

# Ch.9: Phosphorescence in OLEDs

M. Baldo and M. Segal, phys. stat. sol. (a) **201**, 1205 (2004)

2009. 5. 2.

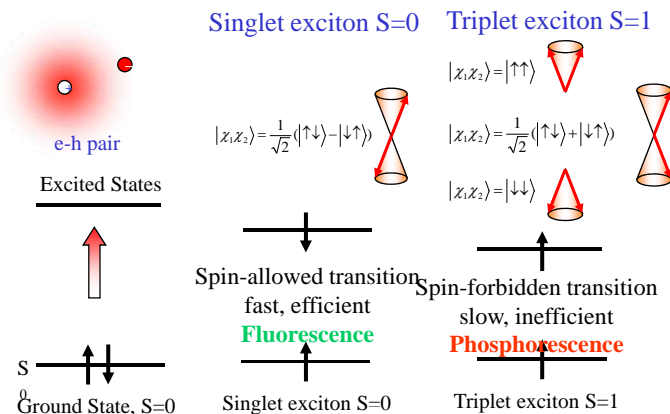
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## Relaxation of Singlet & Triplet Excitons



Fluorescence : Radiation restricted to singlet excitons,  $\rightarrow \eta \sim 25\%$   
 Phosphorescence : Radiation is from triplets  $\rightarrow \eta \sim 100\%$ .

If the excited state is formed from the combination of two uncorrelated electrons, then in a completely random formation process the relative degeneracies of the singlet and triplet states result in a 1 : 3 singlet : triplet ratio, i.e. the fraction of singlet excitons is  $\chi_S = 0.25$ .

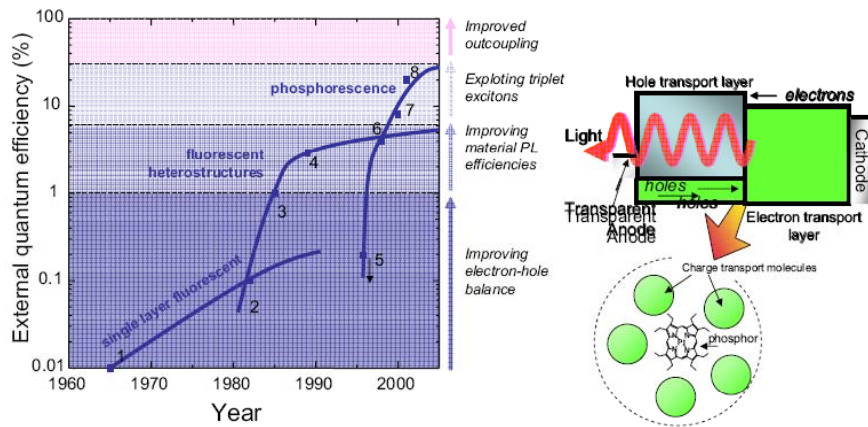
M. Baldo and M. Segal, phys. stat. sol. (a) **201**, 1205 (2004)



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# QE of OLEDs and a brief history

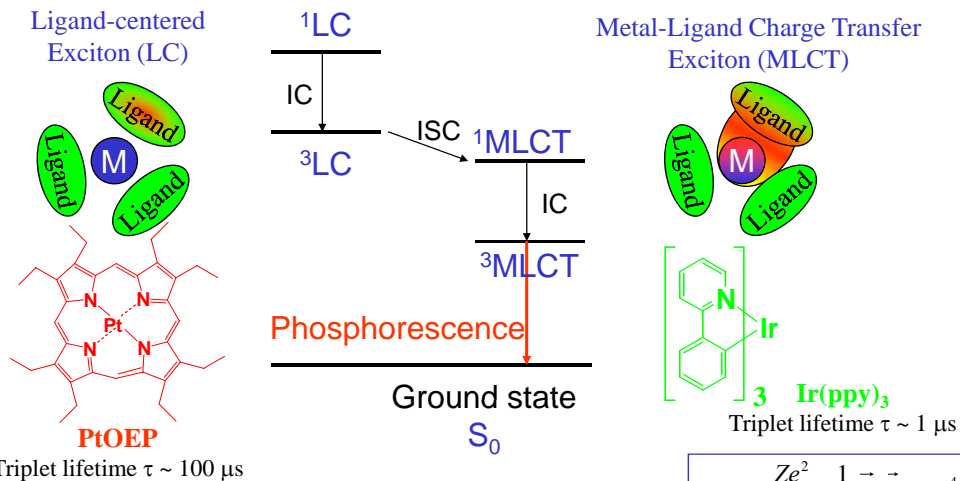


1. Helfrich & Schneider, PRL, **14**, 229 (1965), 2. Vincett, et al. Thin Solid Films, **94**, 171 (1982)
3. Tang & VanSlyke, APL, **11**, 913 (1987), 4. Tang, VanSlyke & Chen, JAP, **65**, 3610, (1989)
5. Hoshino & Suzuki, APL, **69**, 224 (1996), 6. Baldo, et al, Nature, **395**, 151, (1998), 7. Baldo, et al, APL, **75**, 4, (1999), 8. Adachi, et al, JAP, **90**, 5048, (2001)

