# Ch.9: Phosphorescence in OLEDs

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

**2009. 5. 2.**

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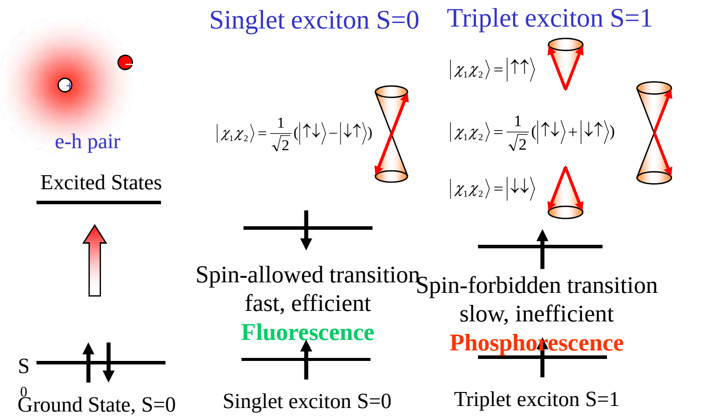
# Relaxation of Singlet & Triplet Excitons





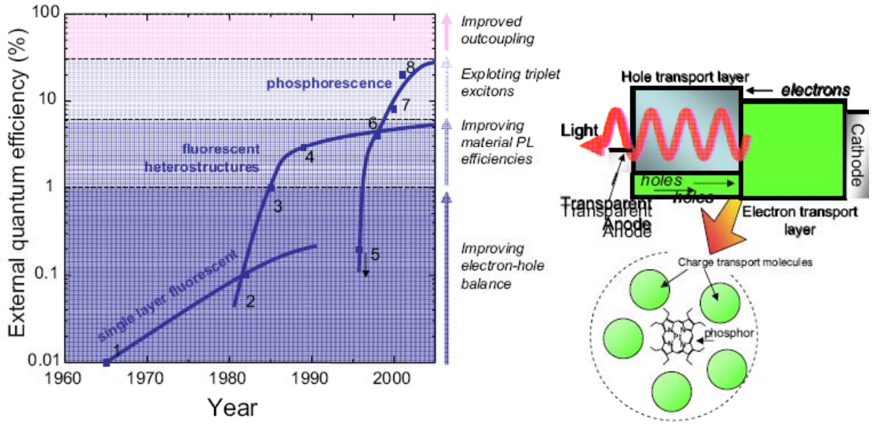

**Fluorescence : Radiation restricted to singlet excitons, → η ~25%**
**Phosphorescence : Radiation is from triplets → η ~ 100%.**

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)

# 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)

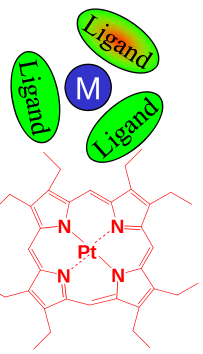
M. Baldo, IMID/IDMC '06 DIGEST, 645-674 (2006)



# Organic Phosphorescent Dyes

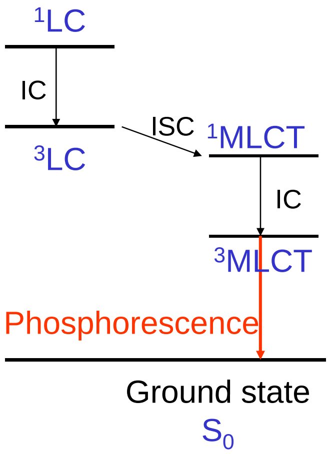
*Organic Semiconductor*
*EE 4541.617A*
*2009. 1st Semester*

Ligand-centered Exciton (LC)

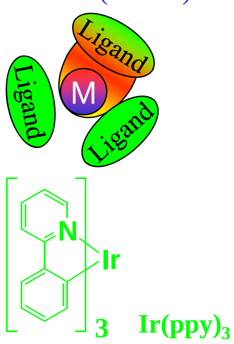



**PtOEP**

Triplet lifetime τ ~ 100 μs




Metal-Ligand Charge Transfer Exciton (MLCT)




