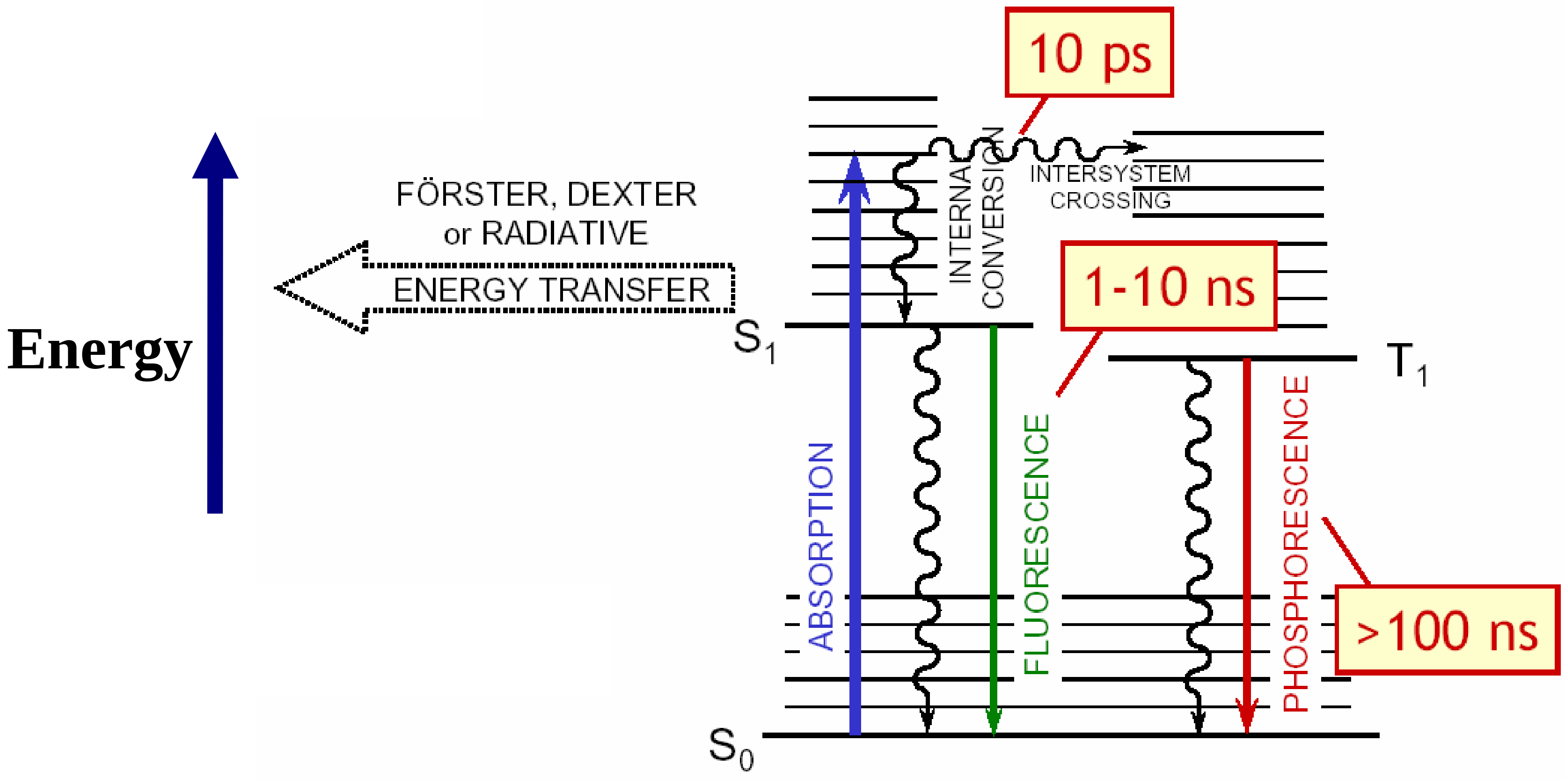
Organic light-emitting diodes

Fluorescent and Phosphorescent OLEDs

Fang-Chung Chen
Department of Photonics and Display Institute
National Chiao Tung University

Typical energy levels and energy-transfer process of a molecule



Why dope dyes in OLEDs?

Tune the color

- **change device color**
- **“tune” the color to a saturated one**

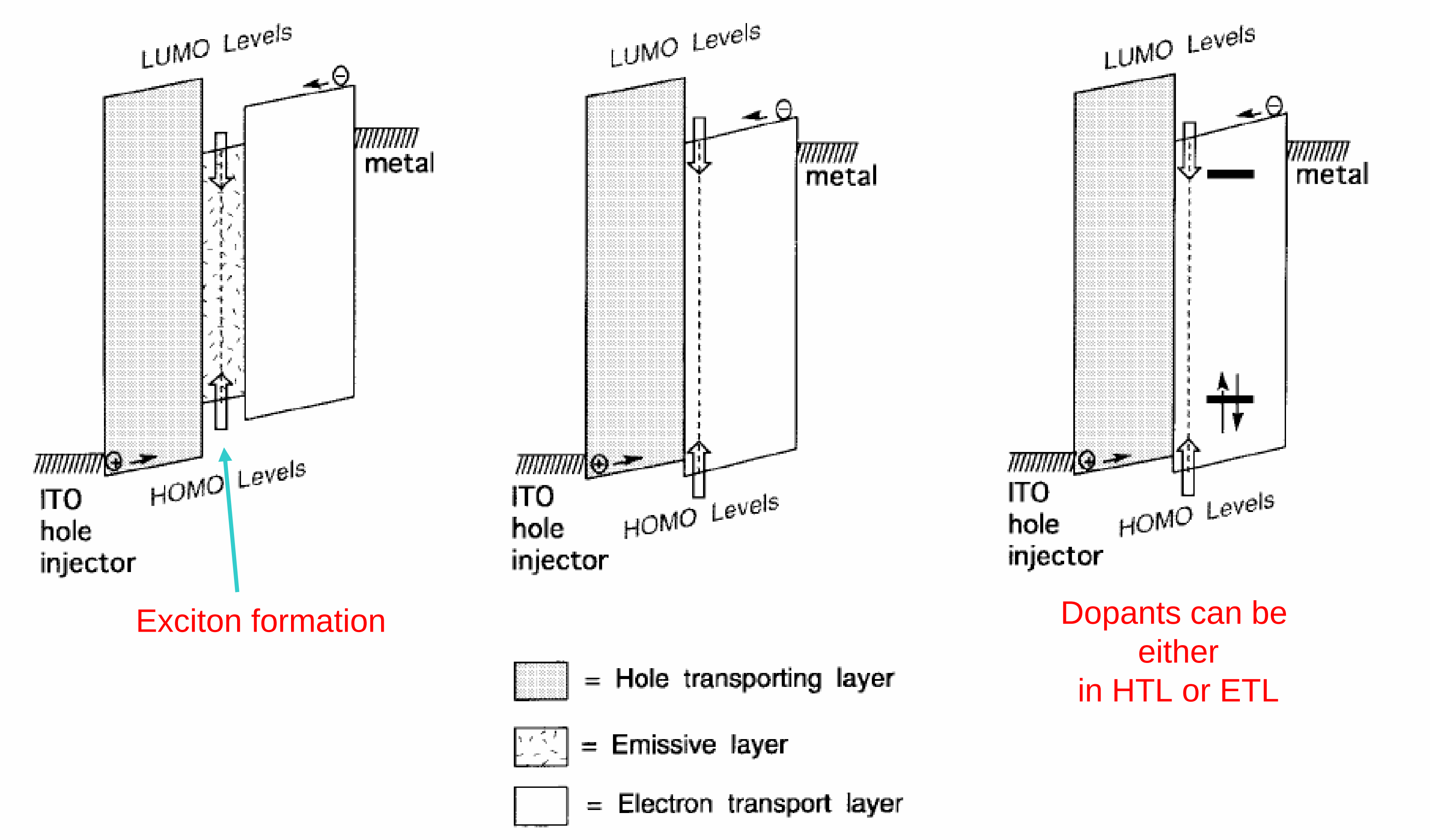
Enhance device efficiency

Enhance the device stability

Device structures with dopants

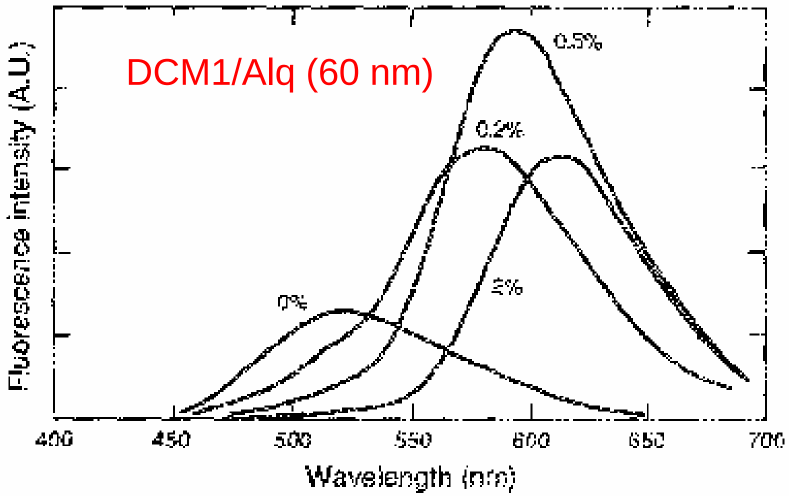
Double heterostructure device

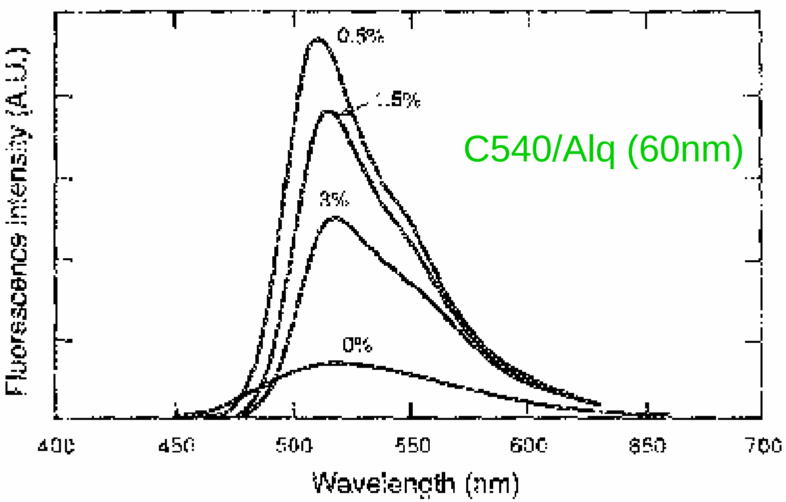
heterostructure device

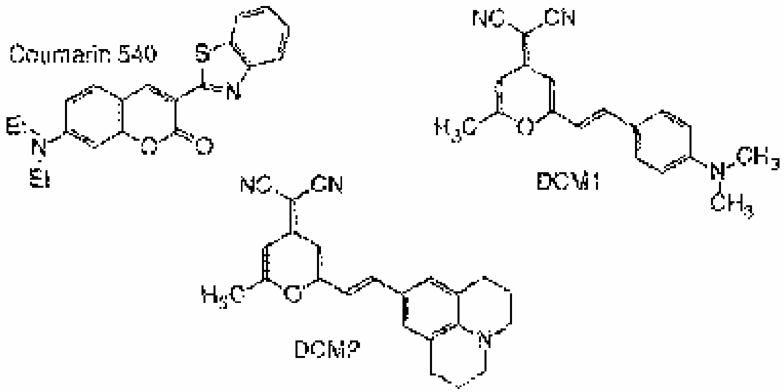


A. A. Shoustikov *et al*. IEEE J. Sel. Top. Qunantum Electronics, 4, 3 (1998)

The photoluminescent spectra of the doped device

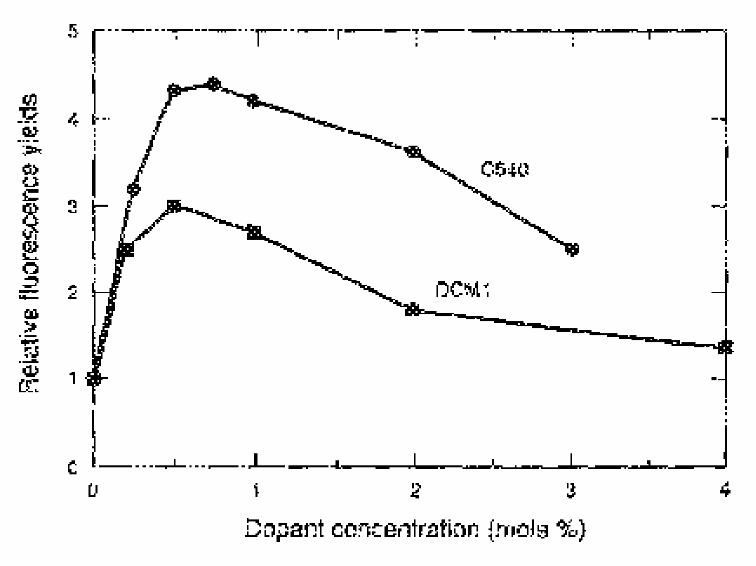




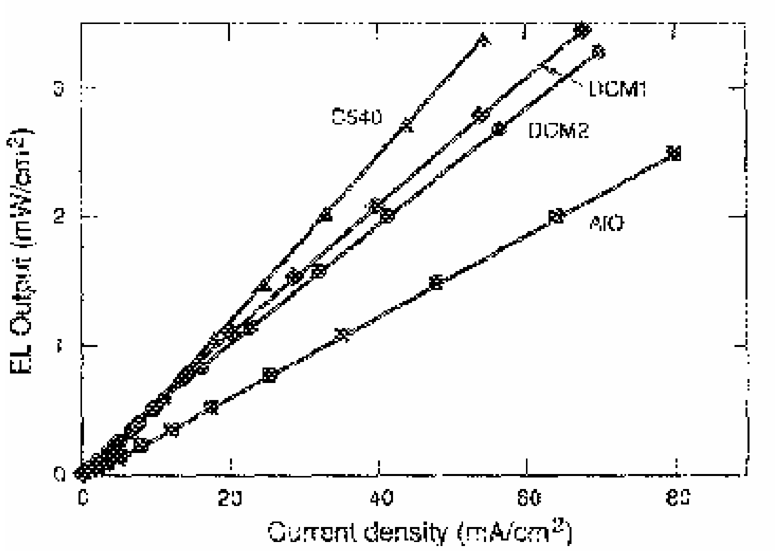


C. W. Tang *et al*. JAP 85, 3610 (1989)

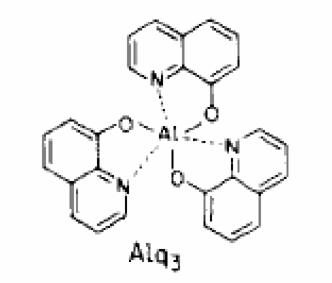
Dye doping level vs Quantum Efficiency



Device Efficiency



Matrix



The Φ_F of pure Alq_3 ~ 8%

$A^* + A \longrightarrow A_2^*$ (A_2^* = excimer)