M. Baldo, IMID/IDMC '06 DIGEST, 645-674 (2006)



# Organic Phosphorescent Dyes



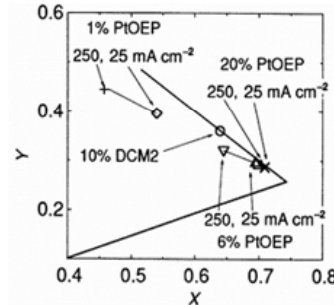
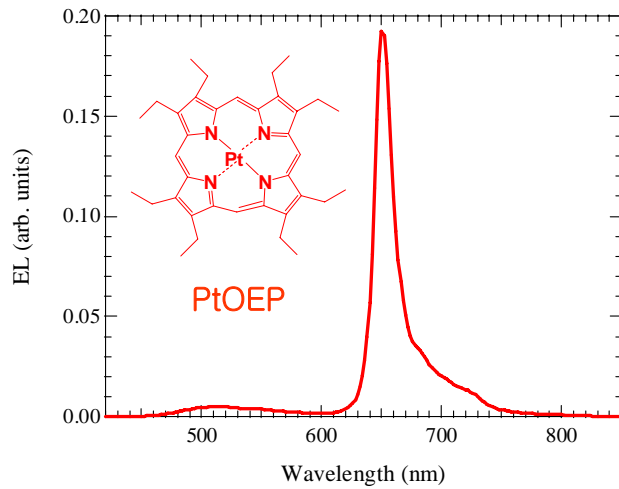
- The emissive state is a mixture of a LC exciton and a MLCT exciton
- The MLCT state has stronger singlet - triplet mixing, due to the overlap with the heavy metal atom.
- For strong spin-orbit coupling, the IC and ISC rates are very fast.

$$H_{\text{SO}} = \frac{Ze^2}{2m^2c^2} \frac{1}{r^3} \vec{L} \cdot \vec{S} \propto Z^4$$



# Phosphorescent Dye OLED

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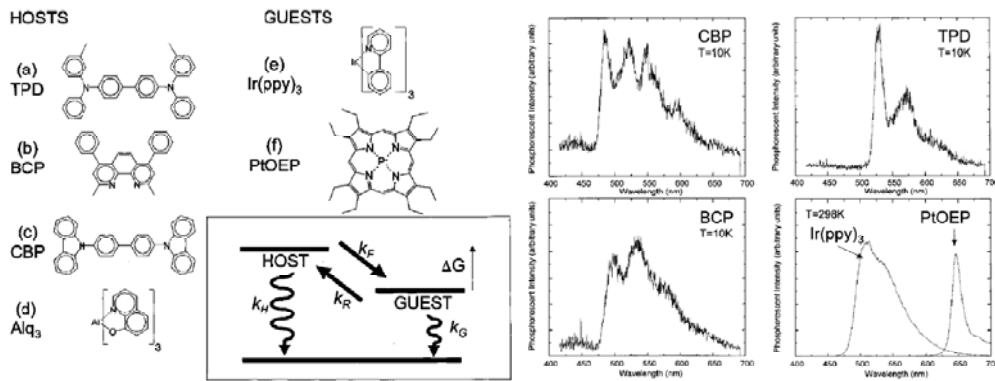
Efficient red EL emission from triplet excitons:  $\eta_{\text{ext}} \sim 2.2\% @ 100 \text{ cd/m}^2$

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



# Triplet energy of R & G phosphors

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Material	Triplet energy ( $\pm 0.1 \text{ eV}$ )	Triplet lifetime	Guest lifetime ( $\mu\text{s}$ )	Host	$\Delta G$ ( $\pm 0.1 \text{ eV}$ )	Host lifetime	Emission lifetime ( $\mu\text{s}$ )	Trapping on guest	EL quantum efficiency
PtOEP	1.9	$110 \pm 10 \mu\text{s}^a$		CBP	-0.7	$> 1 \text{ s}$	$80 \pm 5$	Yes	0%
Ir(ppy) <sub>3</sub>	2.4	$0.8 \pm 0.1 \mu\text{s}^b$		Ir(ppy) <sub>3</sub>	-0.5	$< 0.1 \mu\text{s}$	$80 \pm 5$	?	3%
CBP	2.6	$> 1 \text{ s}$		TPD	-0.4	$300 \pm 50 \mu\text{s}$	$80 \pm 5$	Yes	3%
BCP	2.5	$< 10 \mu\text{s}$		Alq <sub>3</sub>	-0.1	$25 \pm 15 \mu\text{s}$	$40 \pm 5$	No	3%
TPD	2.3	$200 \pm 50 \mu\text{s}$		CBP	-0.2	$> 1 \text{ s}$	$0.4 \pm 0.05$	Yes	8%
Alq <sub>3</sub> <sup>c</sup>	2.0	$25 \pm 15 \mu\text{s}$		TPD	+0.1	$200 \pm 50 \mu\text{s}$	$15 \pm 2$	No	3%
				Alq <sub>3</sub>	+0.4	$25 \pm 15 \mu\text{s}$	$< 0.1$	?	$< 0.1\%$