**$Ir(ppy)_3$**

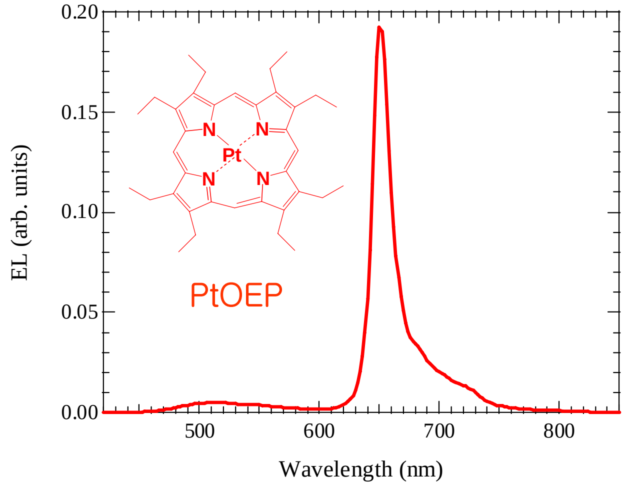
Triplet lifetime τ ~ 1 μs

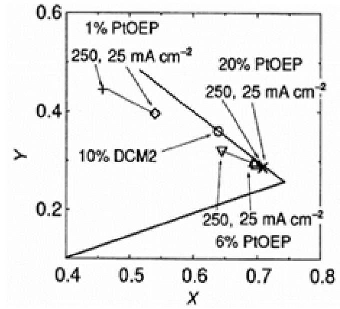
$$H_{SO} = \frac{Ze^2}{2m^2c^2}\frac{1}{r^3}\vec{L}\cdot\vec{S} \propto Z^4$$

- The emissive state is a mixture of a LC exiton 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.

# Phosphorescent Dye OLED





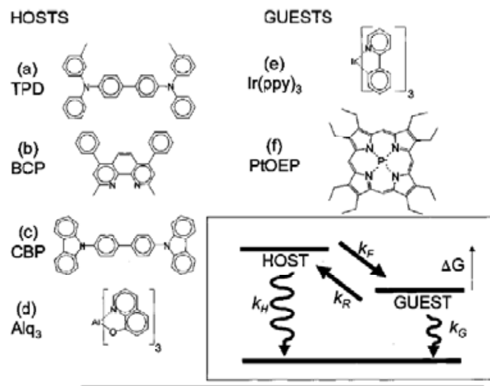

Efficient red EL emission from triplet excitons: $\eta_{ext}$ ~ 2.2% @ 100 cd/m$^2$

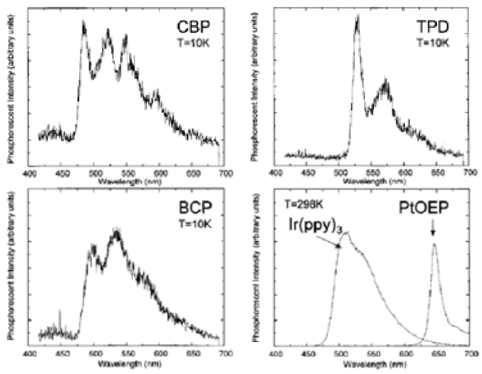
M. A. Baldo, *et al*, Nature **395**, 151 (1998)



