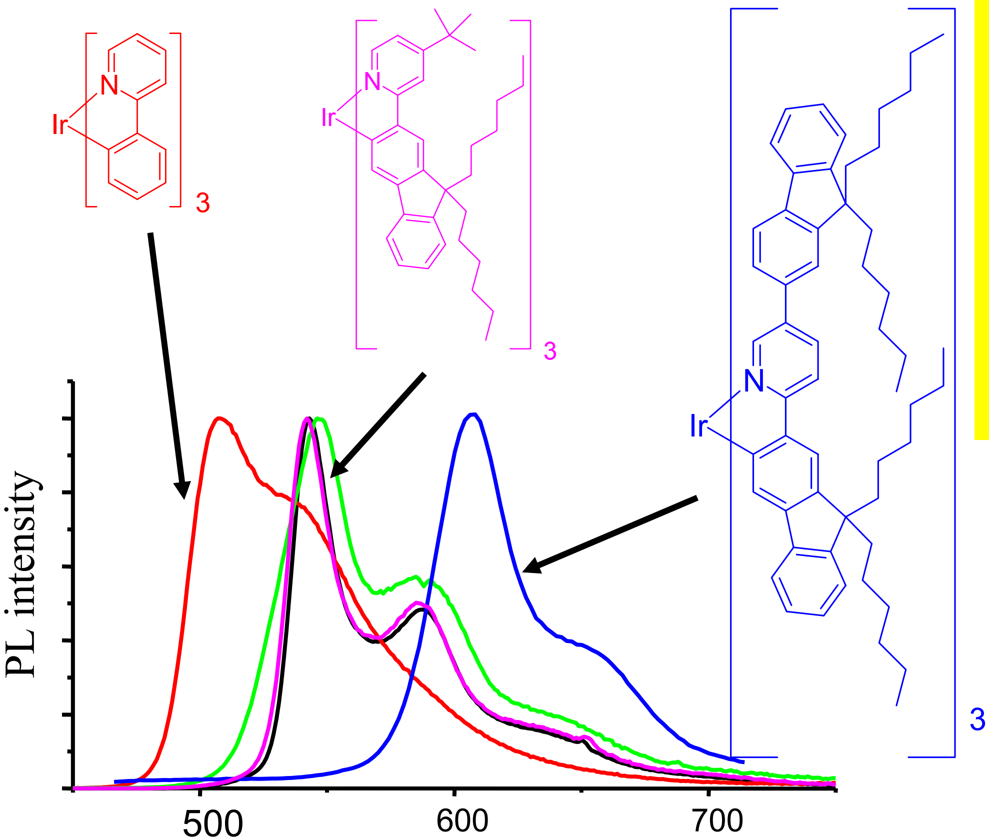
Surface Plasmon Enhanced Light Emitting Devices

Alexander Mikhailovsky, Jacek Ostrowski, Hadjar Benmansour, and Guillermo Bazan

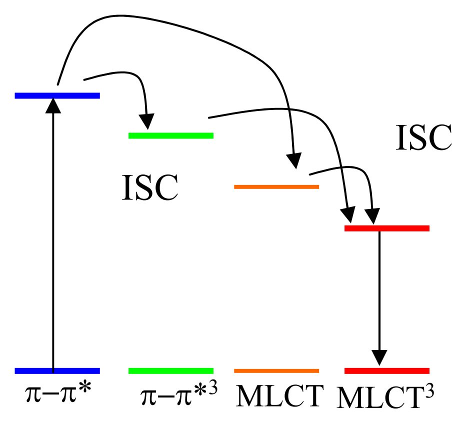
[+]*Department of Chemistry and Biochemistry, University of California Santa Barbara, Santa Barbara, CA 93106*

Triplet Emitters for LED Applications

Organometallic triplet emitters



- Utilizes both singlet and triplet excitations for emission generation (No 25% percent limit for EL efficiency!).
- Can be tuned in very broad range of spectrum by variation of the ligand conjugation length
- High PL (up to 75 %) and EL (15%) efficiencies have been demonstrated
- Radiative life lifetime ~ 1-1000 μS
- LED performance is limited by triplet-triplet annihilation and chromophore saturation