Excimer :dimer formed in the excimeric state; monomers in the ground state

C. W. Tang *et al*. JAP 85, 3610 (1989)

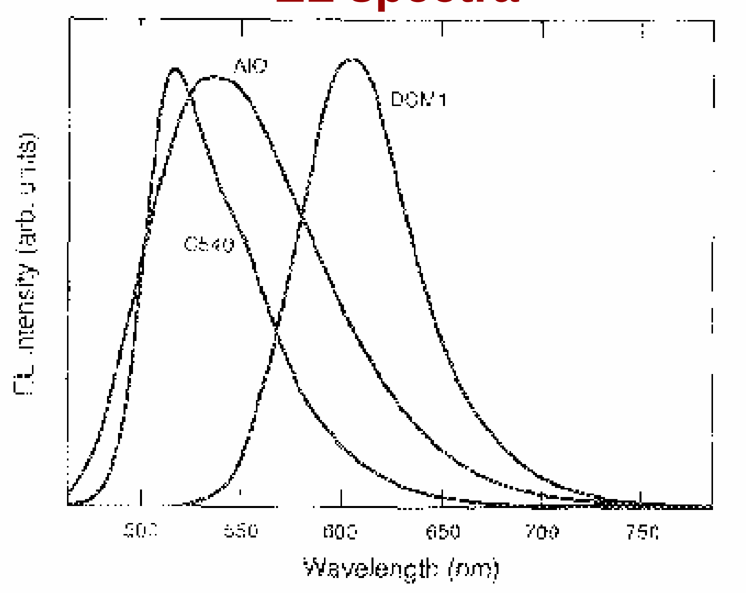
EL spectra and device efficiency

TABLE I. Efficiencies of organic electroluminescent cells.

Emitter	Alq	C540/Alq	DCM1/Alq	DCM2/Alq
Emission wavelength (nm)	540	510	570–620[a]	610–650[a]
EL efficiency (W/A)	0.031	0.061[b]	0.052[b]	0.049[b]
EL quantum efficiency (photon/electron)	0.013	0.025[b]	0.023[b]	0.023[b]

[a]Concentration dependent.
[b]Optimally doped (see text).

EL spectra



C. W. Tang *et al*. JAP 85, 3610 (1989)

The enhancement of the efficiency

$$\eta_{ext} = \eta_{int}\,\eta_p = \gamma\ \eta_r\ \varphi_f\,\eta_p$$

Due to

the enhancement of φ_f

and the probability for hole-electron recombination (γ)

η_{ext} : **external quantum efficiency**

η_{int} : **internal quantum efficiency**

η_p : **light out-coupling efficiency**

γ : **charge carrier balance factor (e/h)**

η_r : **efficiency of exciton production**

φ_f : **internal quantum efficiency luminescence**

Processes lead to the dopant emission

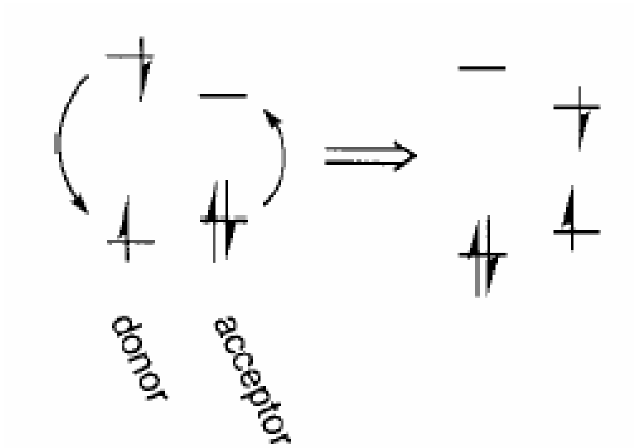
Förster energy transfer

Dexter energy transfer

Carrier trapping

Förster Energy Transfer

A Coulombic interaction between the host exciton and the dopant (donor)



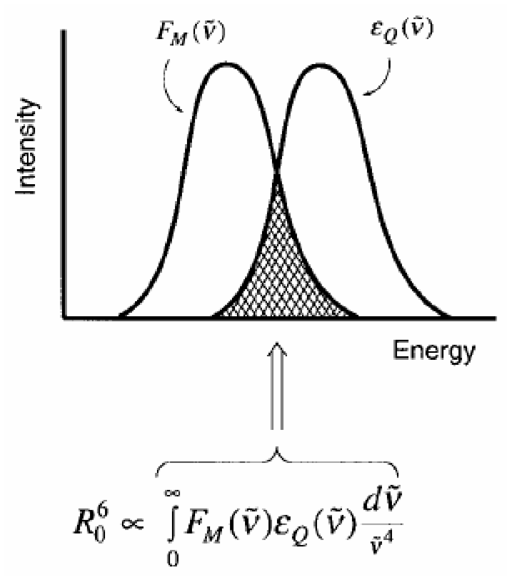
dipole-dipole coupling
fast process (~10^{-12} sec)
long distant process (up to 100 A)

Förster Energy Transfer

Förster energy transfer rate : $$\frac{d}{dt}P_n = \frac{0.5291\kappa^2}{n^4 N_a r^6 \tau_D}\int_0^{\infty} F_D(\tilde{\nu})\varepsilon_A(\tilde{\nu})\frac{d\tilde{\nu}}{\tilde{\nu}^4}$$

The degree of the spectral overlap

κ^2: an orientation factor
n : refraction index
N_a : Avagardro's number
r : the donor acceptor distant
τ_D : donor lifetime
$F_D(\nu)$: fluorescent spectrum of the donor
$\varepsilon_A(\nu)$: absorption spectrum of the acceptor



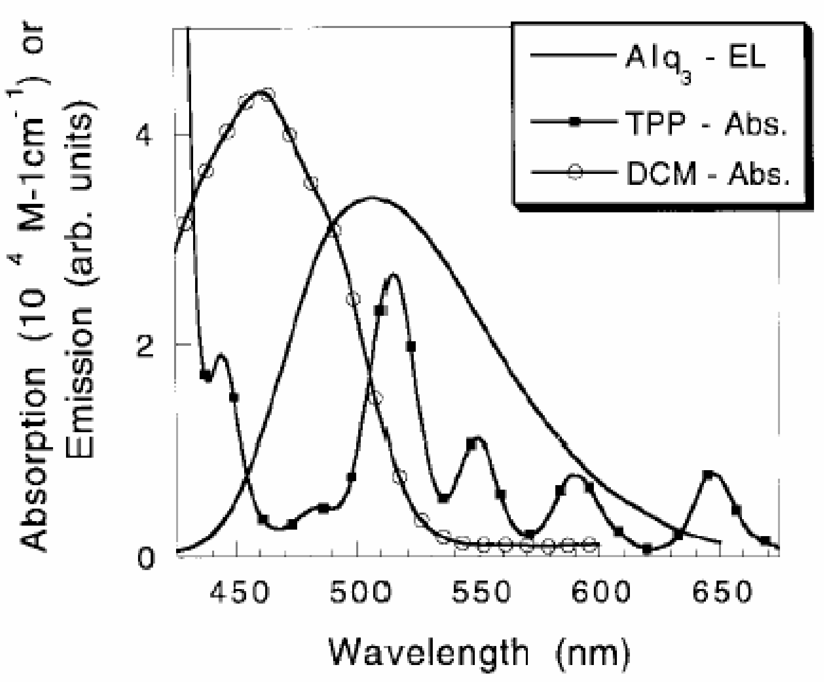
Förster radius : $$R_0^6 = \frac{0.5291\kappa^2}{n^4 N_a}\int_0^{\infty} F_D(\tilde{\nu})\varepsilon_A(\tilde{\nu})\frac{d\tilde{\nu}}{\tilde{\nu}^4}$$

The distance between D&A at which the probability of intermolecular energy transfer equals that of relaxation of the donor by fluorescence

Quantum yield : $$\Phi_{PL} = \int_0^{\infty} F_D(\tilde{\nu})\, d\tilde{\nu}.$$

Förster Energy Transfer -- Example

A = -log (I/I$_o$)
A =εbc
ε: extinction coefficient
b : absorption length
c : concentration



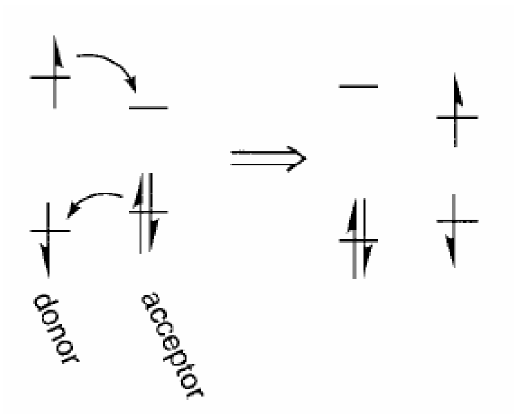
Förster Energy Transfer -- Example

FÖRSTER RADII FOR A SERIES OF DONORS AND ACCEPTORS USED IN OLED'S. SEE SCHEME FOR DESCRIPTIONS OF COMPOUNDS

Extinction coefficient, $mol^{-1}dm^{3}cm^{-1}$, (λ_{max}, solvent)	Acceptor (dye dopant)	Donor (Host)	R_0 (Å)
9.3×10^4 (618nm, DMSO)	Indigo	Alq_3	29
"	"	Alx_3	16
840 (538nm, toluene)	C_{60}	Alq_3	22
3.0×10^4 (634nm, DMSO)	BIS-OH	Alq_3	37
"	BIS-OH	Alx_3	21
2.3×10^4 (516 nm, toluene)	Tetraphenylporphyrin	Alq_3	33
1.0×10^5 (530nm, EtOH)	Rhodamine 6G	Alq_3	41
4.4×10^4 (461nm, toluene)	DCM	Alq_3	33

Dexter Energy Transfer

An electron-exchange interaction between the host exciton and the dopant



require electron exchange

→ short distant process (15-20 A)

Dexter energy transfer rate : $$\frac{d}{dt}P_n = \frac{2\pi}{\hbar}Z^2\int_0^{\infty} E_D(\tilde{\nu})A_A(\tilde{\nu})\,d\tilde{\nu}$$

normalized
spectral overlap

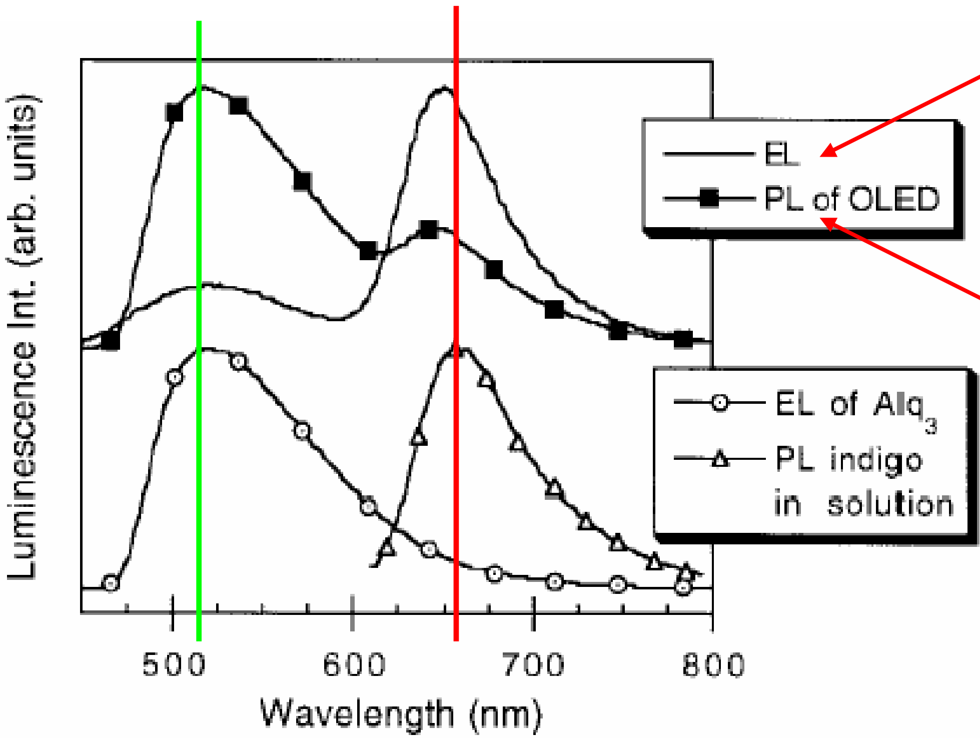
$$Z^2 \propto e^{-2r/L}$$

r : the donor acceptor distant
$E_D(\nu)$: donor emission spectrum
$A_A(\nu)$: acceptor absorption spectrum
L : the sum of the van del Waals radii of the donor and acceptor molecules

