

## Exciton Dynamics and Device Lifetime of Phosphorescent dye doped Polymer Light Emitting Diodes

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### Introduction

Phosphorescence dye doped polymer light emitting devices (PhPLEDs) are expected to give higher efficiency than fluorescent polymers because triplet excitons as well as singlet excitons can be harvested to light using energy transfer and direct charge trapping. PhPLEDs have advantages over phosphorescent dye doped organic light emitting diodes (PhOLED) because polymer allows easy processing for large area and flexible displays using spin coating and ink jet printing. Most of PhPLEDs adopt doping system because of the easiness of synthesis and have used PVK as a host because of the homogeneous dispersion of phosphorescent dopants in the polymer. Even though the PVK based PhPLEDs show higher efficiency than fluorescent PLEDs, they show lower efficiency than small molecule based PhOLEDs. Moreover there are few reports on the lifetime of the devices. In this talk, exciton dynamics and lifetime of PVK based PhPLEDs will be presented.

### Results and discussion

The PL efficiency of Ir(ppy)<sub>3</sub>:PVK for various doping concentrations is shown in figure 1 and compared with Ir(ppy)<sub>3</sub> doped in CBP. The photoluminescence (PL) efficiency of Ir(ppy)<sub>3</sub>:PVK is lower than Ir(ppy)<sub>3</sub>:CBP for the whole range of doping concentration and this low PL efficiency can be a reason of the lower efficiency of PhPLED than PhOLED. Kinetics study of excited state of the phosphorescent dye using a time resolved spectroscopy indicated that the lower efficiency is originated from the large bi-excitonic quenching such as the triplet-triplet annihilation. Reduction of PL efficiency with increasing doping concentration in both systems comes from the dynamic quenching of triplet excitons rather than the static quenching. The dynamic quenching rate is small in CBP:Ir(ppy)<sub>3</sub> in the low doping concentration region below 10 wt% and increases rapidly with increasing doping ratio. In contrast, the dynamic quenching rate is much larger in PVK:Ir(ppy)<sub>3</sub> system than CBP:Ir(ppy)<sub>3</sub> in the low concentration region and weakly increases with increasing concentration. This difference in the dynamic quenching results from the small triplet energy difference between PVK and Ir(ppy)<sub>3</sub> than between CBP and Ir(ppy)<sub>3</sub>.

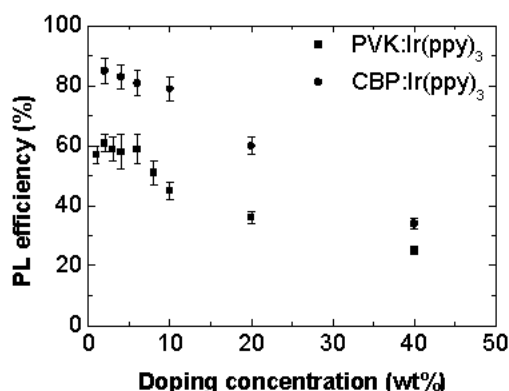


Figure 1. Photoluminescence efficiency of Ir(ppy)<sub>3</sub> doped in PVK and CBP vs. doping concentration.

Three kinds of devices were fabricated to investigate the lifetime and degradation mechanism of PhPLEDs:

- (I) ITO/PEDOT/PVK:Ir(ppy)<sub>3</sub>/BCP/Alq<sub>3</sub>/LiF/Al,
- (II) ITO/PEDOT/CBP:Ir(ppy)<sub>3</sub>/BCP/Alq<sub>3</sub>/LiF/Al, and
- (III) ITO/NPB/CBP:Ir(ppy)<sub>3</sub>/BCP/Alq<sub>3</sub>/LiF/Al.

The lifetime of the devices are displayed in figure 2 which were measured at the initial luminance of 1500 cd/m<sup>2</sup>. The PhPLED with PVK:Ir(ppy)<sub>3</sub> emitting layer show one order of magnitude shorter lifetime than CBP:Ir(ppy)<sub>3</sub> emitting layer with the same device structure as shown in Figure 2. The origin of the short lifetime was investigated based on the morphological instability, oxidation and reduction instability of the consisting materials. No dark spots or phase separation were observed after the accelerated degradation up to 50% of the initial luminance, indicating that the degradation is originated from intrinsic reasons. The change of PL efficiency of hole only devices, and both electron and hole transporting devices with electrical stressing were adopted to examine the electrochemical stability of the PVK, CBP and Ir(ppy)<sub>3</sub> combined with cyclic voltammetry measurement. The injection and transport of holes into PEDOT/PVK system produce irreversible oxidation moieties and carbazyl cross-linking products, which is a part of the shorter lifetime of PVK based devices. The cross-linking property and the change of higher occupied molecular orbital energy level of carbazyl containing materials were confirmed by using the cyclic-voltammetry measurement. When the electrons and holes were injected into the PVK:Ir(ppy)<sub>3</sub> layer, the PL efficiency was reduced gradually with electrical stressing and is reduced to 65% of the initial value after the electric current flow corresponding to the half lifetime. Surprisingly, it was found that Ir(ppy)<sub>3</sub> is unstable under the second reduction process (Ir(ppy)<sub>3</sub><sup>-2</sup>), which is in contrast with the published results. Large difference of the lowest unoccupied molecular orbital energy between PVK and Ir(ppy)<sub>3</sub> (0.5 eV), and low electron mobility of PVK allows electron transport only through Ir(ppy)<sub>3</sub> so that there are large probability for Ir(ppy)<sub>3</sub> to be doubly reduced. In CBP:Ir(ppy)<sub>3</sub>, however, the energy difference is small (<0.1 eV) and the electron mobility of CBP is high so that there is little chance for the Ir(ppy)<sub>3</sub> is doubly reduced. This is the main reason why the PVK:Ir(ppy)<sub>3</sub> based PhPLED gives very short lifetime.

In conclusion, the degradation mechanism of PVK: Ir(ppy)<sub>3</sub> based PhPLEDs include electrochemically unstable PVK<sup>+</sup> host, unstable anionic Ir(ppy)<sub>3</sub><sup>-2</sup> and PEDOT degraded by injected electrons. Improvement of the device lifetime of PhPLEDs requires ambipolar polymers that should have reversible electrochemical property, high triplet energy level, good mixing with dyes and LUMO level close to dopant.

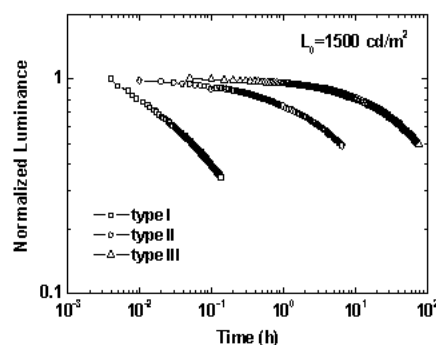


Fig. 2. Reduction of luminance with time for the device structure of ITO/PEDOT/PVK:Ir(ppy)<sub>3</sub>/BCP/Alq<sub>3</sub>/LiF/Al (Type I), ITO/PEDOT/CBP:Ir(ppy)<sub>3</sub>/BCP/Alq<sub>3</sub>/LiF/Al (Type II), and ITO/NPB/CBP:Ir(ppy)<sub>3</sub>/BCP/Alq<sub>3</sub>/LiF/Al (Type III). Initial luminance of the devices was 1500 cd/m<sup>2</sup>.