M. A. Baldo and S. R. Forrest, Phys. Rev. B **62**, 10958–10966 (2000).



# Triplet energy of a blue phosphor and its hosts

Firpic = iridium(III)bis[(4,6-difluorophenyl)-pyridinato-N,C<sup>2'</sup>]picolinate,  $E_t=2.65$  eV

Host

4,4'-N,N'-dicarbazole-biphenyl (CBP),

$E_t=2.56$  eV, a maximum EQE= 5.7%

C. Adachi, R. C. Kwong, P. Djurovich, V. Adamovich, M. A. Baldo, M. E. Thompson, and S. R. Forrest, Appl. Phys. Lett. 79, 2082 (2001)

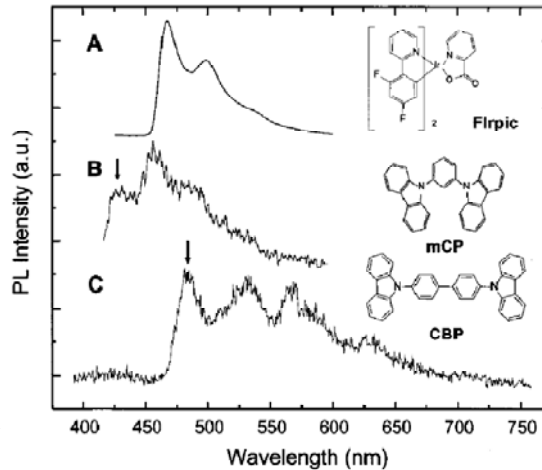
3,5'-N,N'-dicarbazole-benzene (mCP),

$E_t=2.9$  eV, EQE=7.5%

R. J. Holmes, S. R. Forrest, Y. J. Tung, R. C. Kwong, J. J. Brown, S. Garon, and M. E. Thompson, Appl. Phys. Lett. 82, 2422 (2003).

4,4'-bis(9-dicarbazolyl)-2,2'-dimethyl-biphenyl (CDBP),  $E_t=3.0$  eV, EQE=10%

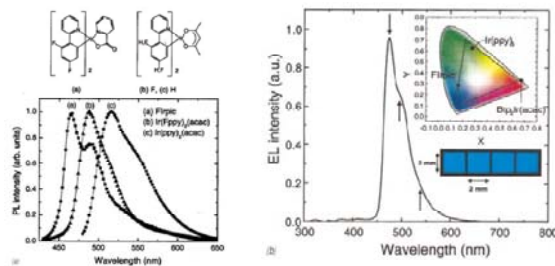
S. Tokito, T. Iijima, Y. Suzuri, H. Kita, T. Tsuzuki, and F. Saito, Appl. Phys. Lett. 83, 569 (2003).



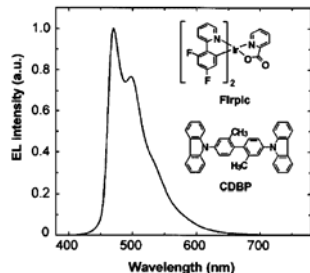
R. J. Holmes, S. R. Forrest, Y. J. Tung, R. C. Kwong, J. J. Brown, S. Garon, and M. E. Thompson, Appl. Phys. Lett. 82, 2422 (2003).



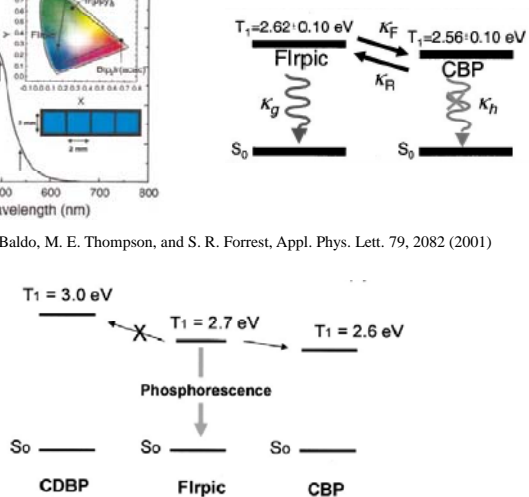
# Blue phosphorescent OLED

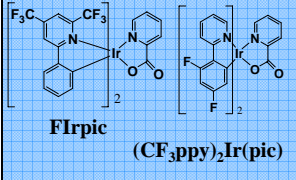
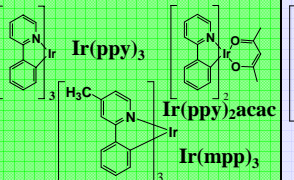
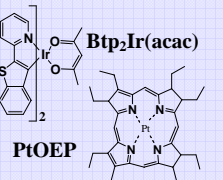
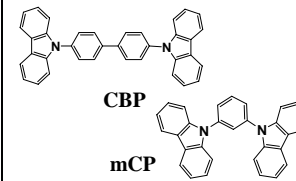
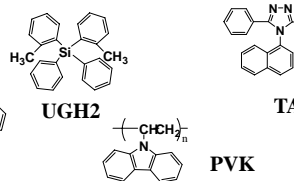
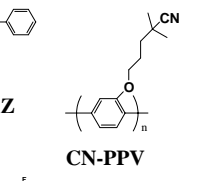
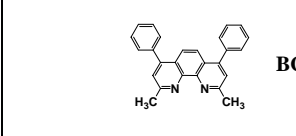
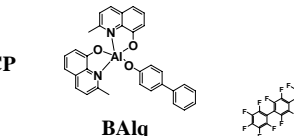
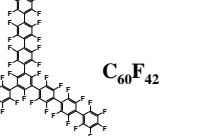