Triplet-Triplet Annihilation in Phosphors

Triplet-triplet annihilation (TTA)

$$T + T \rightarrow S + GS$$

$$T + T \rightarrow T + GS$$

T – triplet exciton, S – singlet exciton

GS – ground state

Rate equation for the excited state kinetics

$$\dot{N} = -(k_R + k_{NR})N - \beta \frac{N^2}{t^s}$$

TTA turns on at high excitation levels or high density of chromophore species

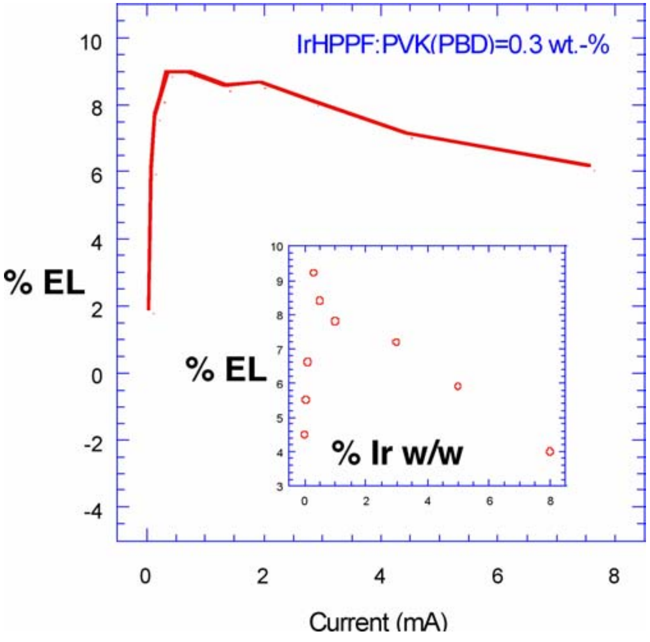
β – TTA coefficient

k_R (k_{NR}) – radiative (non-radiative) decay rate

s – exciton wandering dimensionality parameter

($s = 1$ – no wandering, $s = 0$ – 3D random walk)

TTA – limits performance of phosphorescent light emitting diodes (PhOLEDs) at high current densities



Is There a Way Around TTA?

Steady-state PhOLED operation equation

$$\dot{N} = -(k_R + k_{NR})N - \beta N^2 + \gamma J = 0$$

J – injection current density

γ – efficiency of electron-exciton conversion

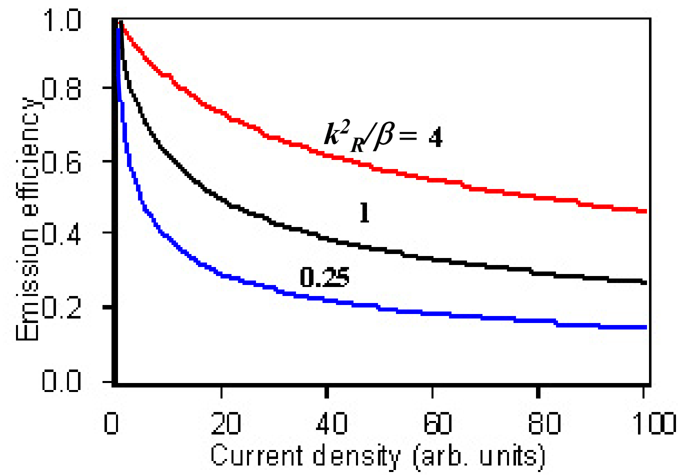
PhOLED efficiciency as a function of current

$$F = -\frac{k_R^2}{\beta}\frac{1}{2QJ} + \sqrt{\frac{k_R^2}{\beta}\frac{\gamma}{J} + \frac{k_R^4}{\beta^2}\frac{1}{4Q^2J^2}}$$

$$Q \equiv \frac{k_R}{k_R + k_{NR}}$$

Phosphorescence quantum yield

Ratio k^2_R/β determines PhOLED's efficiency



PhOLED performance at high current densities can be improved by variation of the emission rate