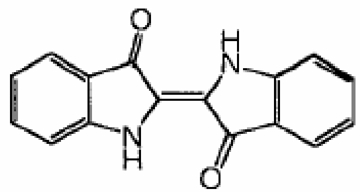
Energy Transfer vs Carrier trapping

energy transfer
+
carrier trapping

energy transfer

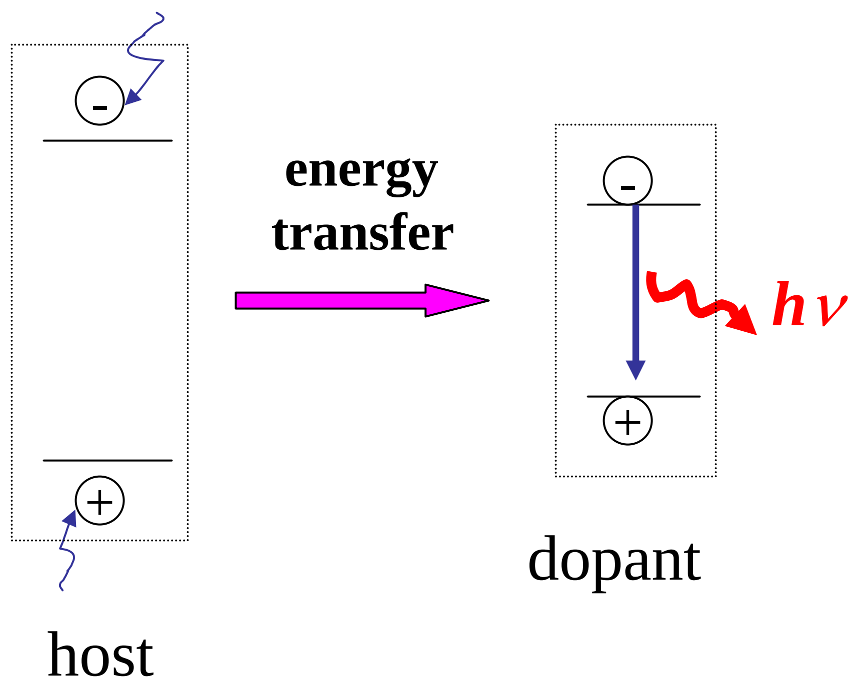


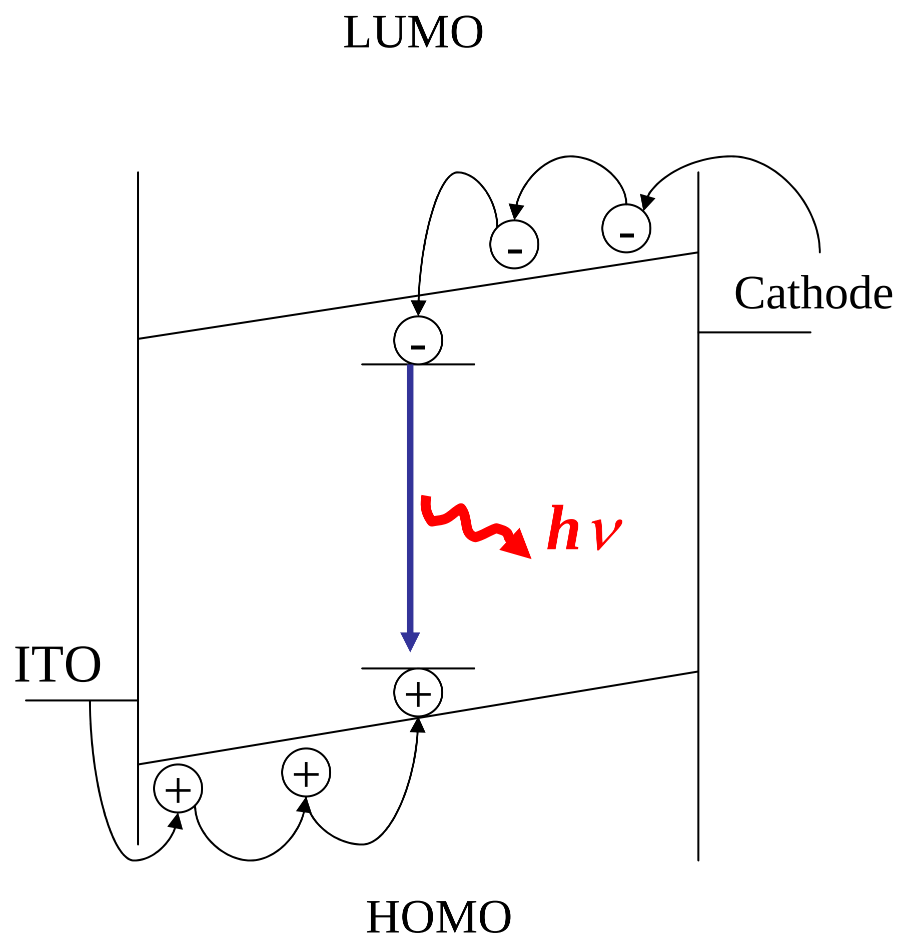
ITO/TPD/Alq_3-indigo/Mg-Ag



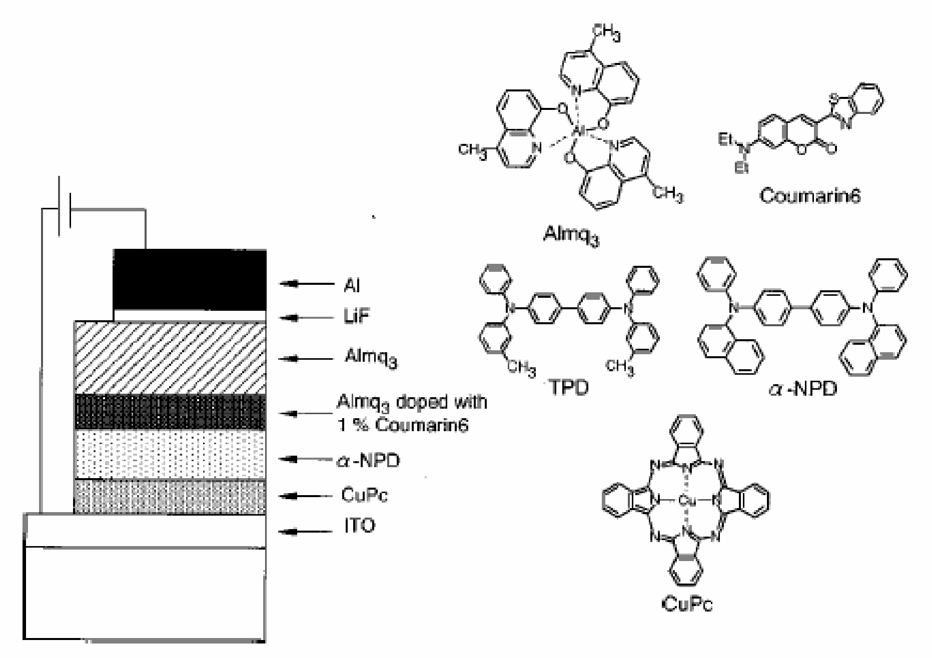
indigo

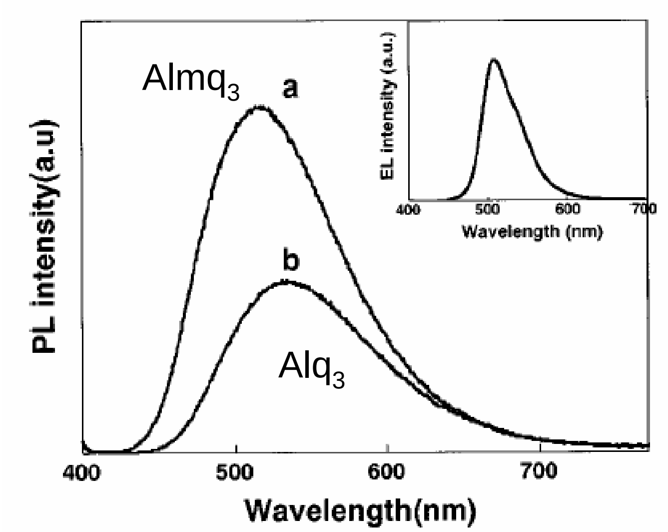
Energy Transfer vs Carrier trapping





Highly efficient organic EL device





QE ~ 7%

24 cd/A

Charge balance
High PL efficiency

T-T annihilation??

J. Kido *et al*. APL 73, 2721 (1998)

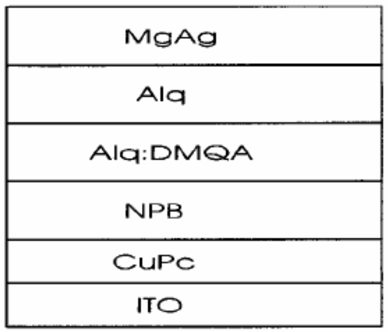
The enhancement of the stability

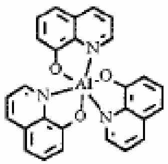
Higher efficiency

To prevent the crystallization of the glassy HTL or ETL

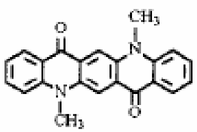
TABLE I. Luminance data of DMQA/Alq EL devices.

DMQA % in Alq	0.00	0.26	0.40	0.80	1.40	2.50
Lum. output (cd/m^2)	518	1147	1322	1462	1287	1027
Efficiency (cd/A)	2.59	5.74	6.61	7.31	6.44	5.14
CIE_x	0.3872	0.3876	0.3785	0.3922	0.4046	0.4095
CIE_y	0.5469	0.5858	0.5995	0.5901	0.5799	0.5742
EL peak (nm)	544	540	540	544	544	544
$T_{1/2}$ (h)	4200	7335	7500	7340	5450	3650