C. Adachi, R. C. Kwong, P. Djurovich, V. Adamovich, M. A. Baldo, M. E. Thompson, and S. R. Forrest, Appl. Phys. Lett. 79, 2082 (2001)



S. Tokito, T. Iijima, Y. Suzuri, H. Kita, T. Tsuzuki, and F. Saito, Appl. Phys. Lett. 83, 569 (2003).

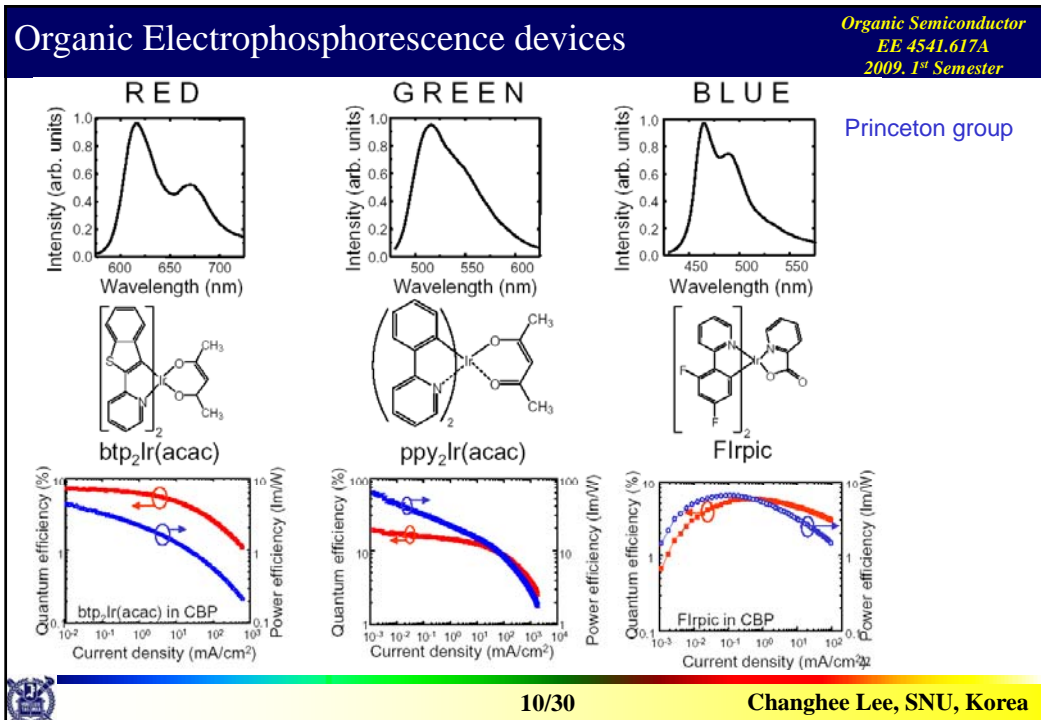


Host and Phosphorescent Dopant Materials				Organic Semiconductor EE 4541.617A 2009, 1 <sup>st</sup> Semester
	Blue	Green	Red	
<b>Dopant</b>	 <p>Flrpic (CF<sub>3</sub>ppy)<sub>2</sub>Ir(pic)</p>	 <p>Ir(ppy)<sub>3</sub> Ir(ppy)<sub>2</sub>acac Ir(mpp)<sub>3</sub></p>	 <p>Btp<sub>2</sub>Ir(acac) PtOEP</p>	
<b>Host</b>	 <p>CBP mCP</p>	 <p>UGH2 PVK</p>	 <p>TAZ CN-PPV</p>	
<b>Hole/Exciton Blocking Materials</b>	 <p>BCP</p>	 <p>BAiq</p>	 <p>C<sub>60</sub>F<sub>42</sub></p>	

Dr. H. N. Cho (InkTek)

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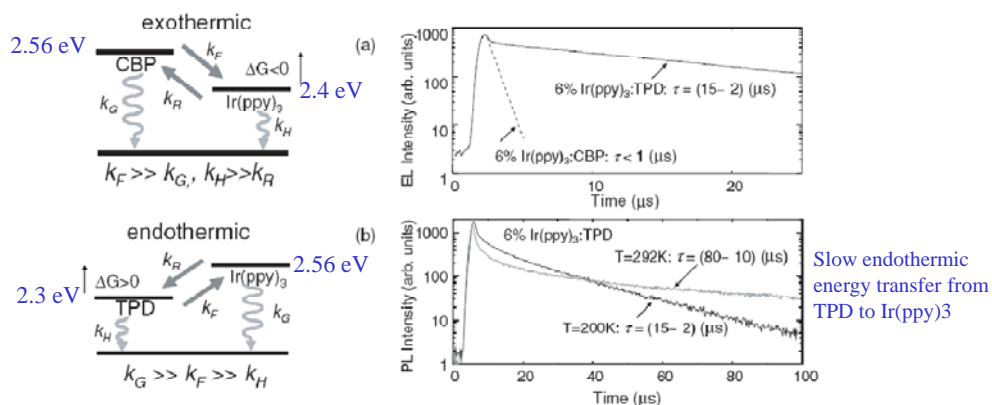
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- endothermic energy transfer
- exothermic energy transfer
- charge trapping