# Triplet energy of R & G phosphors






| Material | Triplet energy (±0.1 eV) | Triplet lifetime |
|---|---|---|
| PtOEP | 1.9 | 110±10 μs[a] |
| Ir(ppy)3 | 2.4 | 0.8±0.1 μs[b] |
| CBP | 2.6 | >1 s |
| BCP | 2.5 | <10 μs |
| TPD | 2.3 | 200±50μs |
| $Alq_3$[c] | 2.0 | 25±15 μs |

| Guest (lifetime) | Host | ΔG (± 0.1 eV) | Host lifetime | Emission lifetime (μs) | Trapping on guest | EL quantum efficiency |
|---|---|---|---|---|---|---|
| PtOEP (110±10 μs) | CBP | −0.7 | >1 s | 80±5 | Yes | 6% |
| | $Ir(ppy)_3$ | −0.5 | <0.1 μs | 80±5 | ? | 3% |
| | TPD | −0.4 | 200±50 μs | 80±5 | Yes | 3% |
| | $Alq_3$ | −0.1 | 25±15 μs | 40±5 | No | 3% |
| $Ir(ppy)_3$ (0.8±0.1 μs) | CBP | −0.2 | >1 s | 0.4±0.05 | Yes | 8% |
| | TPD | +0.1 | 200±50 μs | 15±2 | No | 3% |
| | $Alq_3$ | +0.4 | 25±15 μs | <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,C2']picolinate, $E_t$=2.65 eV

Host

4,4'-N,N'-dicarbazole-biphenyl (CBP), $E_t$=2.56 eV, a maximum EQE= 5.7%

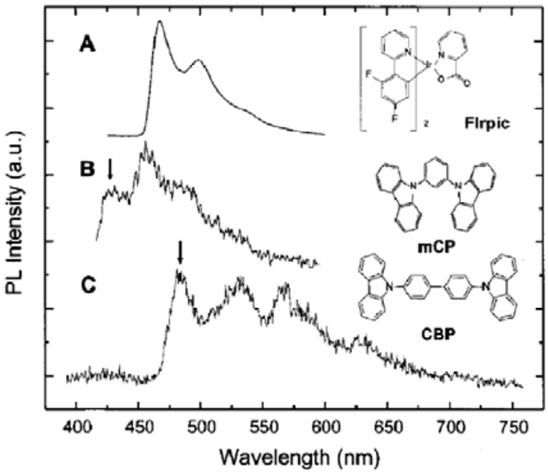
C. Adachi, R. C. Kwong, P. Djurovich, V. Adamovich, M. A. Baldo, M. E. Thompson, and S. R. Forrest, Appl. Phys. Lett. 79, 2082 (2001)

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).

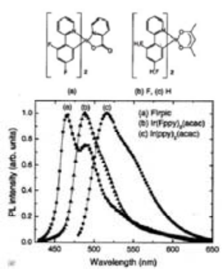


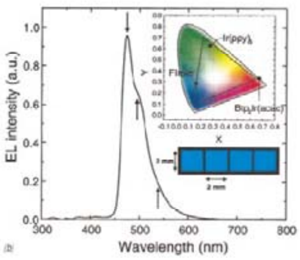

R. J. Holmes, S. R. Forrest, Y. J. Tung, R. C. Kwong, J. J. Brown, S. Garon, and M. E. Thompson, Appl. Phys. Lett. 82, 2422 (2003).