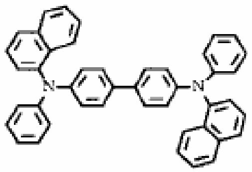




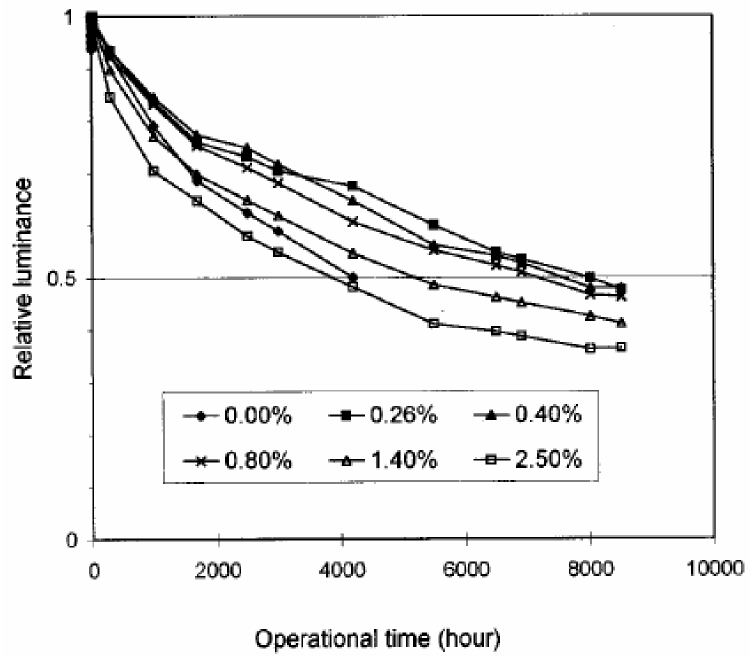
Alq



DMQA

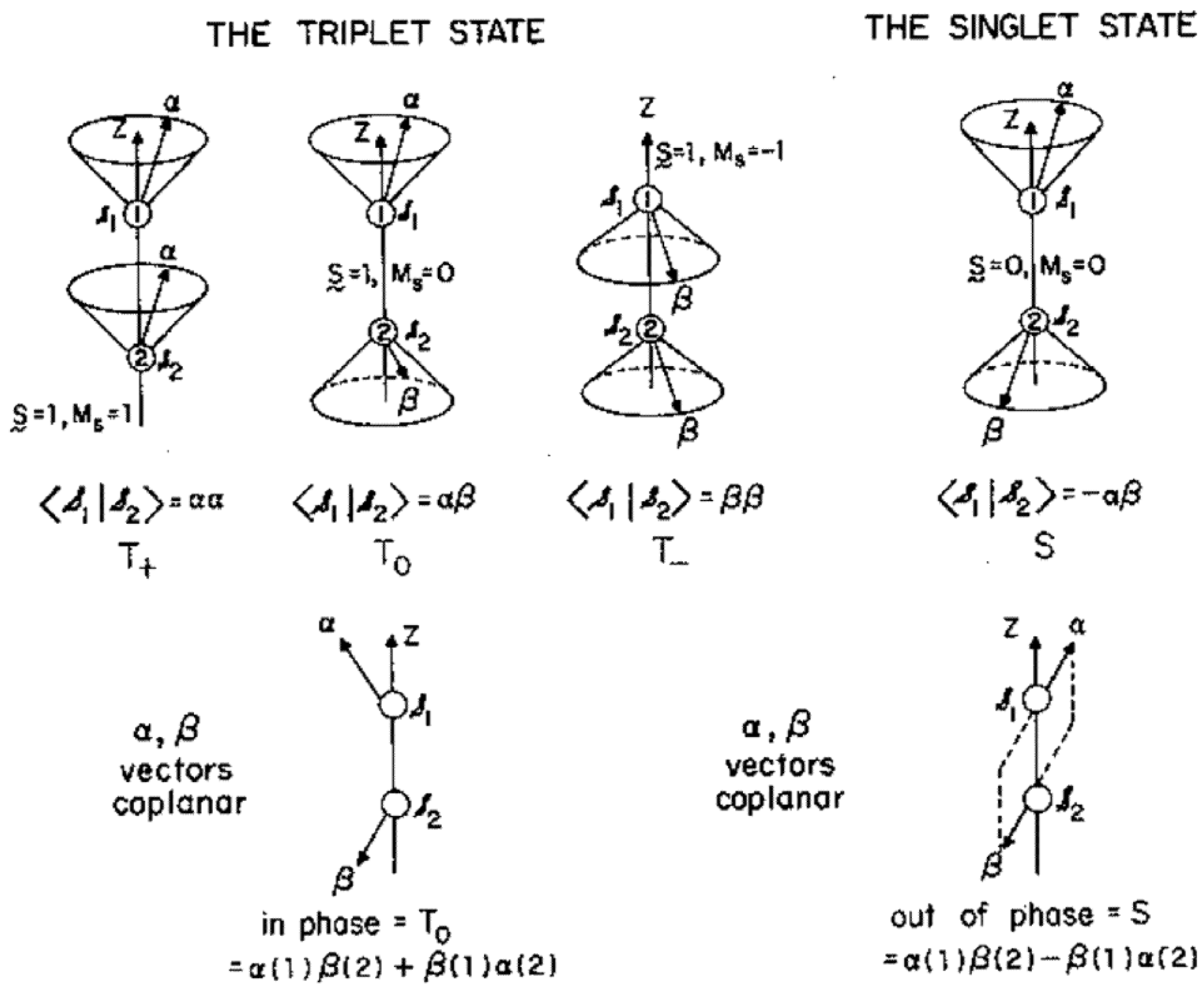


NPB



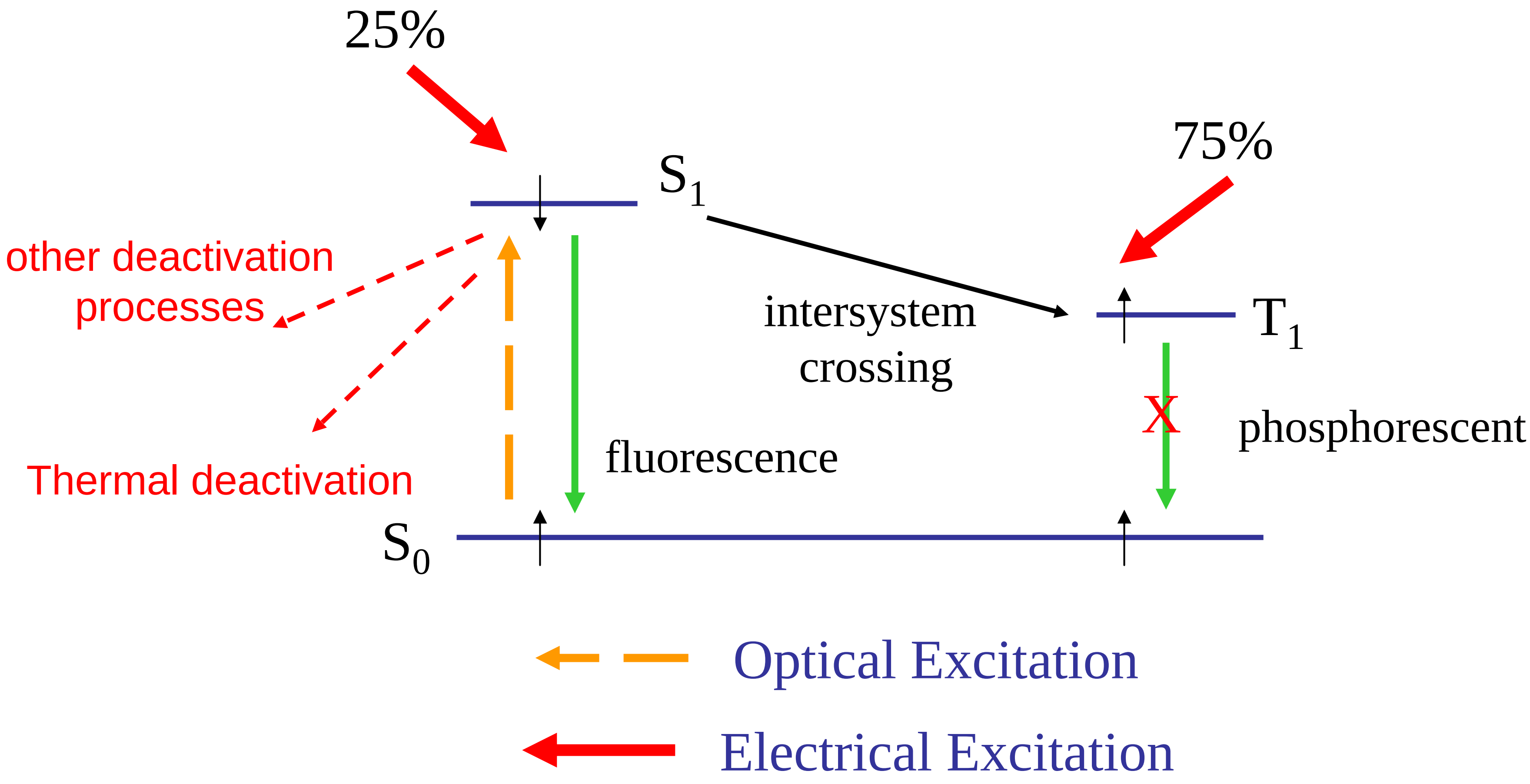
J. Shi & C. W. Tang APL, 70, 1665 (1997)

Singlet and Triplet



N. J. Turro, Modern Molecular Photochemistry, University Science Book, CA, 1991

The limitation of fluorescent OLEDs



internal quantum efficiency is limited at 25%

The enhancement of the efficiency

Phosphorescent dopants are doped into an OLED to harvest both single and triplet excitons

$$\eta_{ext} = \eta_{int}\,\eta_p = \gamma\ \eta_r\ \varphi_l\,\eta_p$$

Due to

the enhancement of η_r

from 25% to 100%

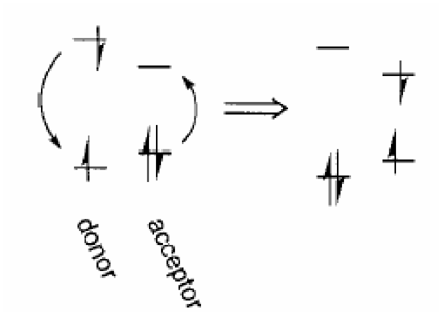
η_{ext} : external quantum efficiency
η_{int} : internal quantum efficiency
η_p : light out-coupling efficiency
γ : charge carrier balance factor (e/h)
η_r : efficiency of exciton production
φ_l : internal luminescent quantum efficiency

Processes lead to the dopant emission

Förster energy transfer
Dexter energy transfer
Carrier trapping

Förster energy transfer

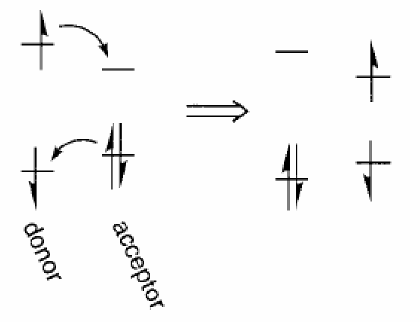
A Coulombic interaction between the host exciton (donor) and the dopant



dipole-dipole coupling
fast process
long distant process (up to 100 A)

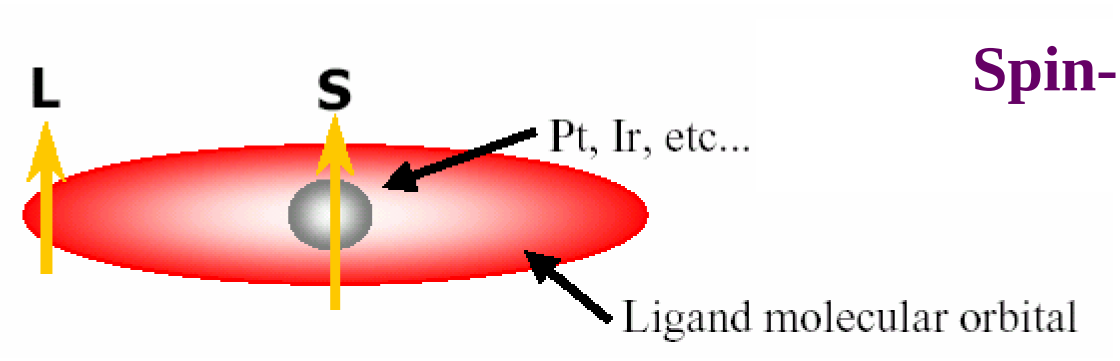
Dexter energy transfer

An electron-exchange interaction between the host exciton and the dopant



require electron exchange
→ short distant process (15-20 A)

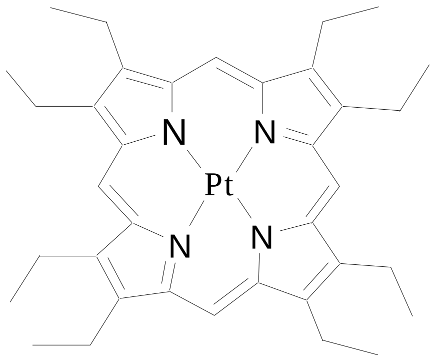
The use of metal-organic complexes with heavy transition metals



Spin-Orbit Coupling

$\propto$ atomic number Z ^{4}

enhance the efficiency of ISC and phosphorescent

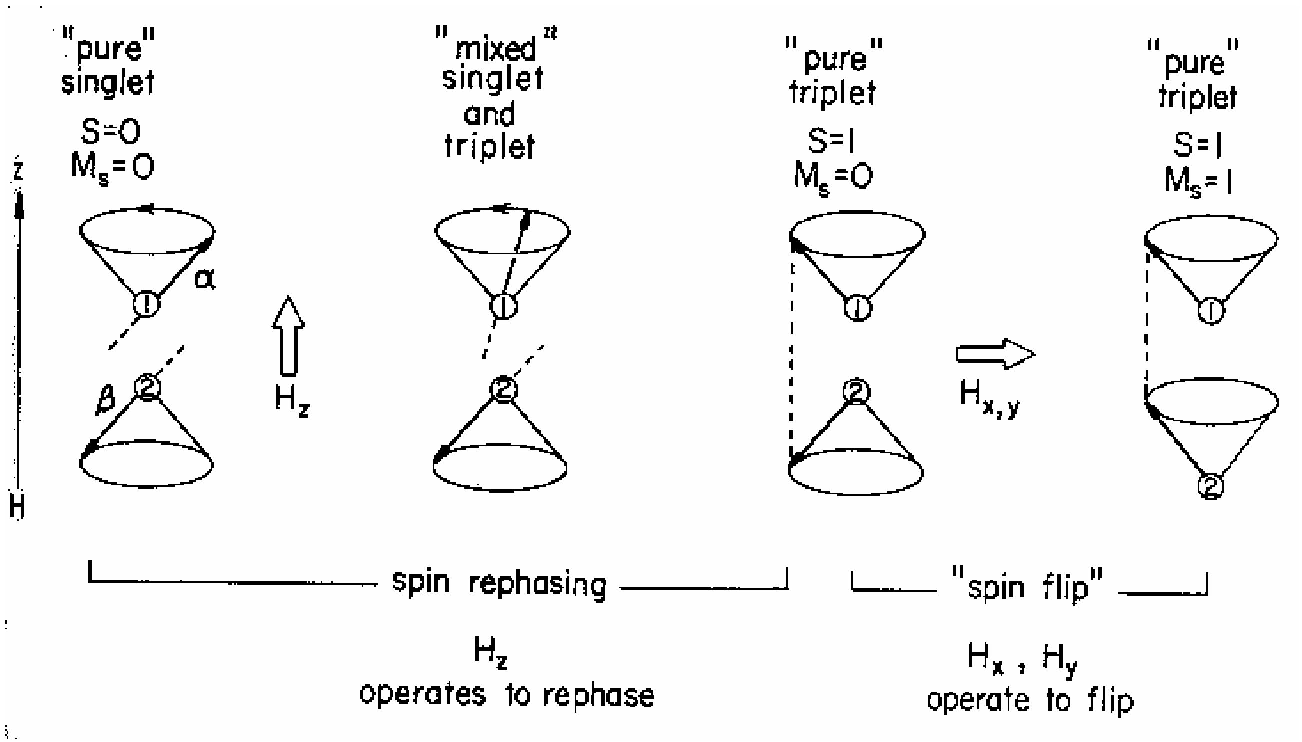


PtOEP

S. R. Forrest's group (Princeton University)
& M. E. Thompson's group
(University of Southern California)

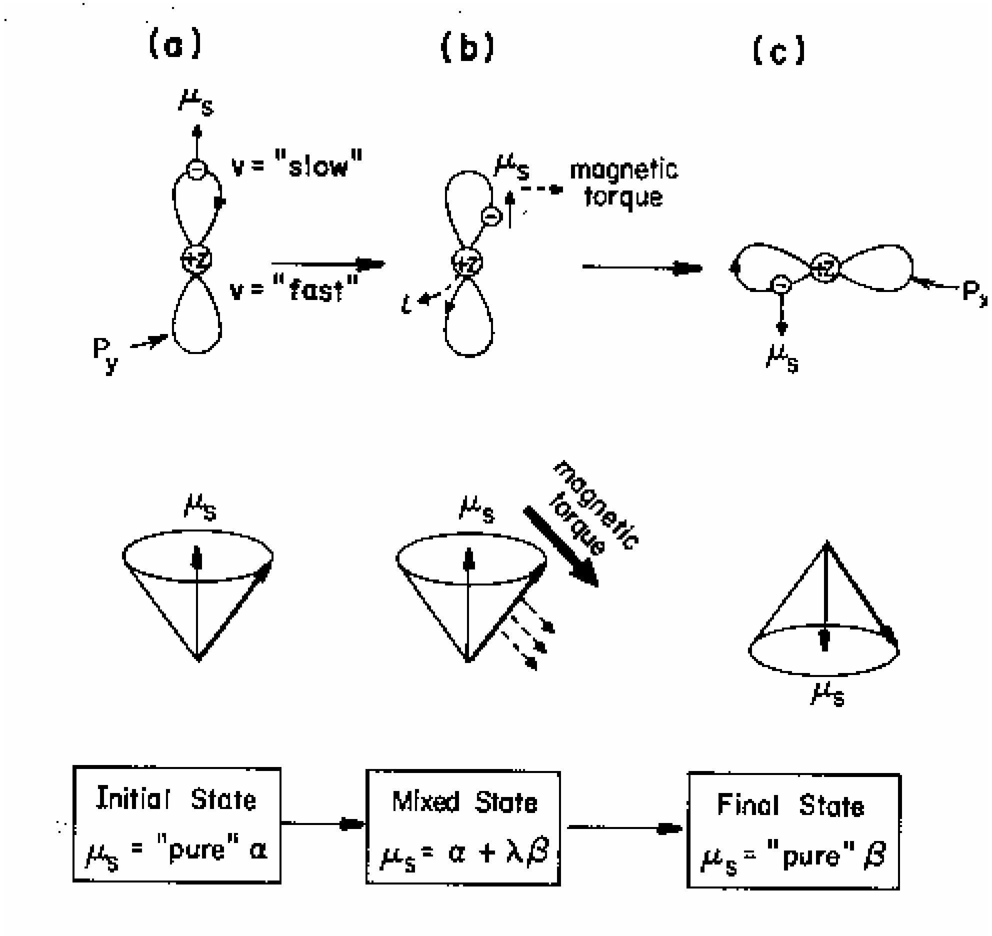
M. A. Baldo *et al*. Nature, **395**, 151 (1998)

