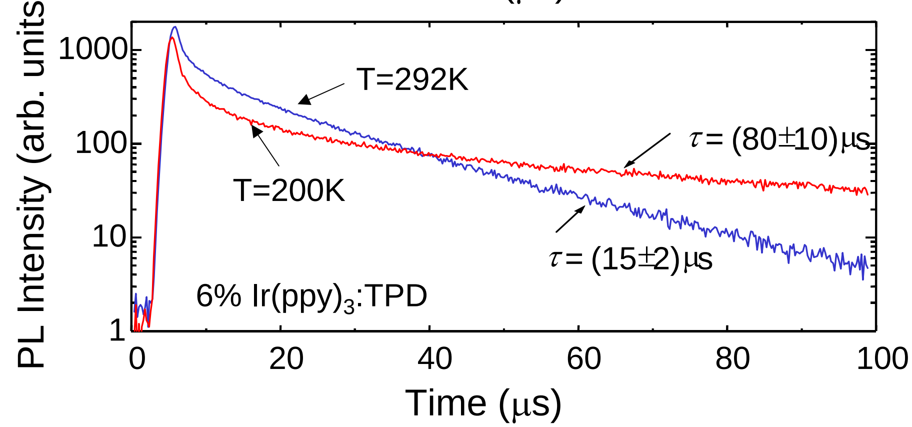
Transient response of endothermic transfer