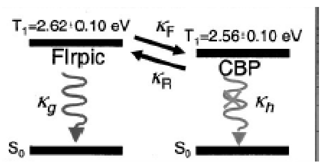


# Blue phosphorescent OLED

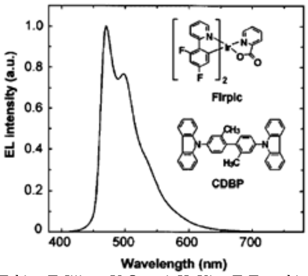


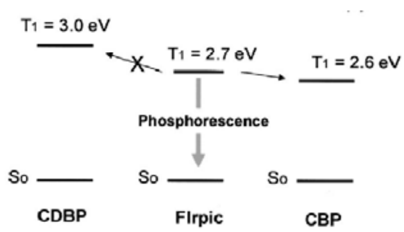


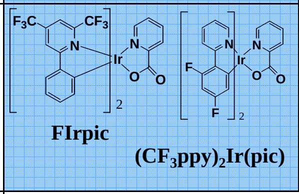
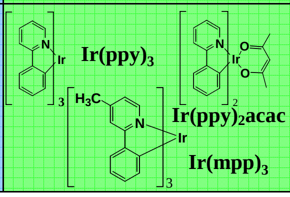
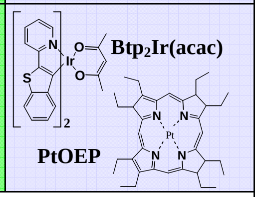
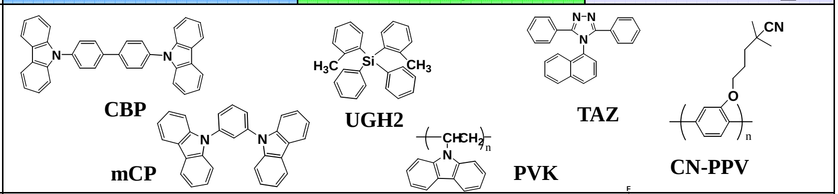
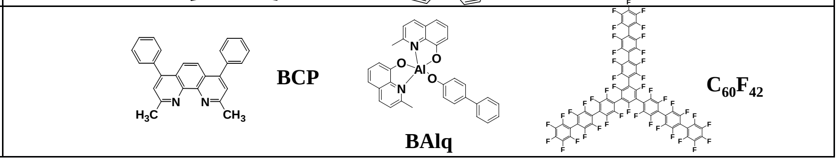

C. Adachi, R. C. Kwong, P. Djurovich, V. Adamovich, M. A. Baldo, M. E. Thompson, and S. R. Forrest, Appl. Phys. Lett. 79, 2082 (2001)




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

# Host and Phosphorescent Dopant Materials

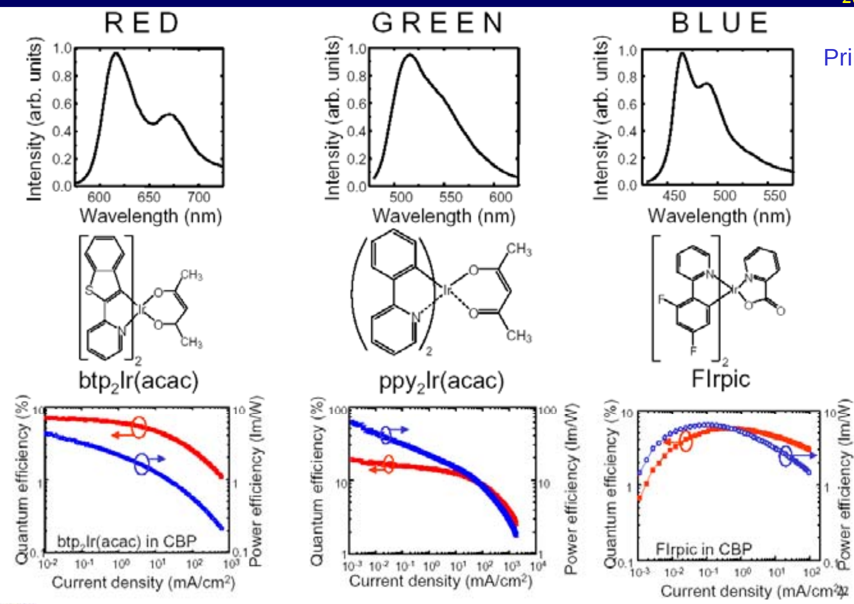
| | Blue | Green | Red |
|---|---|---|---|
| **Dopant** |  **FIrpic** **$(CF_3ppy)_2Ir(pic)$** |  **$Ir(ppy)_3$** **$Ir(ppy)_2acac$** **$Ir(mpp)_3$** |  **$Btp_2Ir(acac)$** **PtOEP** |
| **Host** |  **CBP** **mCP** **UGH2** **PVK** **TAZ** **CN-PPV** | | |
| **Hole/Exciton Blocking Materials** |  **BCP** **BAlq** **$C_{60}F_{42}$** | | |

Dr. H. N. Cho (InkTek)