Spin-Orbital Coupling



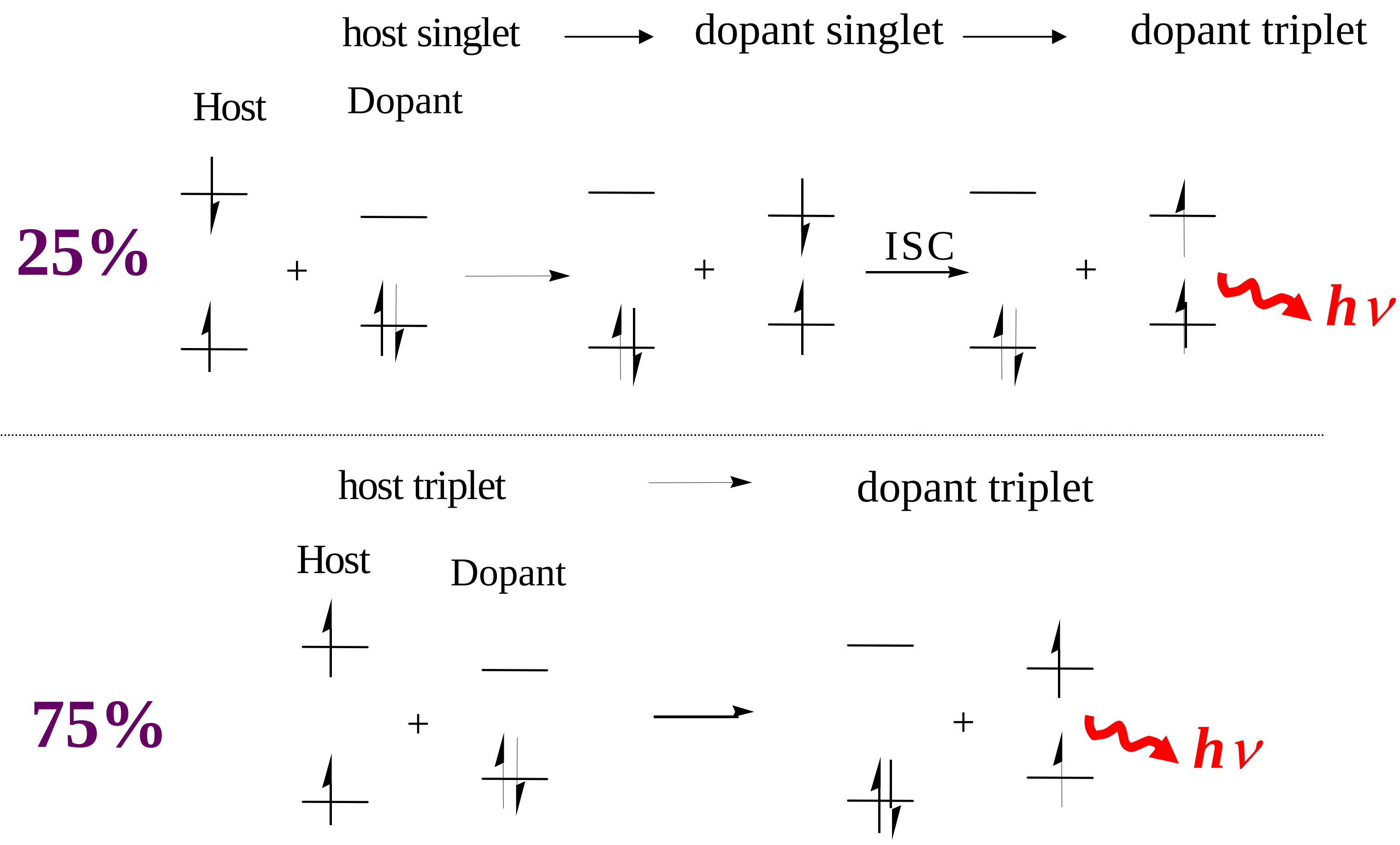
N. J. Turro, Modern Molecular Photochemistry, University Science Book, CA, 1991

Spin-Orbital Coupling



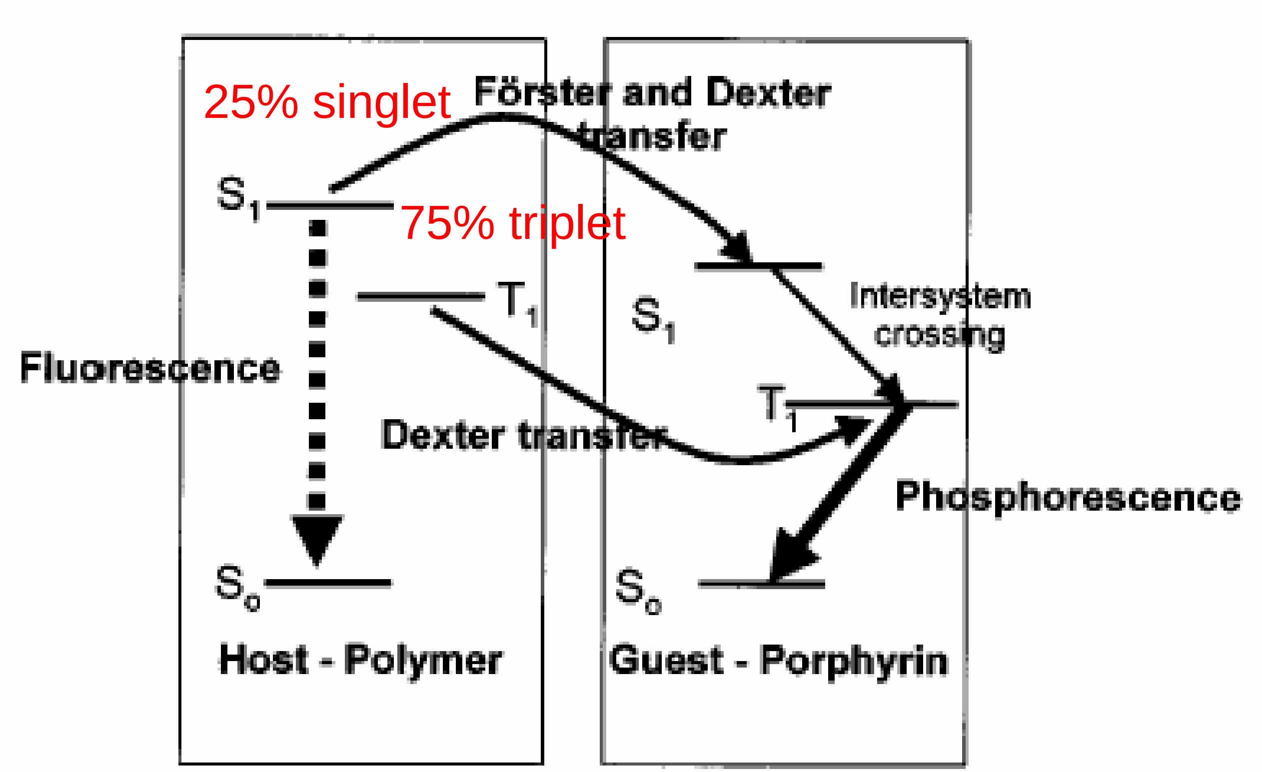
N. J. Turro, Modern Molecular Photochemistry, University Science Book, CA, 1991

Harvest singlet and triplet exctions by doping phosphorescent dye into the host material

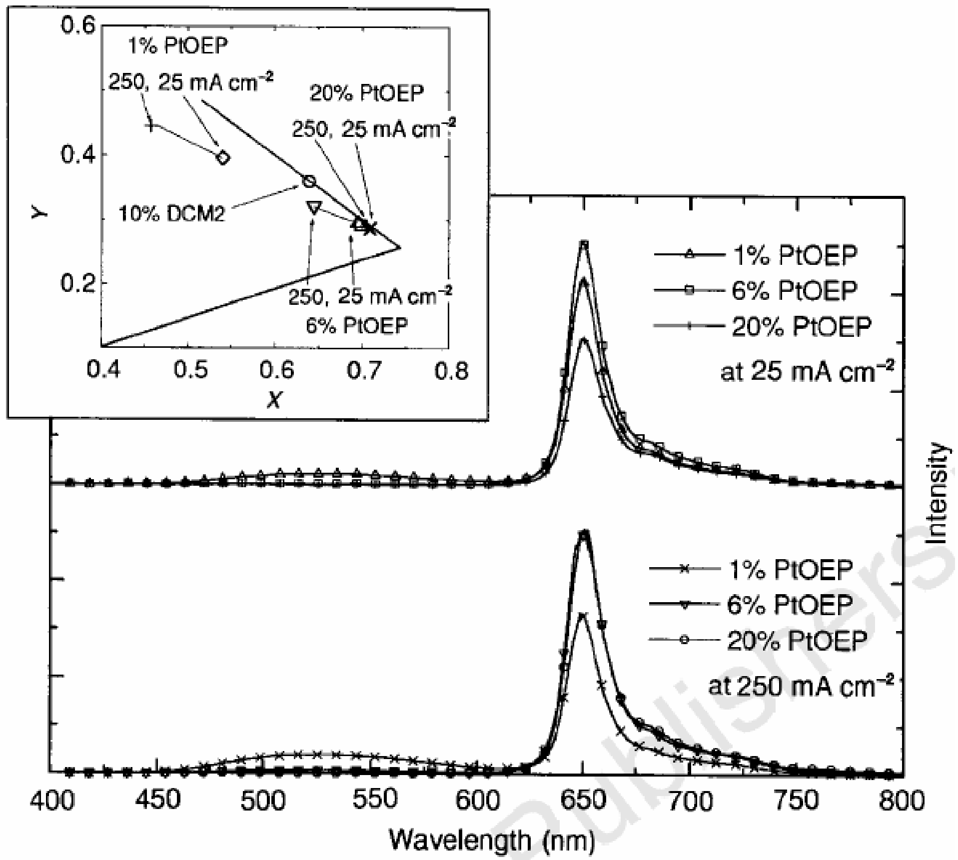


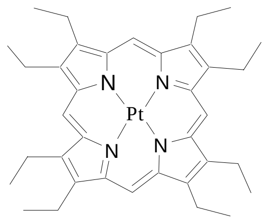
100% of excitons can contribute to EL

Harvest singlet and triplet exctions by doping phosphorescent dye into the host material