## Exothermic and endothermic energy transfer

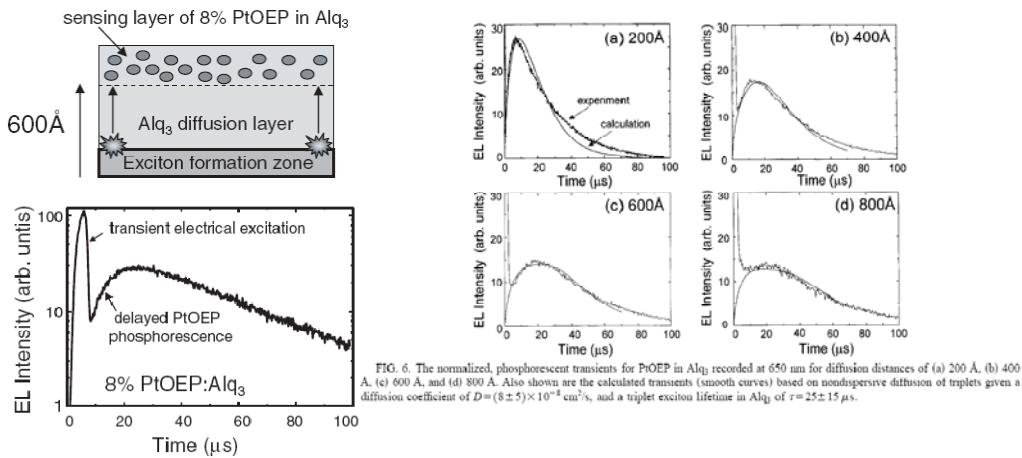


Slow endothermic energy transfer from TPD to Ir(ppy)<sub>3</sub>

**Fig. 5** (a) The electroluminescent response of the endothermic system Ir(ppy)<sub>3</sub>:TPD, as compared to the exothermic system Ir(ppy)<sub>3</sub>:CBP. The lifetime of Ir(ppy)<sub>3</sub> in a TPD host is significantly longer (15  $\mu$ s) than the natural radiative lifetime of Ir(ppy)<sub>3</sub> (<1  $\mu$ s). The initial peak in the response is principally due to fluorescence from TPD. (b) The photoluminescent response of 6% Ir(ppy)<sub>3</sub> in TPD at  $T = 292\text{ K}$  and  $T = 200\text{ K}$ . The lifetime increases at low temperatures, consistent with a thermally activated process such as endothermic energy transfer. However, unlike the EL response, the initial transient in the photoluminescent response is comprised entirely of emission from photo-excited Ir(ppy)<sub>3</sub>. Adapted from Ref. [24].

M. Baldo and M. Segal, phys. stat. sol. (a) **201**, 1205 (2004)



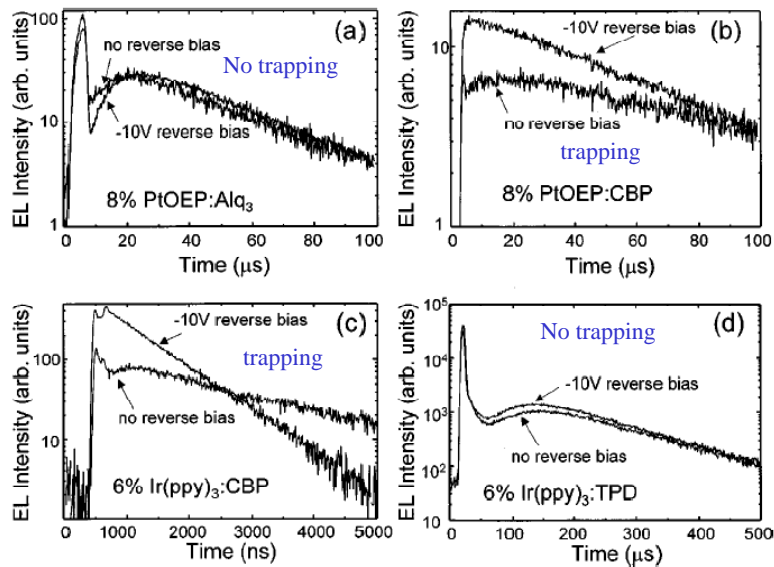


The delay in the PtOEP phosphorescence after an electrical excitation pulse is due to triplet diffusion through the Alq<sub>3</sub> host. The delay is observed to decrease to zero as the excitation formation zone is moved closer to the PtOEP layer, confirming that excitons are formed initially in the Alq<sub>3</sub> host. These experiments were used to estimate the triplet exciton lifetime in Alq<sub>3</sub> to be  $(25 \pm 15) \mu\text{s}$ .