# Organic Electrophosphorescence devices




Princeton group

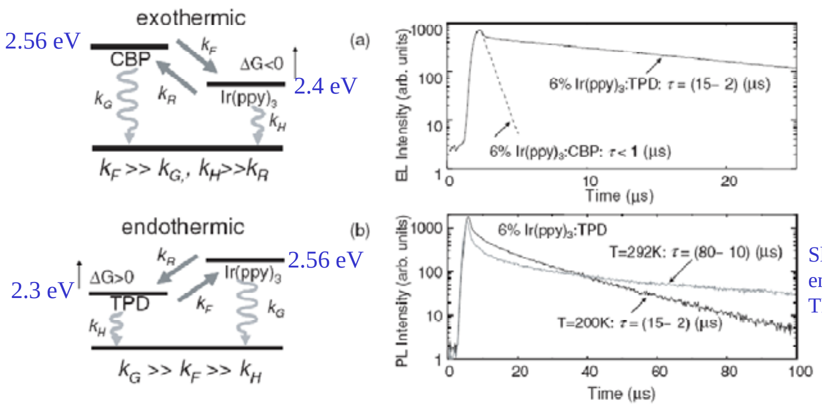
# Energy transfer in blue phosphorescent OLEDs

- endothermic energy transfer
- exothermic energy transfer
- charge trapping





# Exothermic and endothermic energy transfer



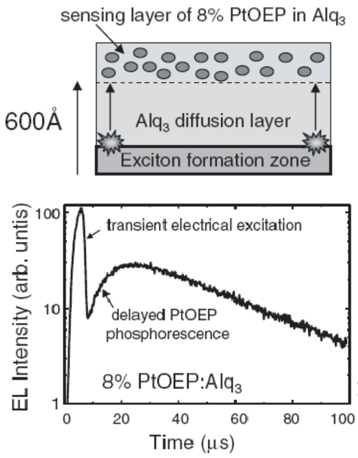

Slow endothermic energy transfer from TPD to Ir(ppy)3

**Fig. 5** a) The electroluminescent response of the endothermic system $Ir(ppy)_3$:TPD, as compared to the exothermic system $Ir(ppy)_3$:CBP. The lifetime of $Ir(ppy)_3$ in a TPD host is significantly longer (15 µs) than the natural radiative lifetime of $Ir(ppy)_3$ (<1 µs). The initial peak in the response is principally due to fluorescence from TPD. (b) The photoluminescent response of 8% $Ir(ppy)_3$ in TPD at $T = 292$ K and $T = 200$ 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 photoexcited $Ir(ppy)_3$. Adapted from Ref. [24].

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

## Exothermic energy transfer from Alq3 to PtOEP and triplet exciton diffusion





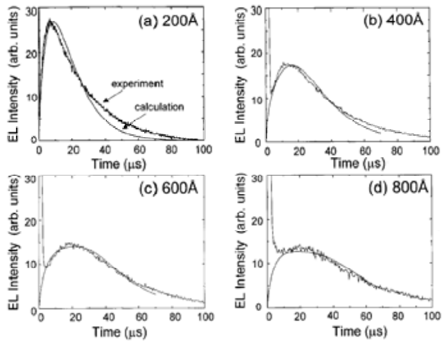




FIG. 6. The normalized, phosphorescent transients for PtOEP in $Alq_3$ recorded at 650 nm for diffusion distances of (a) 200 Å, (b) 400 Å, (c) 600 Å, and (d) 800 Å. Also shown are the calculated transients (smooth curves) based on nondispersive diffusion of triplets given a diffusion coefficient of $D=(8\pm5)\times10^{-8}$ cm$^2$/s, and a triplet exciton lifetime in $Alq_3$ of $\tau=25\pm15$ μs.