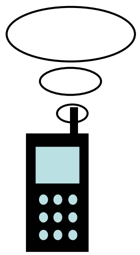
Radiative Decay Control

$$A_{21} = k_R = 1/\tau_R = \frac{\pi\omega}{\hbar n^2}|D|^2 \rho$$

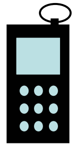
In a continuous medium $\rho \sim n^3$, $k_R \sim n$
However, $n = 1.4 - 1.6$ for most of optical materials and does not allow significant variation of k_R

What if we try to change ρ – local density of states (LDOS) for the electromagnetic field?

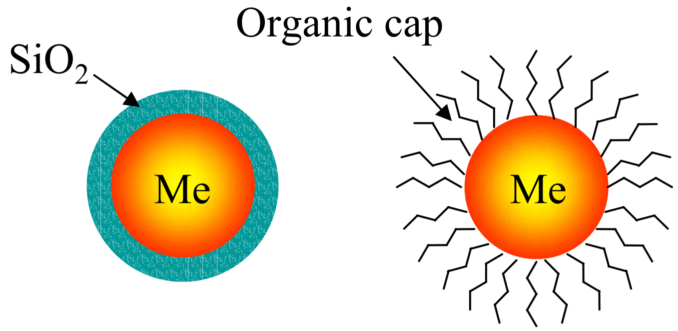
<u>**Possible recipe:**</u> Take metal surface with resonant electromagnetic response (surface plasmon resonance) and place chromophore in its vicinity



SP as a resonant antenna

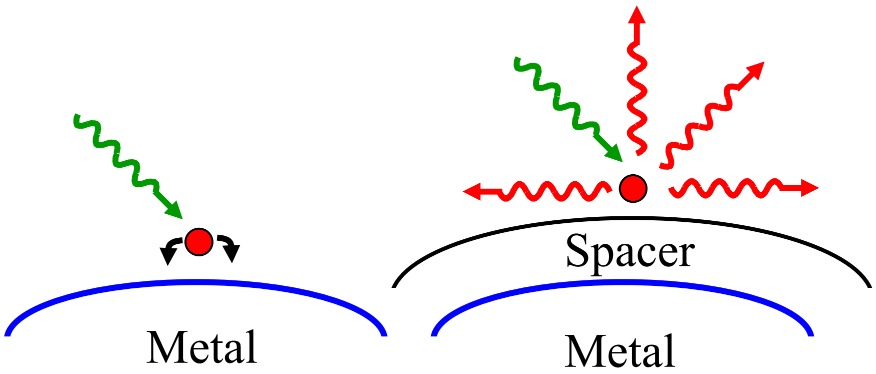


Noble metal (Au, Ag) nanoparticles



- **Surface plasmon resonance (SPR) in the visible range of spectrum**
- **SPR tunable by size and environment variation**
- **SPR coupled directly to light**
- **Easy synthesis and surface modification**