M. Baldo and M. Segal, *phys. stat. sol.* (a) **201**, 1205 (2004) ; M. A. Baldo and S. R. Forrest, *Phys. Rev. B* **62**, 10958–10966 (2000).

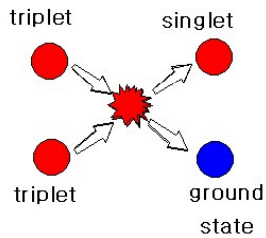


## Charge trapping



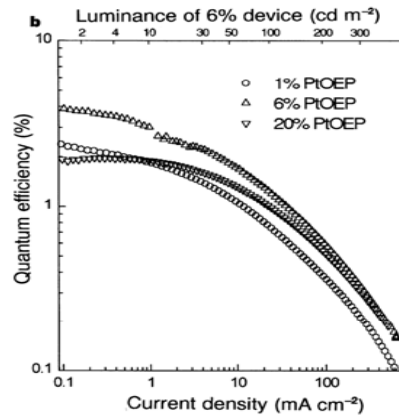


## Triplet – Triplet (T – T) Annihilation



Q.E. decay as current is increased is due to T-T annihilation  
 → decrease the effects of T-T annihilation by:

- short triplet lifetime will decrease T-T annihilation
- decrease dopant aggregation in the thin film

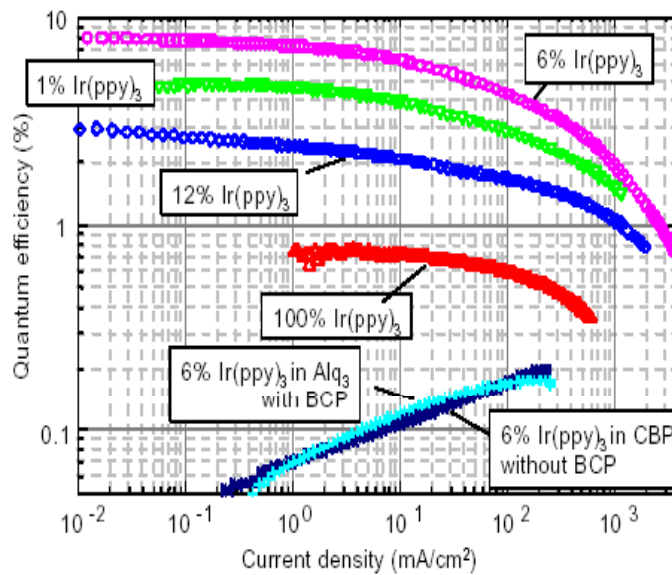


Ref. M. A. Baldo, C. Adachi, and S. R. Forrest, Phys. Rev. B **62**, 10967 (2000)



## Reduced Efficiency Roll-off with Short Triplet Exciton Lifetime

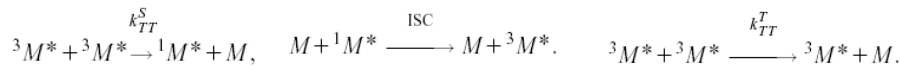
$\text{Ir(ppy)}_3$   
 triplet exciton  $\tau$ :  
 ~500ns (doped in  
 CBP)





## Triplet – Triplet (T – T) Annihilation

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Rate equation for the triplet-triplet annihilation

$$\frac{dn_T}{dt} = -\frac{n_T}{\tau} - k_T n_T^2 + \frac{J}{qd}$$

1) transient  $t > 0, J(t) = 0$

i)  $k_T n_T(0) \ll \frac{1}{\tau} \quad n_T \approx n_T(0) e^{-\frac{t}{\tau}}$

ii)  $k_T n_T(0) \gg \frac{1}{\tau} \quad \frac{dn_T}{dt} \approx -k_T n_T^2$

$$n_T \approx \frac{1}{At + B} \quad \frac{-A}{(At + B)^2} \approx \frac{-k_T}{(At + B)^2} \quad \therefore A = k_T, B = \frac{1}{n_T(0)}$$

$$\therefore n_T \approx \frac{1}{At + B} = \frac{1}{k_T t + \frac{1}{n_T(0)}} = \frac{n_T(0)}{1 + n_T(0)k_T t}$$



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## Transient Solution

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trial solution

$$n_T(t) = \frac{1}{Ae^{\frac{t}{\tau}} + B} \quad \frac{-\frac{A}{\tau} e^{\frac{t}{\tau}}}{(Ae^{\frac{t}{\tau}} + B)^2} = -\frac{\frac{1}{\tau}}{(Ae^{\frac{t}{\tau}} + B)} - \frac{k_T}{(Ae^{\frac{t}{\tau}} + B)^2}$$

$$-\frac{A}{\tau} e^{\frac{t}{\tau}} = -\frac{1}{\tau}(Ae^{\frac{t}{\tau}} + B) - k_T \quad \therefore B = -k_T \tau$$

$$t = 0; n_T(0) = \frac{1}{A + B} \quad \therefore A = \frac{1}{n_T(0)} - B = \frac{1}{n_T(0)} + k_T \tau$$

$$\therefore n_T(t) = \frac{n_T(0)}{[1 + k_T \tau n_T(0)] e^{\frac{t}{\tau}} - k_T \tau n_T(0)}$$