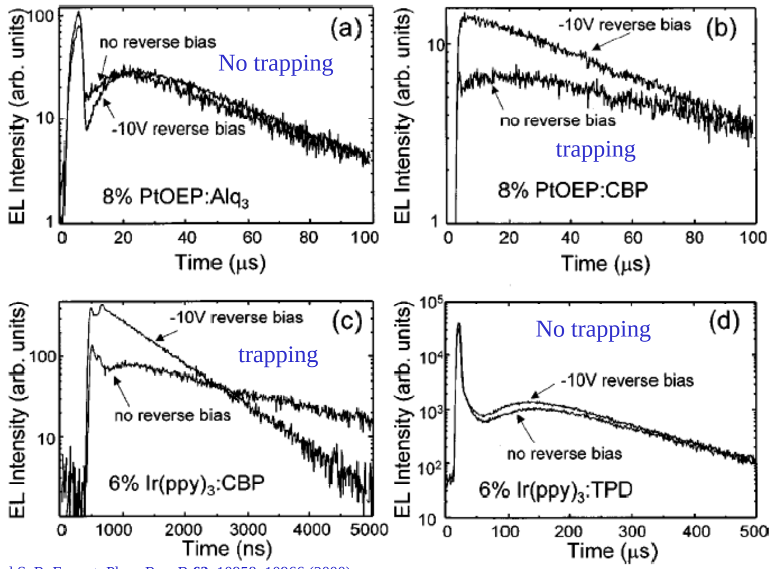
The delay in the PtOEP phosphorescence after an electrical excitation pulse is due to triplet diffusion through the Alq3 host. The delay is observed to decrease to zero as the exciton formation zone is moved closer to the PtOEP layer, confirming that excitons are formed initially in the Alq3 host. These experiments were used to estimate the triplet exciton lifetime in Alq3 to be (25 ± 15) μs.

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

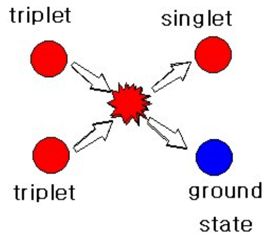


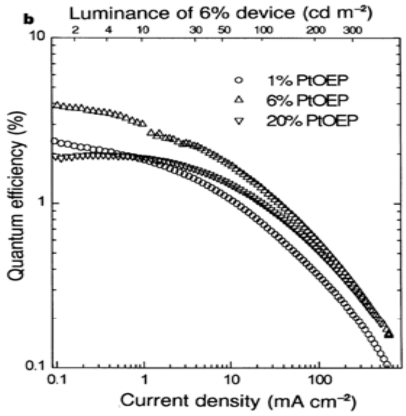



M. A. Baldo and S. R. Forrest, Phys. Rev. B **62**, 10958–10966 (2000).

# Quantum Efficiency *vs* Current

## 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)

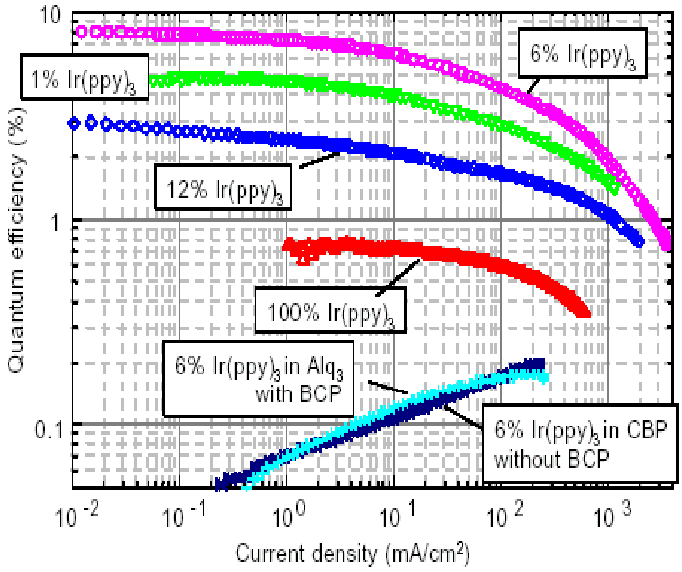




# Reduced Efficiency Roll-off with Short Triplet Exciton Lifetime

Ir(ppy)3

triplet exciton τ: ~500ns (doped in CBP)