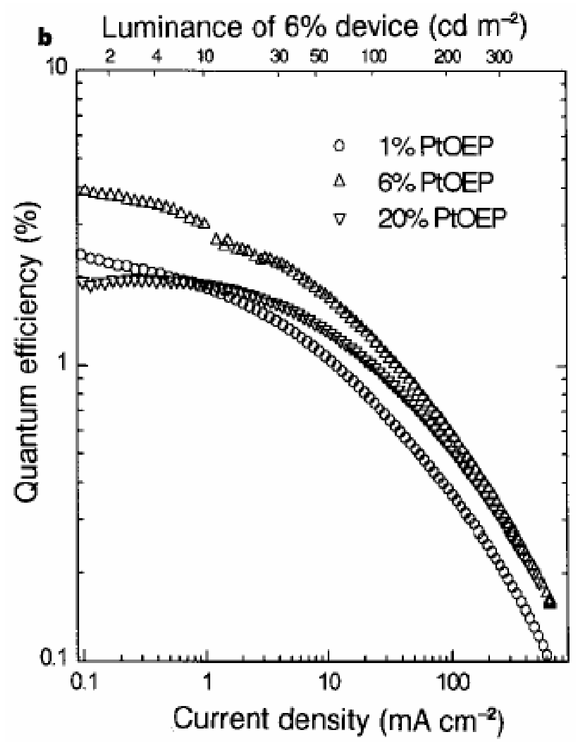


The first efficient phosphorescent OLED





PtOEP



ITO/α-NPD/Alq_3:6% PtOEP/Alq_3/Mg:Ag

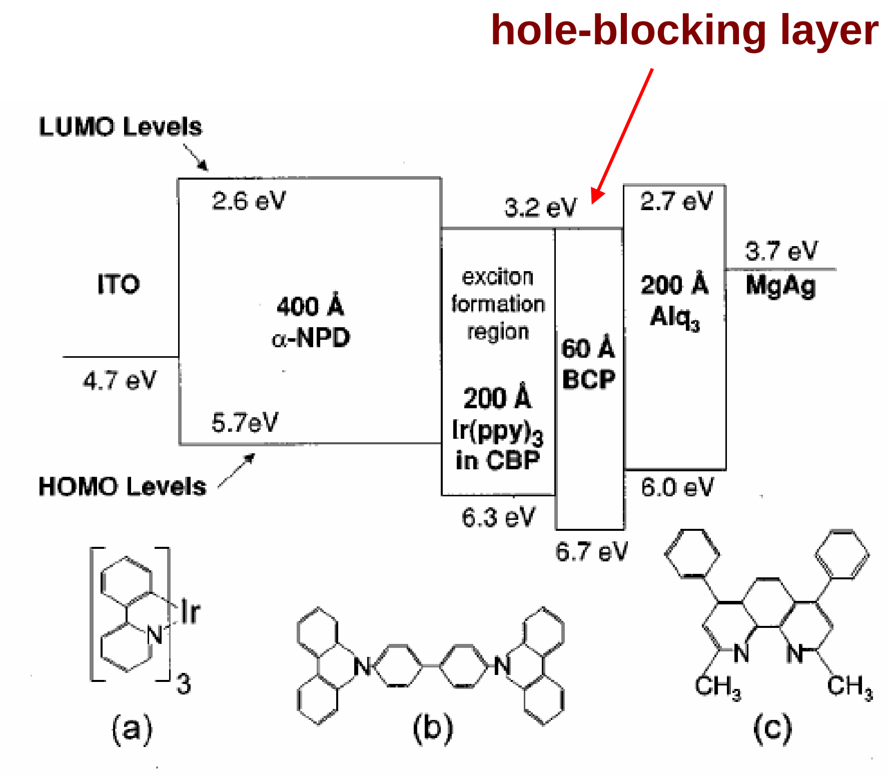
η_{ext} : 4 %

η_{int} : 23 %

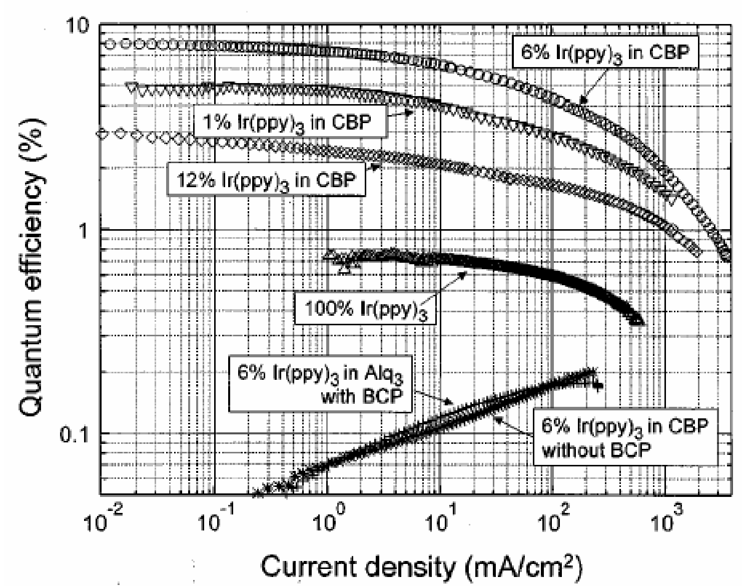
Power efficiency : (8.9±0.9) lm/W

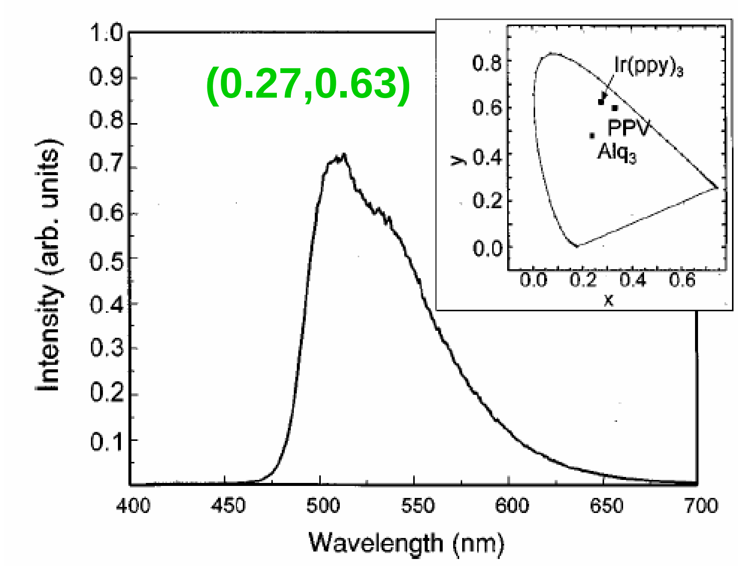
M. A. Baldo *et al*. Nature, **395**, 151 (1998)

Highly Efficient Phosphorescent OLEDs



η_{ext} : 8.0 %
Current efficiency : 28 cd/A
Power efficiency : 31 lm/W

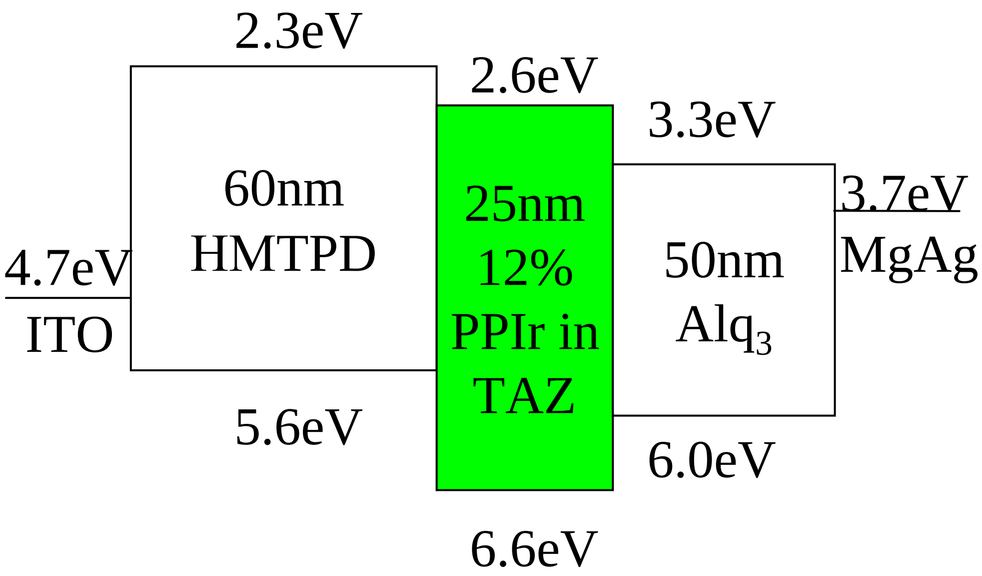


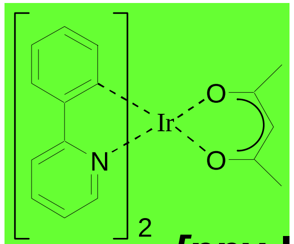


M. A. Baldo *et al.* APL, 75, 4 (1999)

Highly Efficient Phosphorescent OLEDs

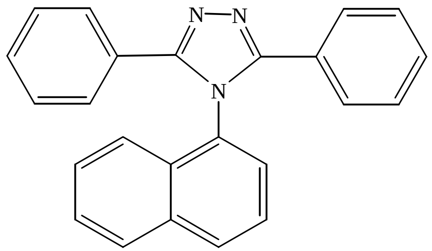
Harvest of singlet and triplet excitons



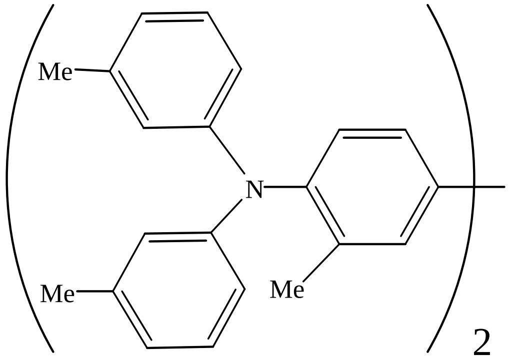


*[ppy$_2$*Ir(acac)]

PPIr



TAZ



HMTPD

ITO/HMTPD/12% PPIr:TAZ/Alq$_3$/Mg:Ag

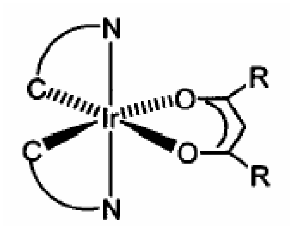
η_{ext} : (19.0±0.5)%

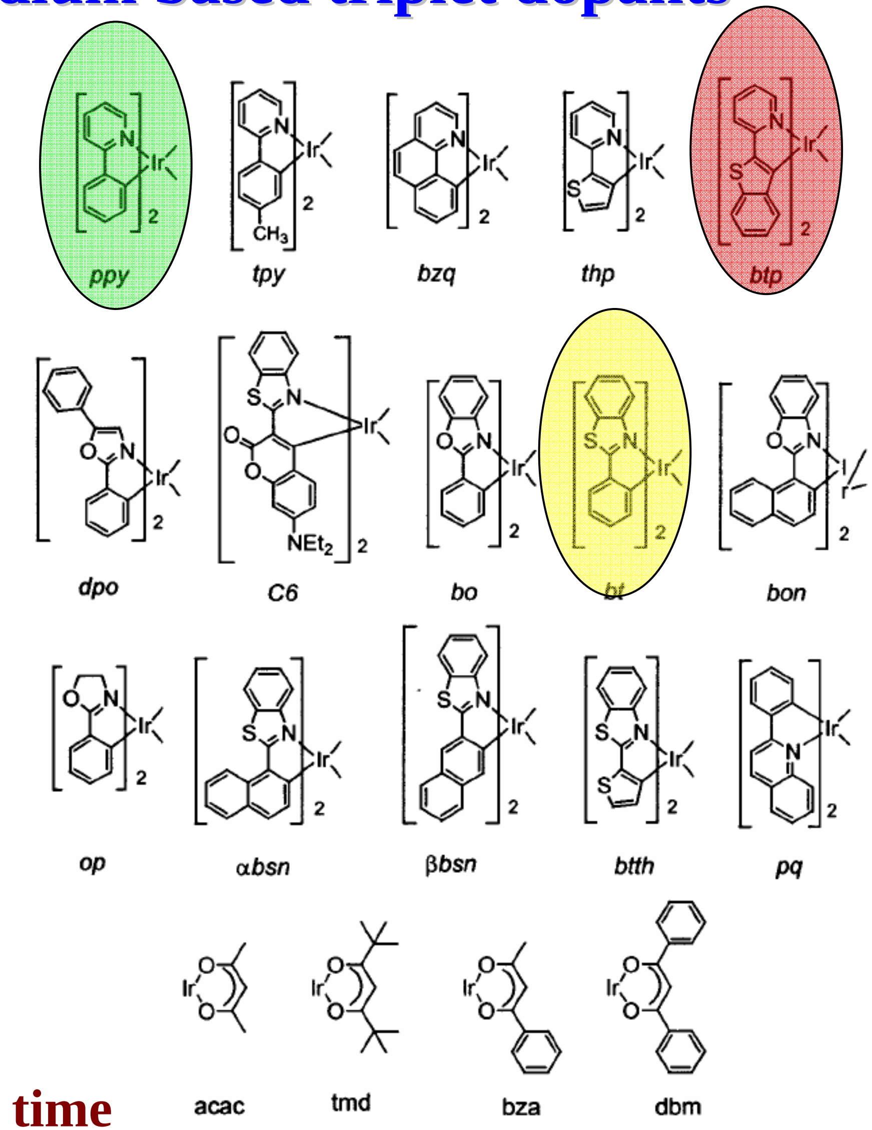
η_{int} : (87±7)% (nearly 100%)