Light emission intensity  $L(t) = \frac{n_T(t)}{\tau} = \frac{L(0)}{(1 + K\tau)e^{\frac{t}{\tau}} - K\tau}$  (let  $k_T n_T(0) = K$ )

M. A. Baldo, C. Adachi, and S. R. Forrest, Phys. Rev. B **62**, 10967 (2000)

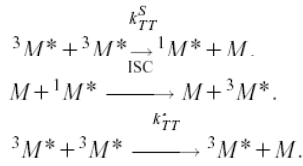


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## T – T Annihilation: Transient behavior

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Rate equation for the T-T annihilation

$$\frac{dn_T}{dt} = -\frac{n_T}{\tau} - k_{TT}n_T^2 + \frac{J}{qd}$$

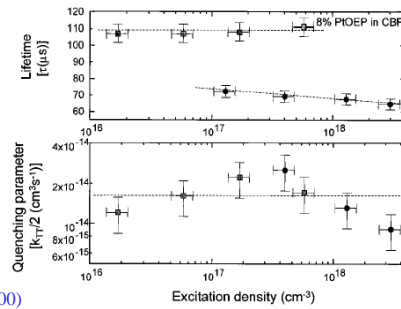
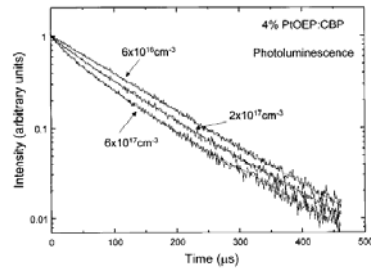
Transient behavior:  $J=0$

$$[^3M^*(t)] = \frac{[^3M^*(0)]}{\left(1 + [^3M^*(0)] \frac{k_{TT}\tau}{2}\right) e^{t/\tau} - [^3M^*(0)] \frac{k_{TT}\tau}{2}}$$

$$K = \frac{1}{2} k_{TT} [^3M^*(0)].$$

$$L(t) = \frac{L(0)}{(1 + K\tau)e^{t/\tau} - K\tau}$$

M. A. Baldo, C. Adachi, and S. R. Forrest, Phys. Rev. B **62**, 10967 (2000)



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## T – T Annihilation: Steady-state solution

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$$\frac{dn_T}{dt} = 0 \quad k_{TT}n_T^2 + \frac{n_T}{\tau} - \frac{J}{gd} = 0$$

(근의 공식)

$$n_T = \frac{-\frac{1}{\tau} + \sqrt{\left(\frac{1}{\tau}\right)^2 + \frac{4Jk_{TT}}{qd}}}{2k_{TT}} = \frac{1}{2k_{TT}\tau} \left[ -1 + \sqrt{1 + \frac{4Jk_{TT}\tau^2}{qd}} \right] = \frac{1}{2k_{TT}\tau} \left[ -1 + \sqrt{1 + \frac{8J}{J_T}} \right] \quad \left( \because \frac{k_{TT}\tau^2}{2qd} = J_T^{-1} \right)$$

Light emission intensity  $L = \frac{n_T}{\tau}$     QE:  $\eta = \frac{L}{J} = \frac{n_T}{J\tau}$

$\eta_0$  :  $k_{TT} = 0$  인 경우, 즉, T-T annihilation이 없는 경우이므로  $\frac{n_T}{\tau} = \frac{J}{gd}$

$$\therefore \eta_0 = \frac{L}{J} = \frac{\frac{n_T}{\tau}}{J} = \frac{1}{gd}$$

$$\frac{\eta}{\eta_0} = \frac{qd}{2k_{TT}\tau^2 J} \left[ -1 + \sqrt{1 + \frac{8J}{J_T}} \right] = \frac{J_T}{4J} \left[ -1 + \sqrt{1 + \frac{8J}{J_T}} \right]$$

M. A. Baldo, C. Adachi, and S. R. Forrest, Phys. Rev. B **62**, 10967 (2000)



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# Efficiency Roll-off

Steady-State:  $d[{}^3M]/dt=0$

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

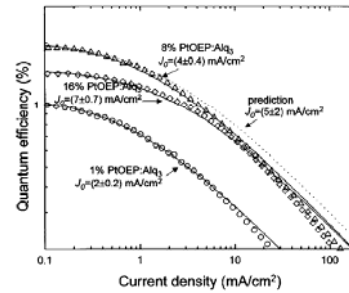
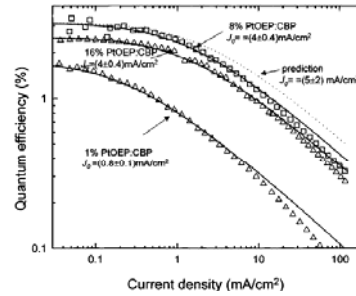
$$J_0 = \frac{4qd}{k_{TT}\tau^2}$$

current density required to excite every phosphorescent molecule (i.e., the onset of saturation)

$$J_s = \frac{[M]qd}{\tau}$$

TABLE I. Current densities at the onset of T-T annihilation ( $J_0$ ) as compared to predictions based on transient decays, and the estimated current density required to saturate the phosphors.