## Triplet – Triplet (T – T) Annihilation



$$^3M^* + ^3M^* \xrightarrow{k_{TT}^S} {}^1M^* + M, \quad M + {}^1M^* \xrightarrow{\text{ISC}} M + {}^3M^*. \quad {}^3M^* + {}^3M^* \xrightarrow{k_{TT}^T} {}^3M^* + M.$$

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

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

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

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



## Transient Solution



trial solution

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

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

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

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

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

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

# T – T Annihilation: Transient behavior



$$^3M^* + {}^3M^* \xrightarrow[\text{ISC}]{k_{TT}^S} {}^1M^* + M.$$

$$M + {}^1M^* \longrightarrow M + {}^3M^*.$$

$$^3M^* + {}^3M^* \xrightarrow{k_{TT}'} {}^3M^* + M.$$

Rate equation for the T-T annihilation

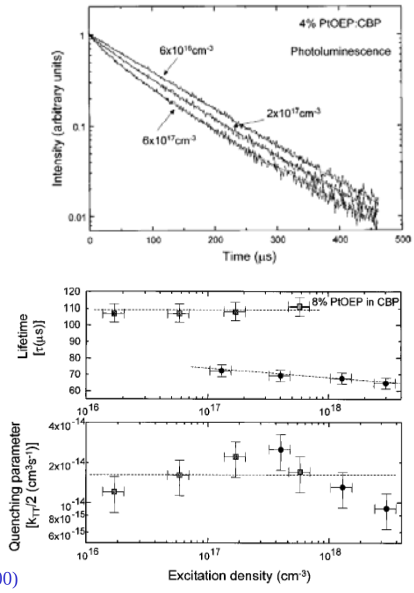
$$\frac{dn_T}{dt} = -\frac{n_T}{\tau} - k_T n_T{}^2 + \frac{J}{qd}$$

Transient behavior: J=0

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

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

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




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



# T – T Annihilation: Steady-state solution



$$\frac{dn_T}{dt} = 0 \qquad k_T n_T{}^2 + \frac{n_T}{\tau} - \frac{J}{gd} = 0$$

(근의 공식)

$$n_T = \frac{-\frac{1}{\tau} + \sqrt{(\frac{1}{\tau})^2 + \frac{4Jk_T}{qd}}}{2k_T} = \frac{1}{2k_T\tau}\left[-1+\sqrt{1+\frac{4Jk_T\tau^2}{qd}}\right] = \frac{1}{2k_T\tau}\left[-1+\sqrt{1+\frac{8J}{J_T}}\right] \qquad (\because \frac{k_T\tau^2}{2qd} = J_T{}^{-1})$$

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

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

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

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

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

# Efficiency Roll-off



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

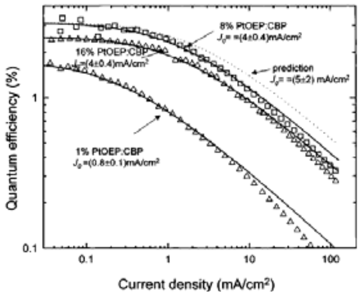
$$\frac{\eta}{\eta_0}=\frac{J_0}{4J}\left(\sqrt{1+8\frac{J}{J_0}}-1\right), \qquad J_0=\frac{4qd}{k_{TT}\tau^2}$$

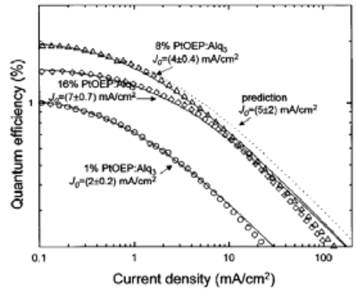
current density required to excite every phosphorescent molecule (i.e., the onset of saturation)