Firpic in CBP



Ir(ppy)$_3$ in TPD

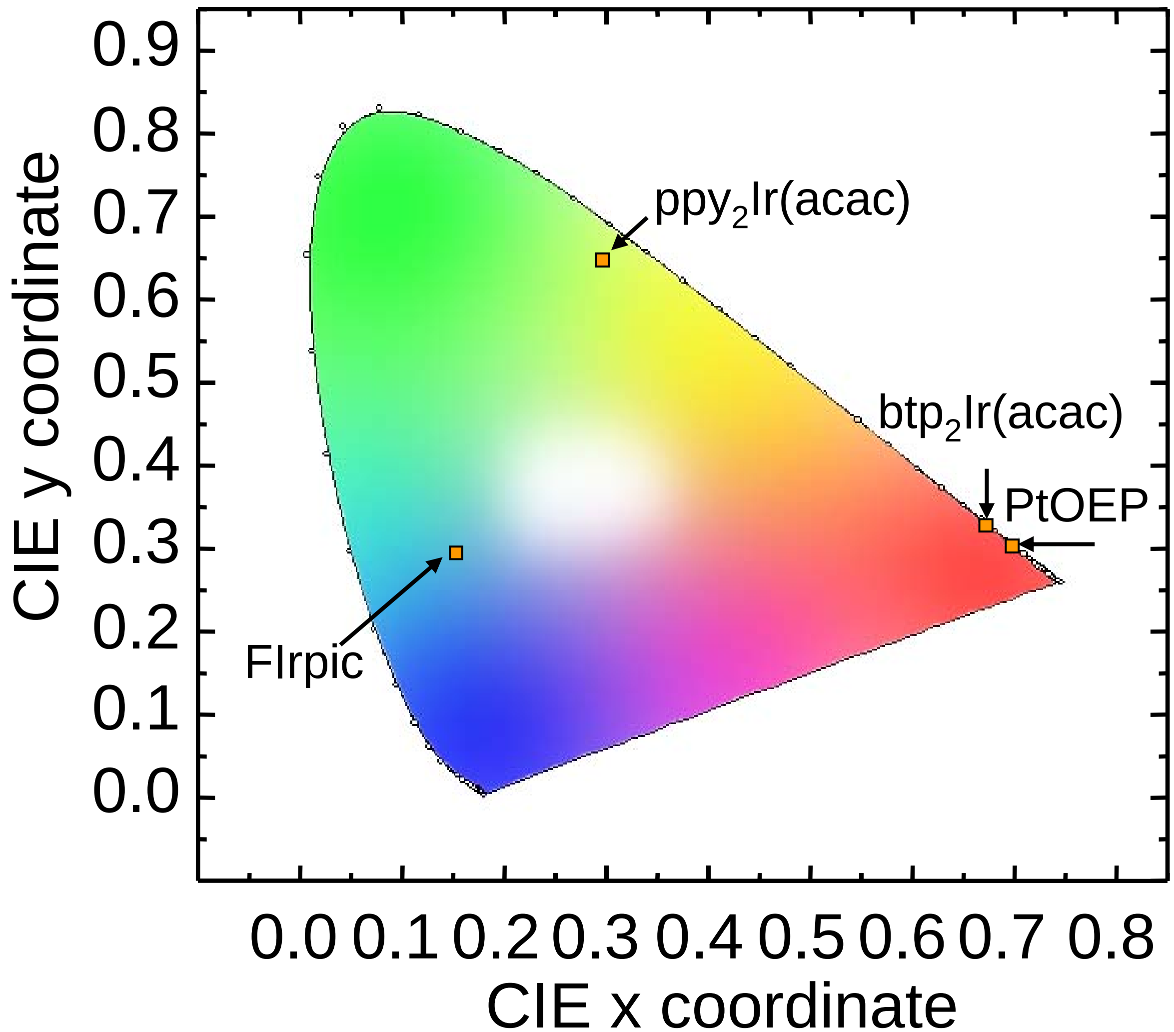




Efficiency of luminescence decreases below T=200K as energy transfer to phosphor is frozen out.

Transient response is also consistent with endothermic transfer:
At T=200K, apparent transient lifetime of FIrpic (includes endothermic transfer) >> natural lifetime (~10μs)

COLOR PURITY



Organic materials have broad luminescent spectra. Overcome in red and blue by shifting toward non-visible wavelengths.

OLED SUMMARY

Peak power efficiency in green is 60 lm/W
Peak quantum efficiency is 19%
(corresponds to ~100% internal)

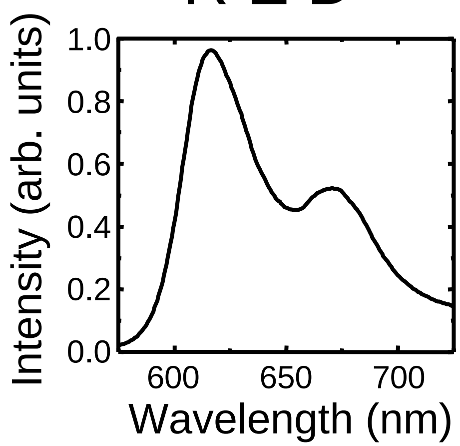
Largest remaining problem is operating voltage

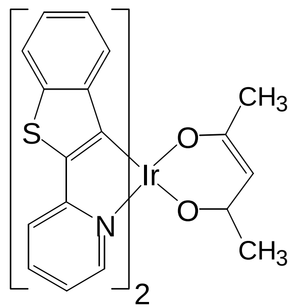
			J = 1 μA/cm^2				J = 1 mA/cm^2			
phosphor	host	Φ (lm/W)	η_P (lm/W)	$\eta_{Q\,ext}$	$\eta_{Q\,int}$	V_λ/V	η_P (lm/W)	$\eta_{Q\,ext}$	$\eta_{Q\,int}$	V_λ/V
$ppy_2Ir(acac)$	TAZ	530	60	0.19	0.87	0.60	20	0.15	0.68	0.25
btpIr(acac)	CBP	170	4	0.07	0.32	0.34	2.2	0.06	0.27	0.22
FIrpic	CBP	260	1.3	0.006	0.027	0.83	5.0	0.057	0.23	0.34
PtOEP	CBP	60	0.3	0.056	0.23	0.09	0.2	0.042	0.19	0.08