	1% PtOEP in CBP	1% PtOEP in Alq <sub>3</sub>	8% PtOEP in CBP	8% PtOEP in Alq <sub>3</sub>	16% PtOEP in CBP	16% PtOEP in Alq <sub>3</sub>
$J_0$ from steady-state response (mA/cm <sup>2</sup> )	0.8 ± 0.1	2.4 ± 0.2	4.4 ± 0.4	3.8 ± 0.4	4.4 ± 0.4	7.4 ± 0.7
$J_0$ from transient response (mA/cm <sup>2</sup> )	7 ± 2	8 ± 3	5 ± 2	5 ± 2	4 ± 1	6 ± 2
Saturation threshold current density (mA/cm <sup>2</sup> )	40 ± 20	200 ± 100	400 ± 80	800 ± 200	800 ± 200	1000 ± 300



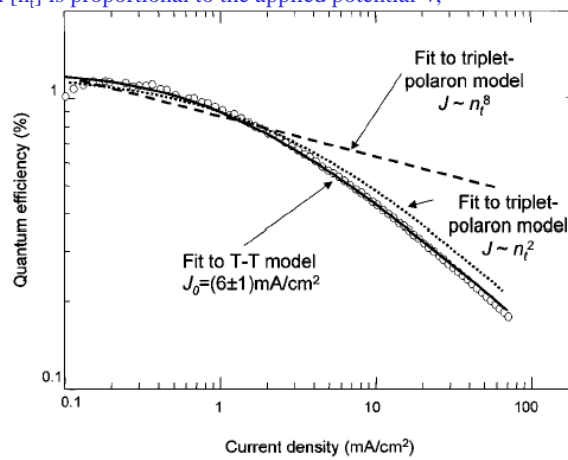
# Triplet-polaron annihilation

$$\frac{d[{}^3M^*]}{dt} = -\frac{[{}^3M^*]}{\tau} - k_e[{}^3M^*][n_t] + \frac{J}{qd}$$

Assuming bulk limited transport, then  $[n_t]$  is proportional to the applied potential  $V$ ,

$$\frac{\eta}{\eta_0} = \frac{1}{1 + \alpha V^l}$$

$$J \propto V^{l+1}$$



# Triplet-polaron annihilation

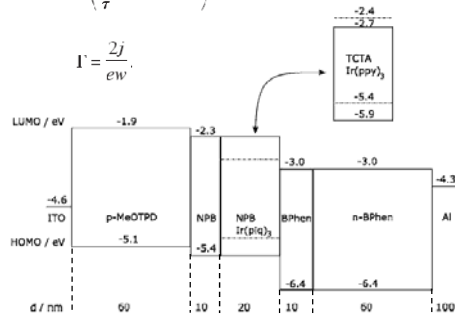
$$\frac{d[n_{ex}]}{dt} = -\frac{[n_{ex}]}{\tau} - \frac{1}{2}k_{TT}[n_{ex}]^2 - k_p \left[ \frac{\rho_c(j)}{e} \right] [n_{ex}] + \frac{j}{eW}$$

$$\frac{\eta(j)}{\eta_0} = \Theta \left[ \sqrt{\frac{\Delta^2 + \Gamma k_{TT}}{k_{TT}^2}} - \frac{\Delta}{k_{TT}} \right]$$

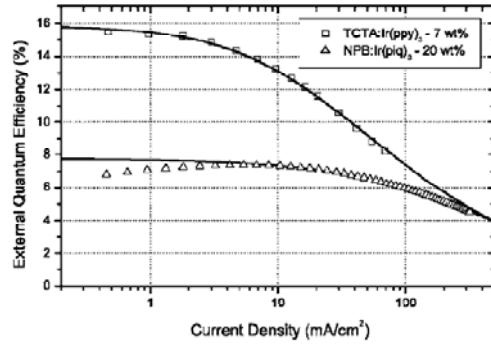
$$\Theta = \frac{eW}{\tau j}$$

$$\Delta = \Delta(k_p) = \left( \frac{1}{\tau} + k_p C_j^{l(l+1)} \right)$$

$$\Gamma = \frac{2j}{eW}$$



	$\tau$ [ $\mu$ s]	$k_{TT}$ [ $10^{-12}$ cm <sup>3</sup> s <sup>-1</sup> ]	$k_{p,e}$ [ $10^{-12}$ cm <sup>3</sup> s <sup>-1</sup> ]	$k_{p,h}$ [ $10^{-12}$ cm <sup>3</sup> s <sup>-1</sup> ]	$\eta_0$ [%]	$w$ [nm]
TCTA:Ir(ppy) <sub>3</sub>	(1.58 ± 0.05)	(3 ± 2)	(0.2 ± 0.1)	(0.3 ± 0.2)	15.8	10
NPB:Ir(piq) <sub>3</sub>	(1.10 ± 0.05)	(1.4 ± 0.6)	(0.7 ± 0.2)	(0.2 ± 0.2)	7.6	19



S. Reineke, K. Walzer, and K. Leo, Phys. Rev. B 75, 125328 (2007)