Emission-Quenching Competition

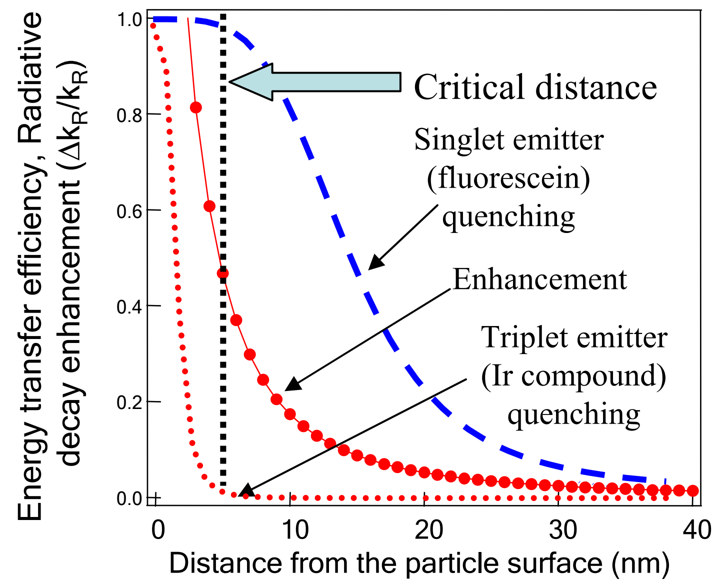


$$k_Q \propto f / r^m$$

m = 6 for point dipoles
m ~ 4 for metal nanoparticels*
m = 3 for a plain metal surface

In order to avoid quenching, the metal and the chromophore have to be separated spatially.
How will it affect the emission rate enhancement?

*G.Strouse, private communications



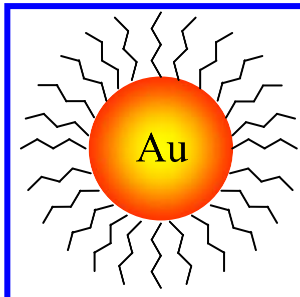
Quenching distance depends on the oscillator strength

$$f_S / f_T = \tau_S / \tau_T = 1 \text{ ns}/10\,\mu\text{s} = 10000$$

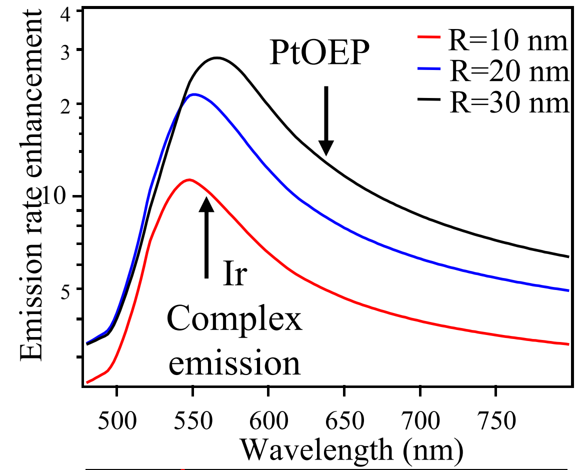
$$\boxed{R_Q^T / R_Q^S \approx 0.1}$$

Triplet emitters can be placed close to the surface, without loss of emission

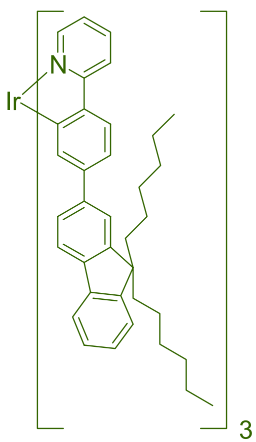
Blends Preparation



Dodecanethiol overcoated Au NPs
- Cap thickness ~ 2 nm
- Size 10 – 50 nm (broad size distribution)
- Soluble in non-polar organic solvents