Table of phosphorescent device operating parameters

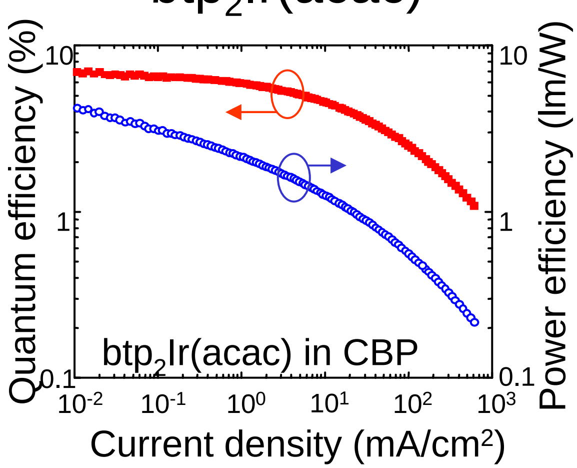
PHOSPHORESCENT DEVICE PERFORMANCE

R E D

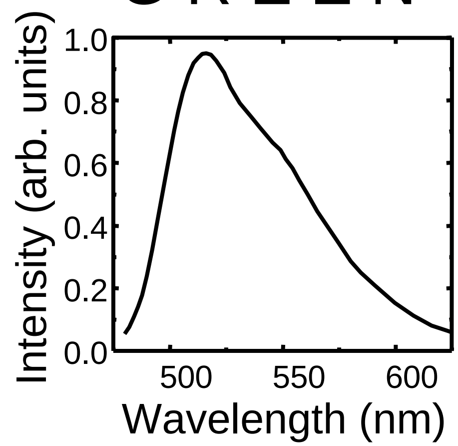


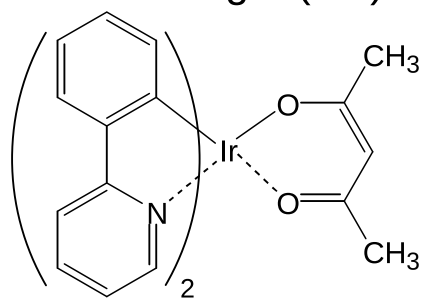


$btp_2Ir(acac)$

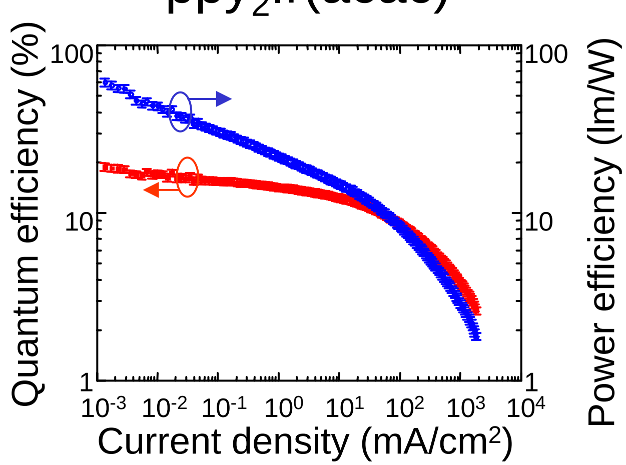


G R E E N

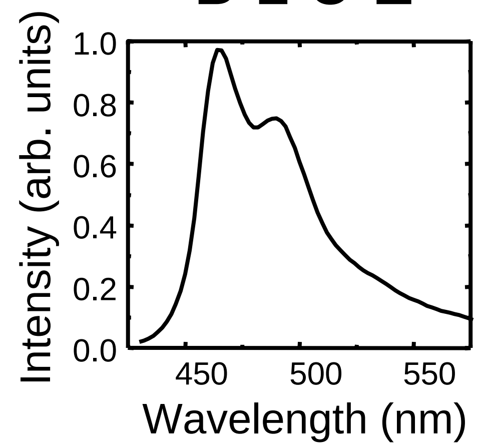


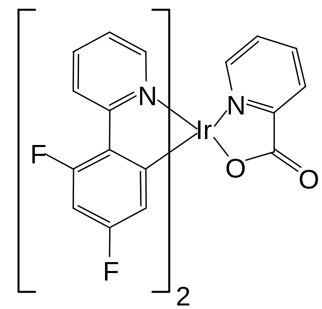