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

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 $Alq_3$ | 8% PtOEP in CBP | 8% PtOEP in $Alq_3$ | 16% PtOEP in CBP | 16% PtOEP in $Alq_3$ |
|---|---|---|---|---|---|---|
| $J_0$ from steady-state response ($mA/cm^2$) | 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 ($mA/cm^2$) | 7±2 | 8±3 | 5±2 | 5±2 | 4±1 | 6±2 |
| Saturation threshold current density ($mA/cm^2$) | 40±20 | 200±100 | 400±80 | 800±200 | 800±200 | 1000±300 |






# Triplet-polaron annihilation

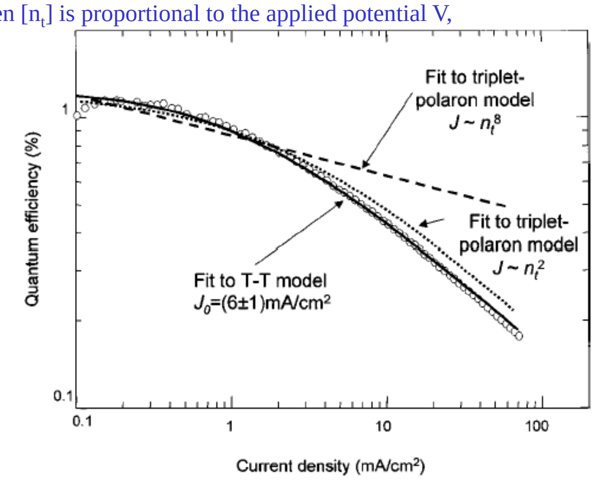
*Organic Semiconductor*
*EE 4541.617A*
*2009. 1st Semester*

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

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

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

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



# Triplet-polaron annihilation

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

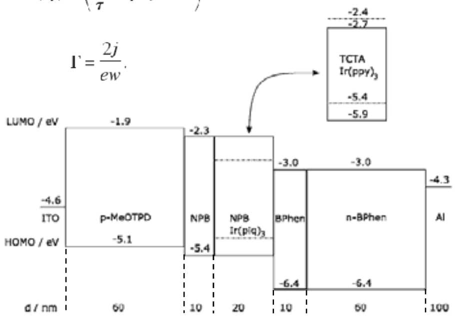
$$\frac{\eta(j)}{\eta_0} = \Theta\left[\sqrt{\frac{\Delta^2 + \Gamma k_{TT}}{k_{TT}^2}} - \frac{\Delta}{k_{TT}}\right]$$

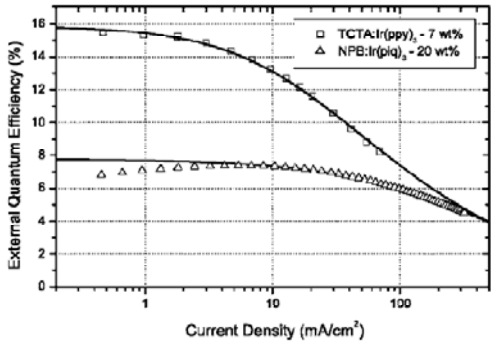
$$\Theta = \frac{ew}{\tau j},$$

$$\Delta \equiv \Delta(k_P) = \left(\frac{1}{\tau} + k_P C j^{1/(l+1)}\right)$$

$$\Gamma = \frac{2j}{ew}.$$

| | $\tau$ [$\mu$s] | $k_{TT}$ [$10^{-12}$ cm$^3$ s$^{-1}$] | $k_{P,e}$ [$10^{-12}$ cm$^3$ s$^{-1}$] | $k_{P,h}$ [$10^{-12}$ cm$^3$ s$^{-1}$] | $\eta_0$ [%] | $w$ [nm] |
|---|---|---|---|---|---|---|
| TCTA:Ir(ppy)$_3$ | **(1.58±0.05)** | (3±2) | (0.2±0.1) | **(0.3±0.2)** | **15.8** | 10 |
| NPB:Ir(piq)$_3$ | **(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)