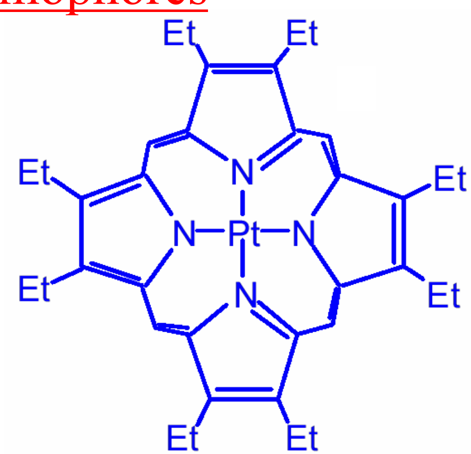


Chromophores



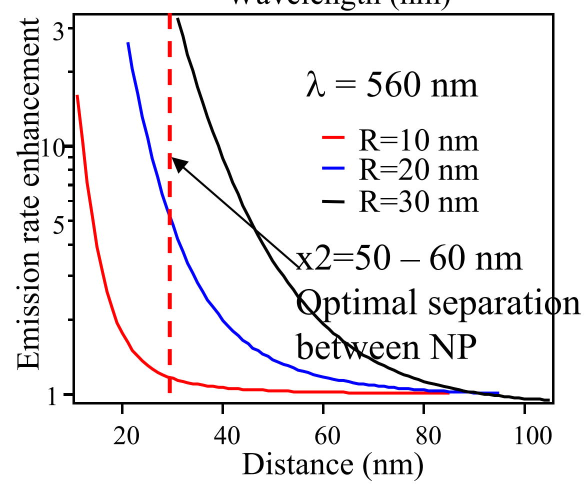
Ir complex

$\tau_R \sim 6\ \mu s$



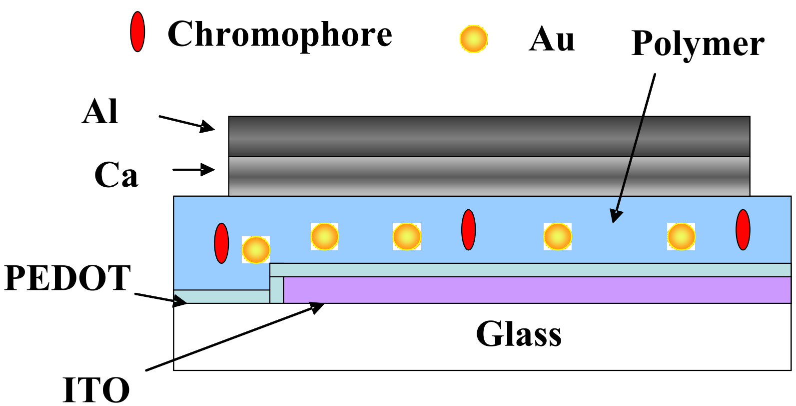
PtOEP

$\tau_R \sim 100 \mu s$



Chew, H., *J. Chem. Phys.*, **1987**, 87, 1355

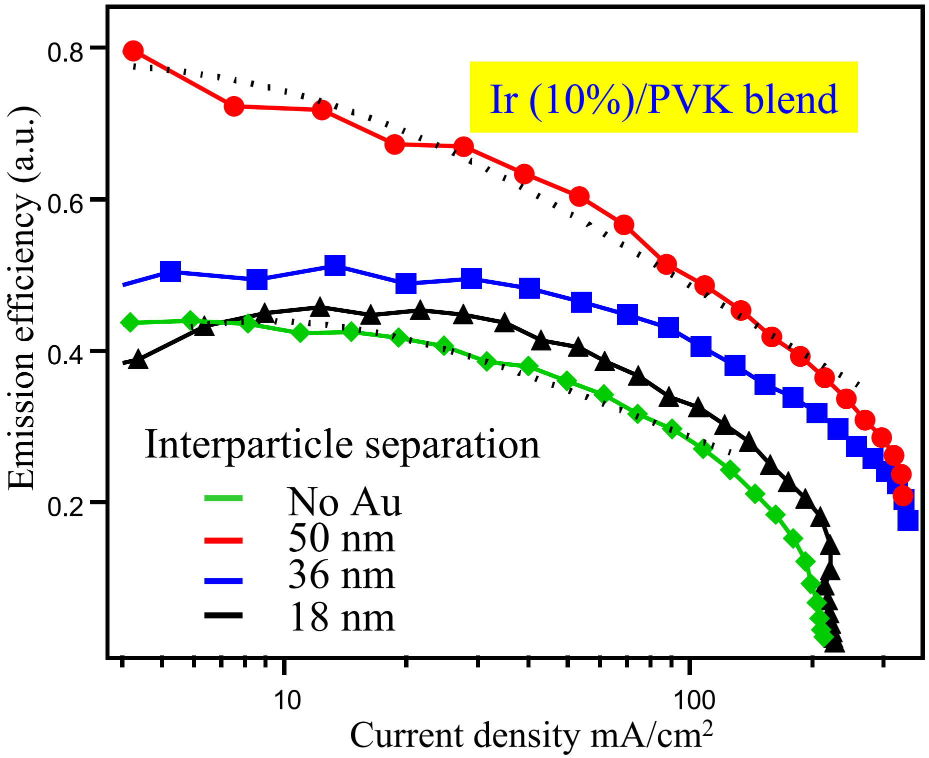
Au Nanoparticles-Doped PhOLEDs I



Fitting formula

$$F = -\frac{k_R^2}{\beta}\frac{1}{2QJ} + \sqrt{\frac{k_R^2}{\beta}\frac{\gamma}{J} + \frac{k_R^4}{\beta^2}\frac{1}{4Q^2J^2}}$$