$ppy_2Ir(acac)$

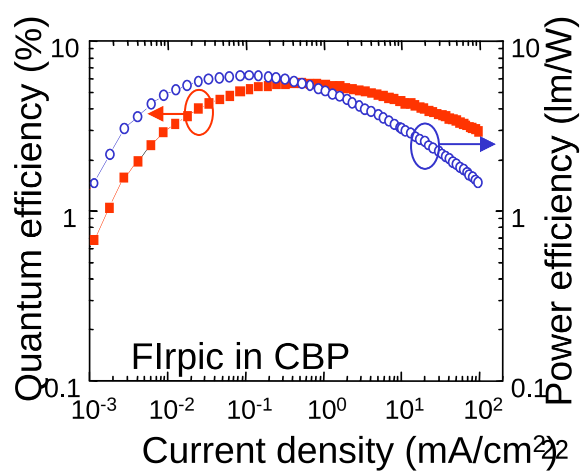


B L U E



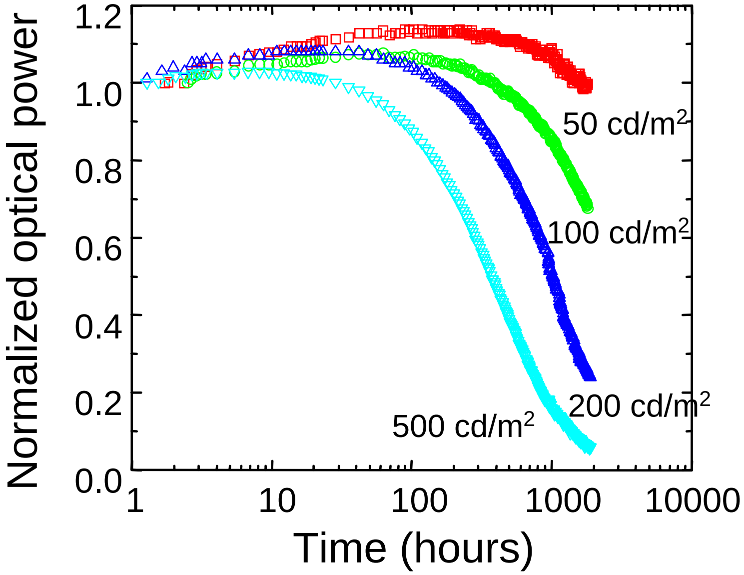


FIrpic

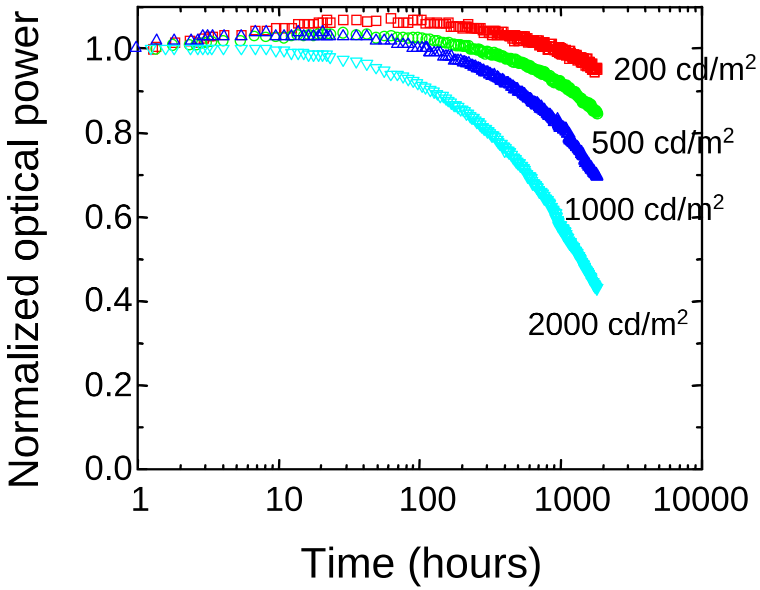


PHOSPHORESCENT STABILITY

Courtesy Ray Kwong and UDC



Red: BtpIr(acac) in CBP



Green: $(ppy)_2Ir(acac)$ in CBP

Phosphors should improve OLED stability
by rapidly removing triplet excitons
and lowering drive current required.