Power efficiency : (60±5) lm/W

C. Adachi *et al*. JAP, 90, 5048 (2001)

Iridium based triplet dopants



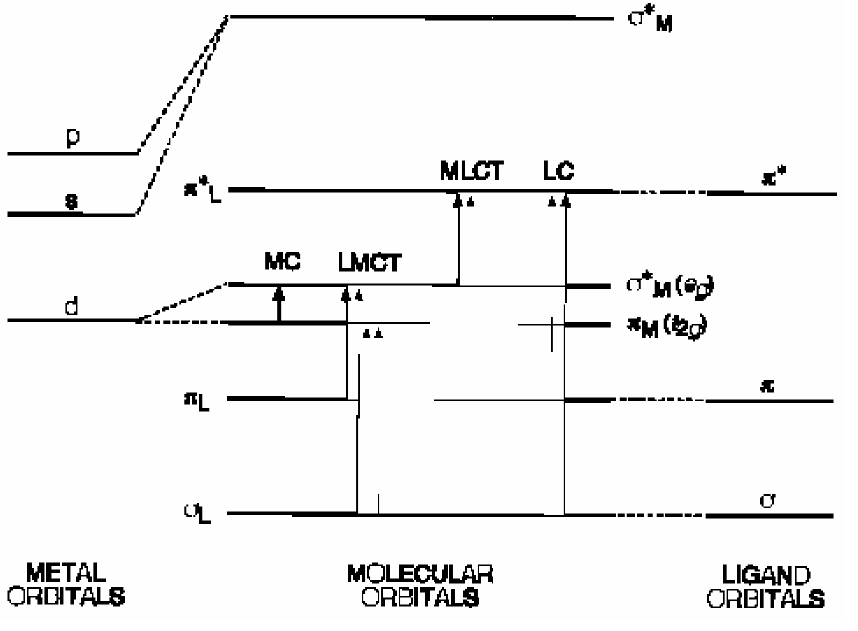


Short life time

-- due to strong spin-orbital coupling

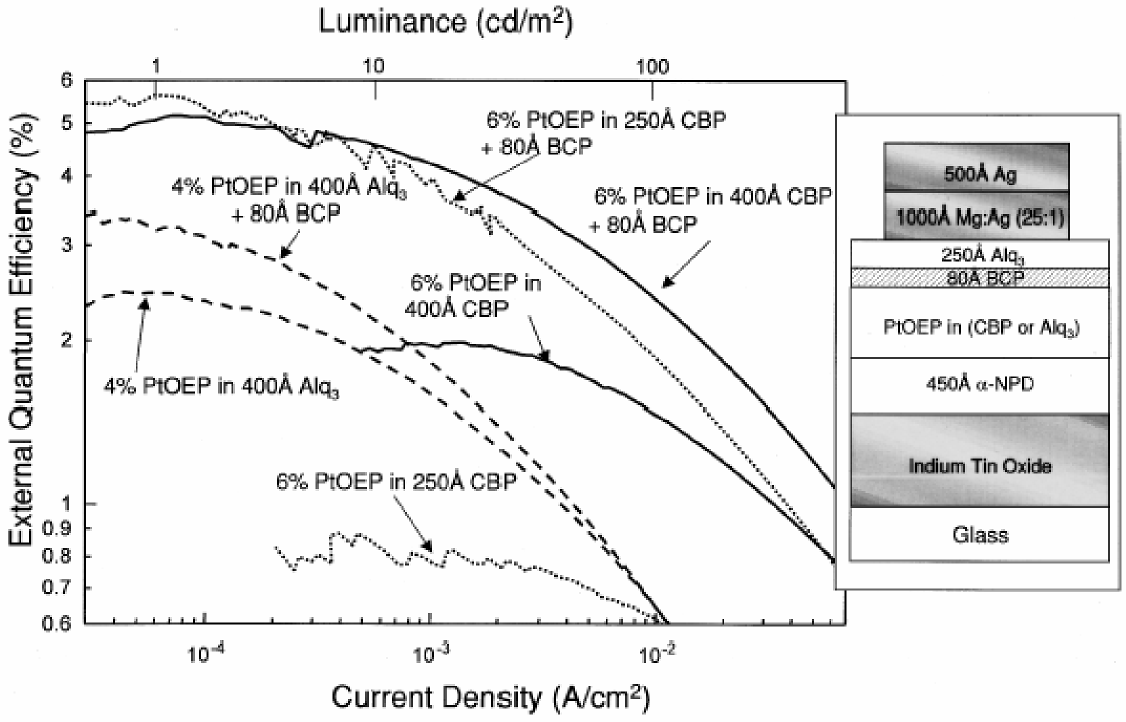
Lamansky *et al*. JACS, 123, 4304 (2001)

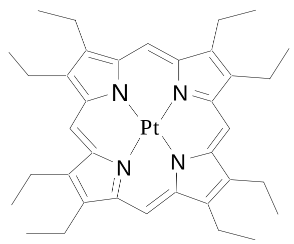
Energy level diagram for a transition metal complex



V. Balzani *et al*. Chem. Rev., 96, 759 (2001)

Red Phosphorescent OLEDs





PtOEP

Triplet life time:
in CBP : ~100 μsec
in Alq_3 : ~45 μsec
double lifetime

ITO/α-NPD/6% PtOEP:CBP/BCP/Alq_3/Mg:Ag
η_{ext} : (5.6±0.1)%

D. F. O'Brien *et al*. APL, 74, 442 (1999)

Triplet – Triplet annihilation

The roll-off of efficiency at high current region

Dopant site saturation???

$\eta_{ext} \propto 1/J$ (J : current density)

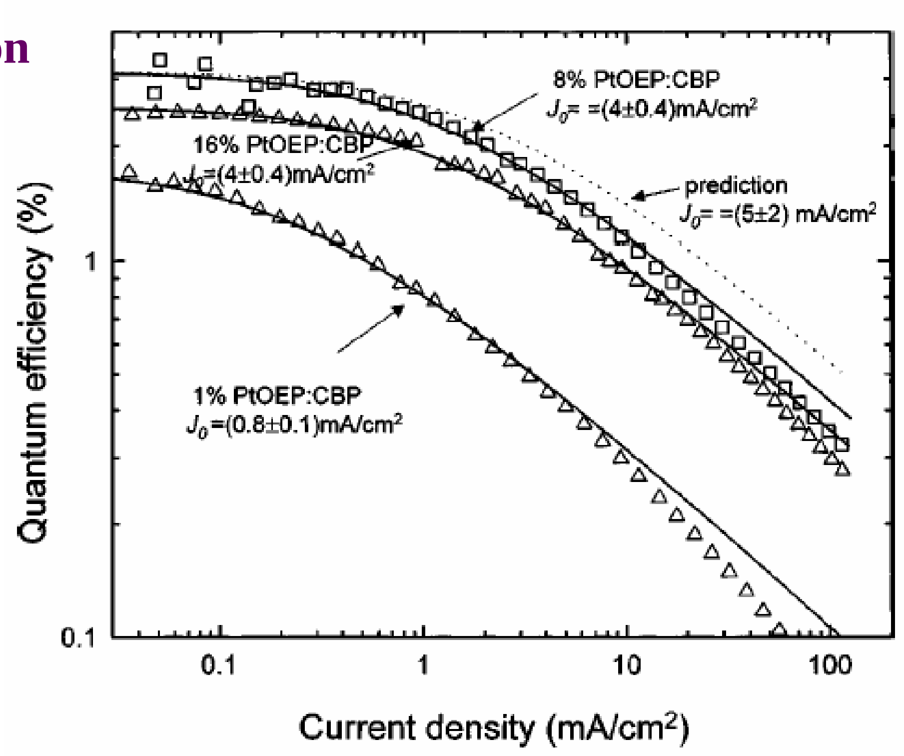
T-T annihilation : $T^3 + T^3 \rightarrow S^0 + S^1$

$$\frac{\eta}{\eta_0} = \frac{J_0}{4J}\left(\sqrt{1 + 8\frac{J}{J_0}} - 1\right)$$

η_0 : quantum efficiency in the absent of TT annihilation

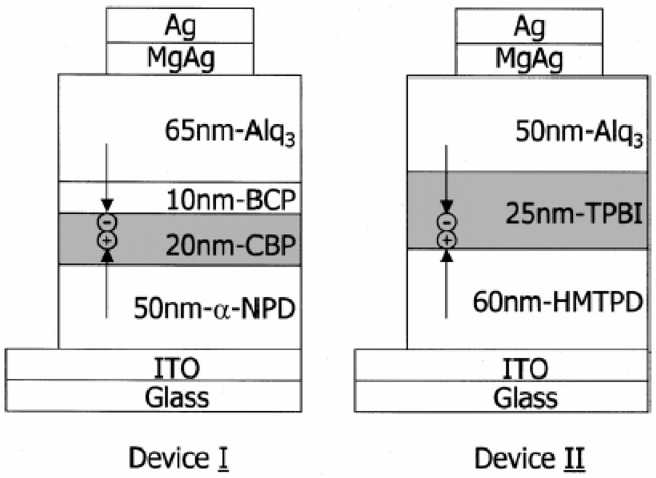
J_0 : onset current density at $\eta = \eta_0 / 2$

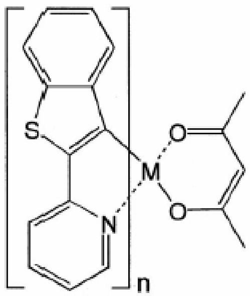
$$J_0 = \frac{4qd}{k_{TT}\tau^2}$$

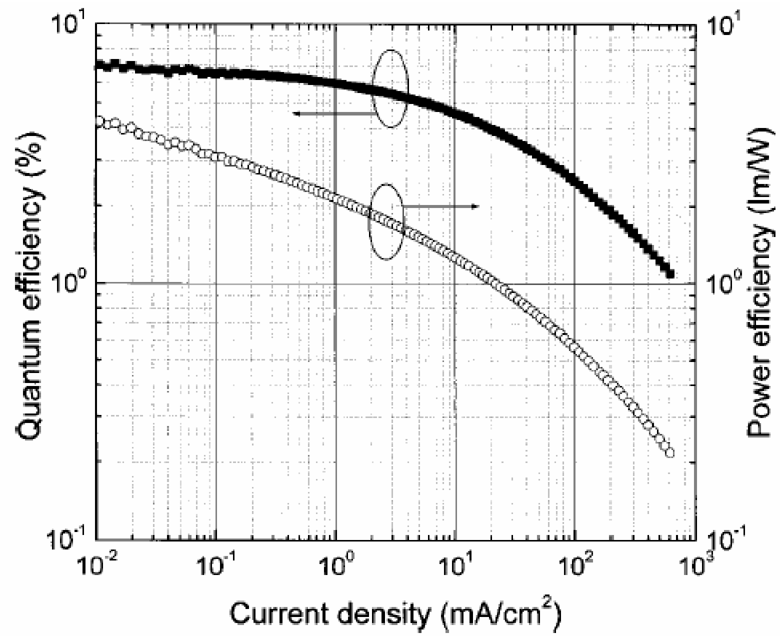


M. A. Baldo *et al*. Phys. Rev. B, 62, 10967 (2000)

Red Phosphorescent OLEDs





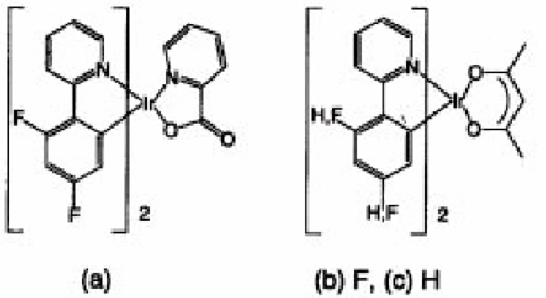


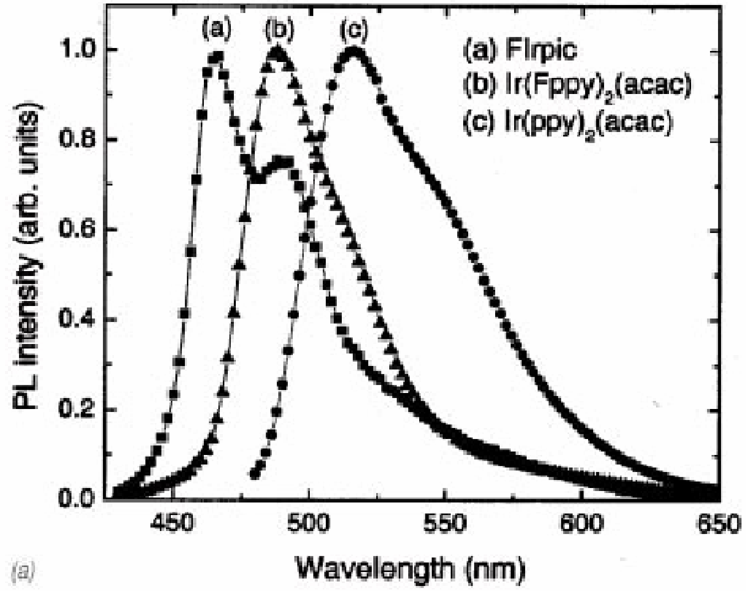
Triplet lifetime ~ 4 μsec
vs ~80 μsec for PtOEP

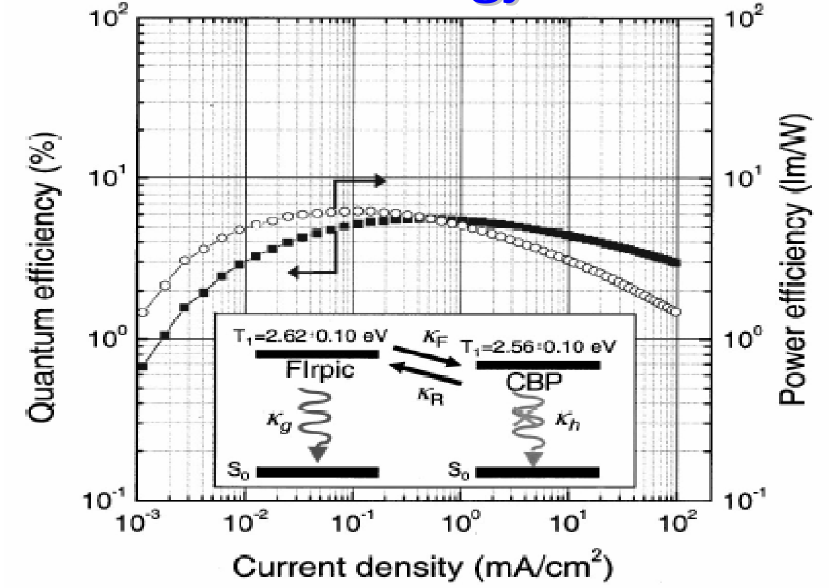
ITO/α-NPD/7% BtpI:6% CBP/BCP/Alq_3/Mg:Ag
η_{ext} : (7.0±0.5)%
Power efficiency : (4.6±0.5) lm/W

C. Adachi *et al*. APL, 78, 1622 (2001)

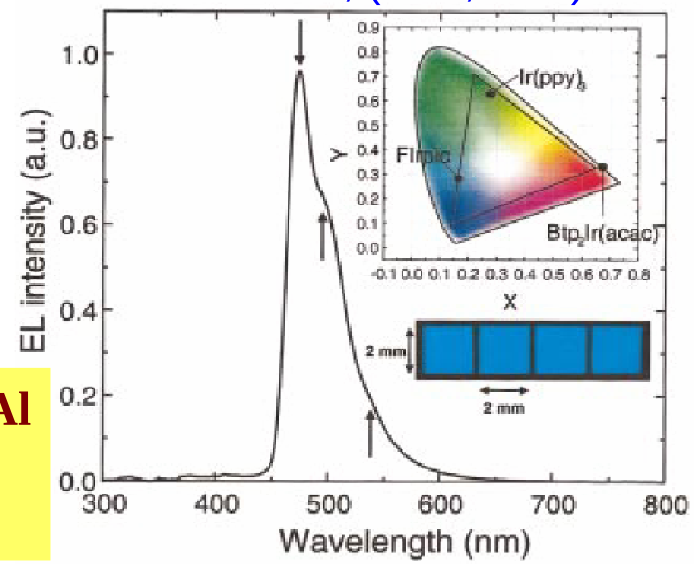
Blue Phosphorescent OLEDs – endothermic energy transfer