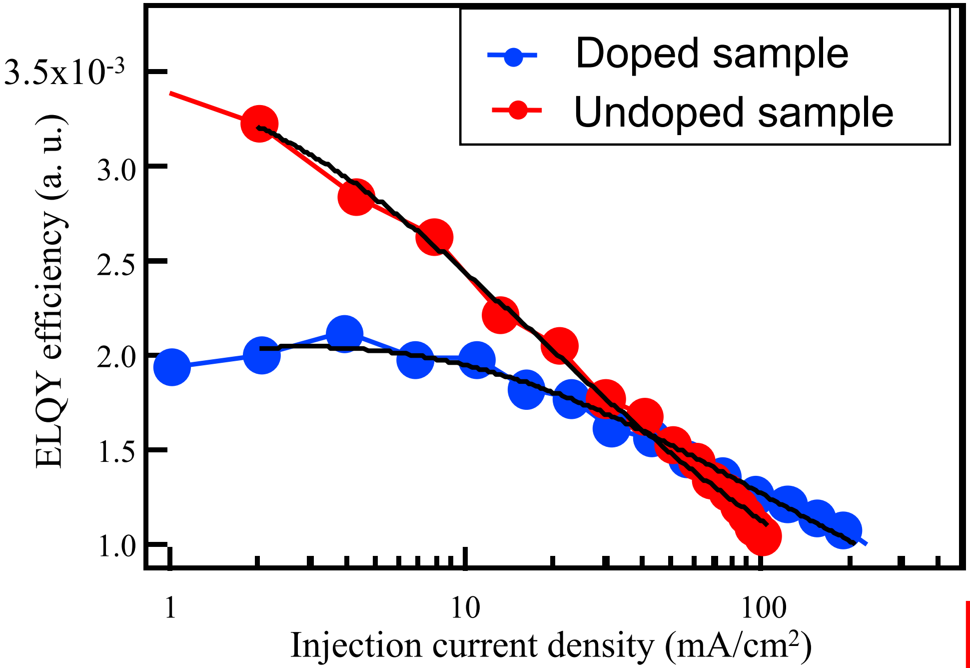
$$k_R^{Au} / k_R \approx 2.4$$



SiO_2 Nanoparticles-doped PhOLEDs do no exhibit enhanced performance

Au Nanoparticles-Doped PhOLEDs II

PtOEP/PFO devices



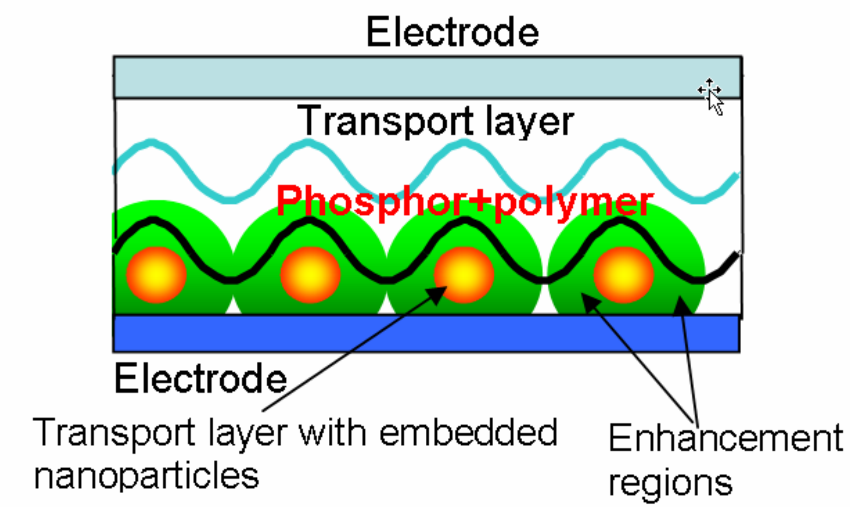
- Quite poor repeatability of devices
- Different slope indicates faster relaxation in Au-doped devices
- Optical excitation measurements indicate two-fold increase of the emission yield
- Doped devices have significantly higher turn on voltage