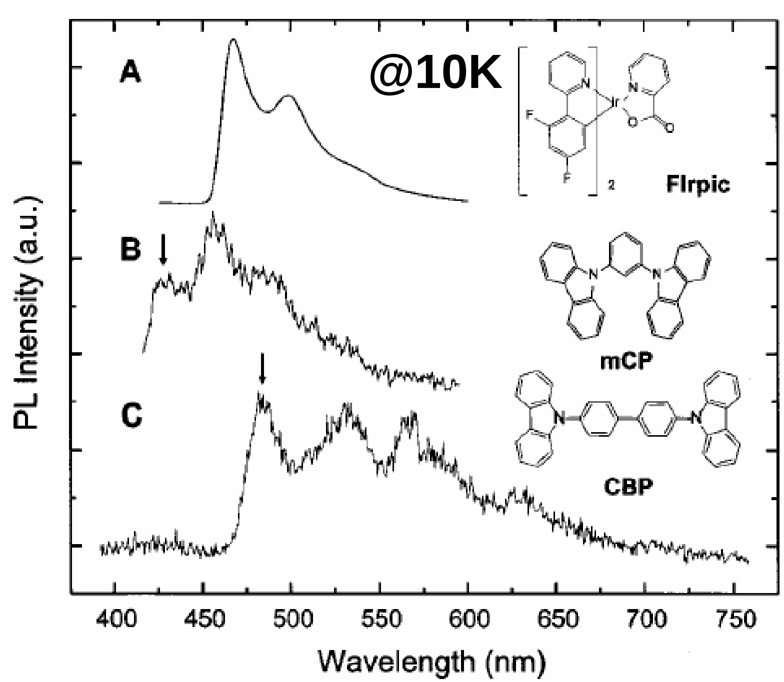
475 nm, (0.16, 0.29)



ITO/CuPC/α-NPD/CBP:6% FIrpic/BAlq$_3$/LiF/Al
η_{ext} : (5.7±0.3)%
Power efficiency : (6.3±0.3) lm/W

C. Adachi *et al*. APL, 79, 2082 (2001)

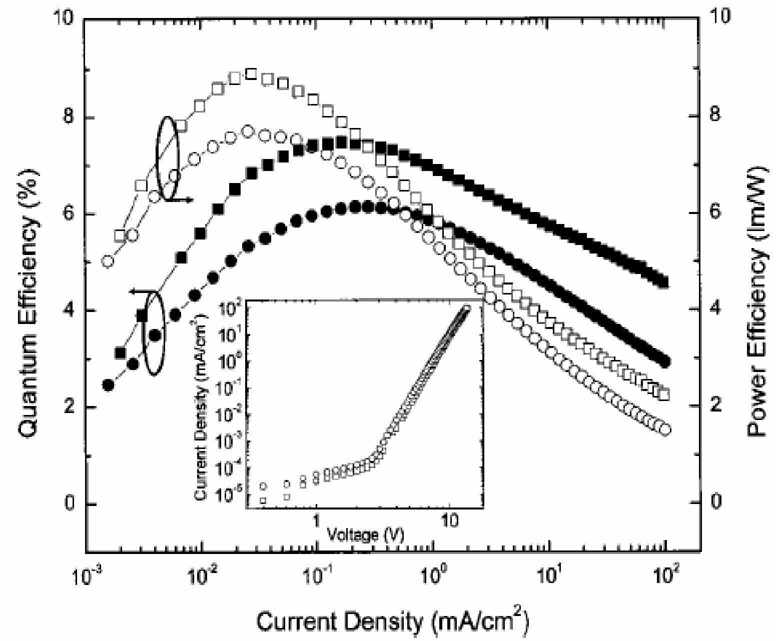
Blue Phosphorescent OLEDs with enhanced efficiency – exothermic energy transfer



(2.62±0.10)eV

(2.90±0.10)eV

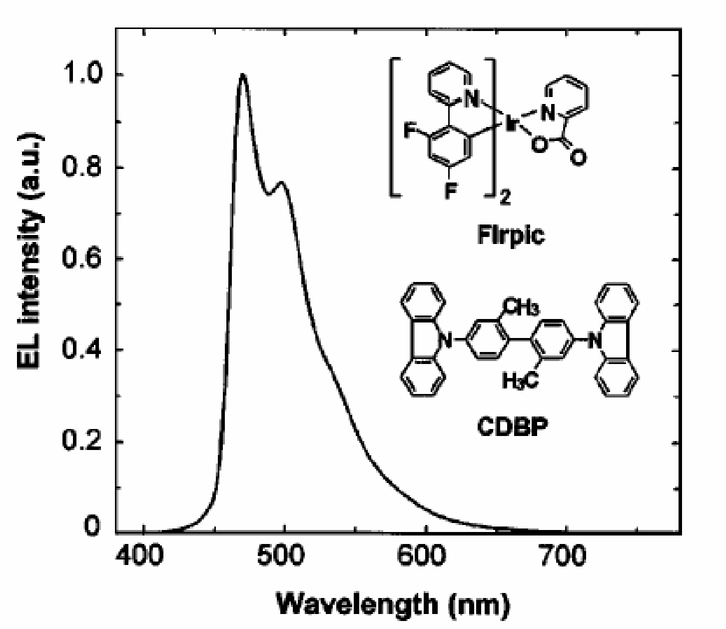
(2.56±0.10)eV

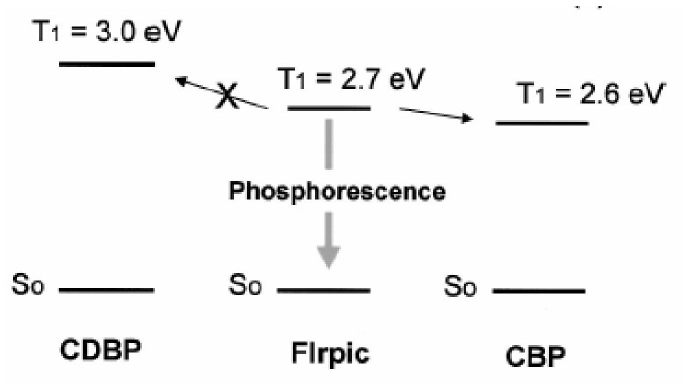


ITO/CuPC/α-NPD/mCP:6% FIrpic/BAlq$_3$/LiF/Al
η_{ext} : (7.5±0.8)%
Power efficiency : (8.9±0.9) lm/W

R. J. Holmes *et al*. APL, 82, 2422 (2003)

Blue Phosphorescent OLEDs



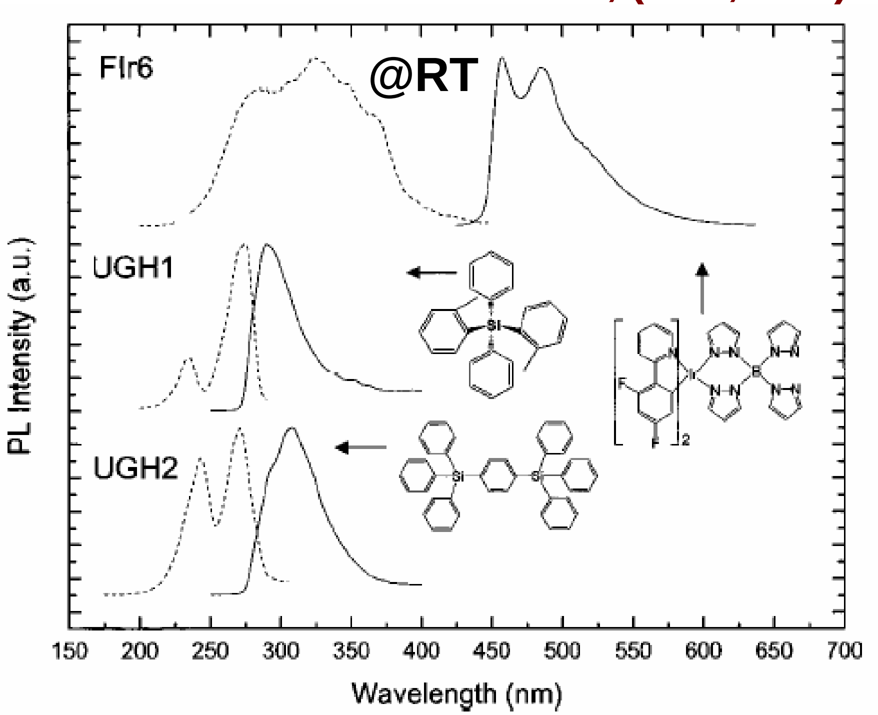


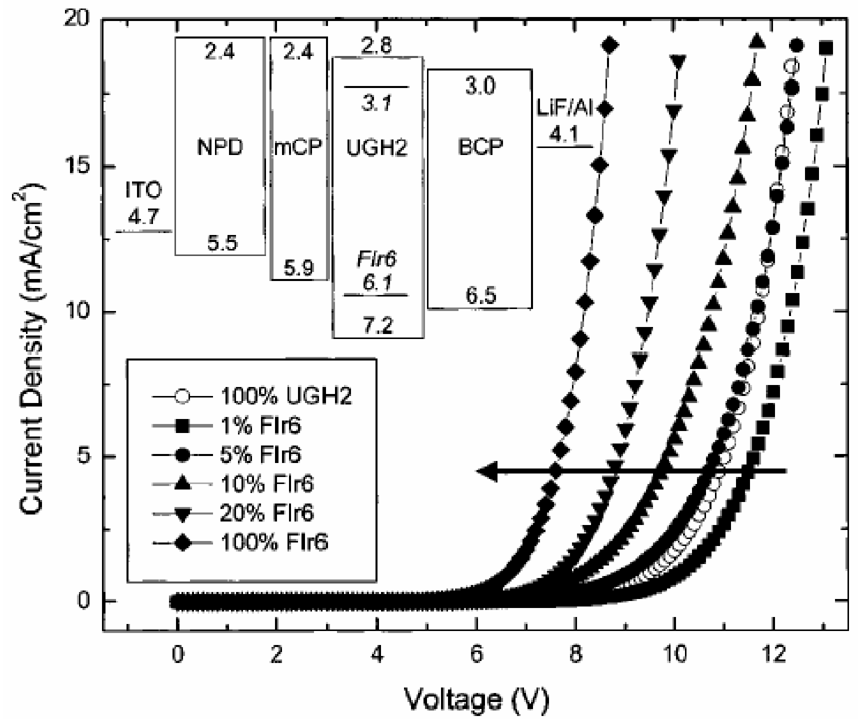
ITO/PEDOT/α-NPD/CDBP:3% FIrpic/BAlq$_3$/LiF/Al
η_{ext} : 10.4 %
Current efficiency : 20.5 cd/A
Power efficiency : 10.5 lm/W

S. Tokito *et al*. APL, 83, 569 (2003)

Deep Blue Phosphorescent OLEDs

457 nm, (0.16, 0.26)





@77K
UGH1 : 393 nm
UGH2 : 390 nm

ITO/α-NPD/mCP/UGH2:10% FIr6/BCP/LiF/Al
η_{ext} : (11.6±1.2)%
Power efficiency : (13.9±1.4) lm/W

R. J. Holmes *et al*. APL, 83, 3818 (2003)

Power Efficiency

	Singlet	Triplet (expected)
Blue	5~8 lm/W	20~30 lm/W
Green	10~15 lm/W	40~60 lm/W
Red	1~3 lm/W	4~10 lm/W
White	10~15 lm/W	40~60 lm/W

PHOLED Materials		Color Coordinates CIE [x, y]	Luminous Efficiency [cd/A]	Operational Lifetime [hrs]	Luminance [cd/m²]
Commercial	RD15	(0.67, 0.33)	12	100,000	500
	RD07	(0.65, 0.35)	18	40,000	500
	GD29	(0.30, 0.63)	24	10,000	600
	GD33	(0.31, 0.64)	40	20,000	1,000
	GD48	(0.32, 0.63)	37	25,000	1,000
Development	RD61	(0.62, 0.38)	30	40,000	500
	GD107	(0.35, 0.60)	40	25,000	1,000
	YD85	(0.41, 0.58)	65	under test	1,000
Research	New Green	(0.32, 0.63)	80	15,000	1,000
	New Green	(0.32, 0.63)	57	40,000	1,000
	New Blue	(0.16, 0.37)	22	15,000	200
	New Blue	(0.14, 0.13)	9	under development	200
	New Blue	(0.16, 0.10)	3	under development	200

Data by July 2005

http://www.universaldisplay.com/

OLED Displays

AUO – world first 4” a-Si AMOLED (2003)

Parameter	Features
Display Size	4-inch
Resolution	160×(RGB)×234
Sub-Pixel Pitch	171um×264um
Driving Method	2-TFT Voltage Programming
Color Number	262K (6 bits)
Brightness	300 cd/m^2
Power Cons.	670 mW
Substrate	a-Si TFT
Contrast ratio	>250
Module thickness	1.8 mm
Emission Type	Bottom Emission

Commercial Phosphorescent OLEDs

The Fujitsu F505iGPS cellular phone uses a Pioneer full-color PM subdisplay that incorporate UDC's red-emitting PHOLED material. The subdisplay has 1.1" diagonal, 96x72 pixels, and 4096 colors.

Cover of Information Display, June, 2004