$$k_R^{Au} / k_R \approx 2$$

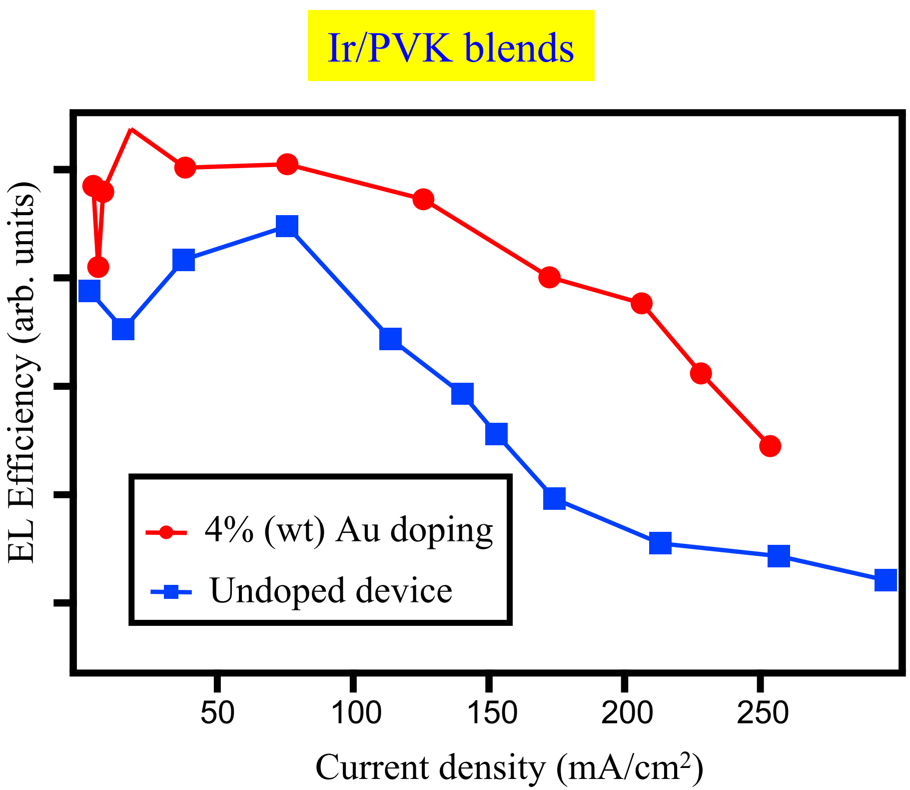
$$\gamma^{Au} / \gamma \approx 0.43$$

Improved decay rate, but worse charge-exciton conversion efficiency (phase separation?)

PhOLEDs With Doped Transport Layer



- PhOLEDs with doped transport layer exhibit increase of performnace
- Effect is not due to increase of outcoupling efficiency (different slope of E-I curve)
- Increased ohmic losses in doped devices lead to thermal damage at high current density



Conclusions

- Surface plasmon-based techniques for radiative decay control in PhOLEDs have been developed
- Interplay of different processes affecting singlet and triplet chromophore's performance in the vicinity of metal surfaces has been analyzed
- Two configurations of the surface plasmon enhanced PhOLEDs were developed and tested
- Two-fold enhancement of EL yield and efficient operation at high current densities have been demonstrated in Au nanoparticles-doped devices.