Red Electrophosphorescence from Polyacetylene-Based Light Emitting Diodes

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ABSTRACT

A new carbazole-containing polyacetylene (PA) was used as a host material in the construction of red phosphorescent LEDs with a configuration of ITO/PEDOT:PSS/host:btp$_2$Ir(acac)/BCP/Alq$_3$/LiF/Al. Compared with PVK as a host in the same device, The PA as a host has enhanced the quantum efficiency up to 1.4 fold. The efficiency of the device can be further improved 4.5 fold by using a BAlq layer instead of BCP/Alq$_3$ layers, and external quantum efficiency of 4.1% photons/electron has been achieved.

INTRODUCTION

Recently, the use of phosphorescent dyes has been popular in organic light-emitting devices (OLEDs) to overcome the fluorescent efficiency limit (25%) imposed by the formation of triplet excitons [1]. Phosphorescence in these dyes is strong due to the incorporation of a heavy metal atom with strong spin-orbit coupling which mixes singlet and triplet states. As the result, the internal quantum efficiency can theoretically reach 100% for such phosphorescent dye doped devices.

Although an effective external quantum efficiency of 19% photons/electron and a luminance power efficiency of 70 L/W have been demonstrated in OLEDs based on small molecules [2,3], the results in polymers have been not as encouraging.

Polymers have an important advantage over their small-molecule counterparts in that they can be solution processed [4]. This potentially allows a lower cost of production using room temperature spin-coating, screen printing or ink-jet printing techniques. However, there are only a few reports on utilizing polymer as host matrix in electrophosphorescent LEDs. So far most work has been done with poly(vinylcarbazole) (PVK) [5–8] and poly(fluorene) (PF) derivatives [9–11] as hosts. Recently, Gong et al [5] and Xie et al [6] reported external quantum efficiency of 10% from green-emitting Ir(PPy)$_3$-doped PVK devices. This important result demonstrated that phosphorescent dye-doped polymer host could provide very high efficiency as in the case of small molecule as well.

For red-emitting phosphorescent polymer LEDs, the host studied is mainly focused on PVK.[7-8] By doping btp$_2$Ir(acac) into PVK, Chen et al [8] achieved an external quantum efficiency of 3.3%, which was clearly less than the results on green-emitting devices. The probable reason is the generally low absorption of btp$_2$Ir(acac) molecule in the blue spectral region of PVK. Therefore, in order to realize full color display based on phosphorescent polymer LEDs, it is very important to develop new polymer host materials which can give efficient energy transfer from the host to the red dye. In this paper, a new carbazole-containing polyacetylene (PA; Fig. 1) is introduced as the host instead of PVK. Using the same device configuration, we show that the quantum efficiency can be increase by up to 1.4 times.

Since the performance of an OLED is sensitive to both the arrangement and the choice of the constituent organic layers, further improvement is quite possible. In this work, we modify the device configuration by using a BAlq layer (Fig. 1) instead of BCP/Alq$_3$ layers, which resulted in a great improvement in its EL performances. When the thickness of a BAlq reach its optimal value, a high external quantum efficiency of 4.1% ph/el can be obtained.

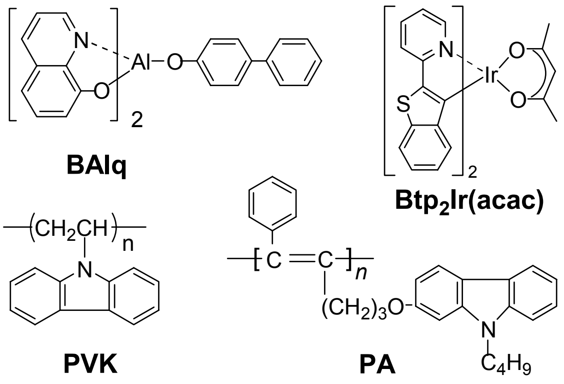

Fig. 1. Chemical structures of the molecules.

EXPERIMENTAL

Glass coated with 70nm, 30 Ω/□ indium-tin oxide (ITO) was used as the starting substrate. The sequence of pre-cleaning prior to the deposition of the organic layers consisted of a 50°C ultrasonic detergent soak for 30min, de-ionized water spray for 10min, ultrasonic de-ionized water soak for 30min, 110°C oven bake dry for 1-2hr and ultra-violet/ozone illumination for 10min. Sequential spin-coatings of 12nm PEDOT:PSS and 50nm btp2Ir(acac)-doped PVK or PA at room temperature under ambient conditions were followed by 54°C vacuum oven solvent evaporation and bake dry for 2hr.

Subsequently, for device Type A, 20nm Alq_3, 20nm BCP 1nm LiF and 150nm Al were in turn deposited by thermal vacuum evaporation in a chamber with a base pressure of 1 μTorr. The layer thickness during evaporation was measured in situ using a quartz crystal monitor. A Tencor P-10 Surface Profiler was used to determine the thickness of the spin-coated films. For device Type B, the processes are same as device A but using a BAlq layer instead of BCP and Alq_3 layers.

Photoluminance (PL) and Electroluminescence (EL) photometric characteristics were measured using a Kollmorgen Instrument PR650 photo-spectrometer. Current-voltage characteristics were measured using a Hewlett-Packard HP4145B Semiconductor Parameter Analyzer.

RESULTS AND DISCUSSIONS

We firstly studied the absorption and photoluminescence (PL) spectra of $btp_2Ir(acac)$, PVK and PA in their film states. As shown in Fig. 2, the $btp_2Ir(acac)$ exhibited a strong absorption peak at 486nm owing to its metal to ligand charge transfer (MLCT) absorption. Upon photoexcitation the PVK and PA emitted a blue light peaked at 408 and 452nm, respectively. There is a complete overlap between the PL spectrum of PA and the MLCT absorption of $btp_2Ir(acac)$, which is much larger than that between PVK and $btp_2Ir(acac)$, thus resulting the more efficient Fo¨rster energy transfer from the singlet-excited state of PA to the MLCT band of $btp_2Ir(acac)$. So a stronger red emission from $btp_2Ir(acac)$ is anticipated in the $btp_2Ir(acac)$-doped PA system.

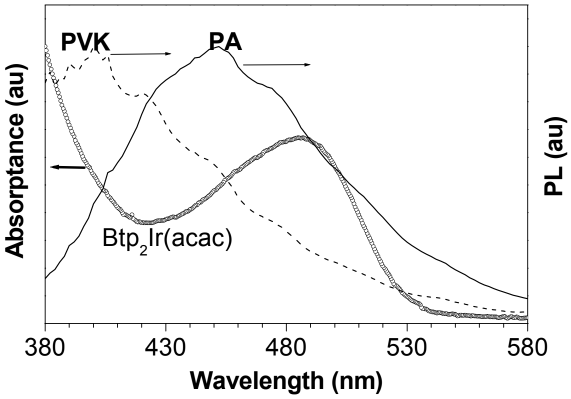

Fig. 2. Normalized absorption and photoluminescence spectra of thin solid films of $btp_2Ir(acac)$, PVK and PA.

Excited at 337nm, the normalized PL spectra of PVK and PA doped with various doping concentrations of $btp_2Ir(acac)$ are shown in Fig. 3. PL peaks are observed at ~400nm for PVK singlet emission and at 620nm for $btp_2Ir(acac)$ triplet emission (Fig. 3A). The blue emission at ~400nm from PVK reduces significantly with increasing dopant concentration from 5 to 15 wt %, indicating that Fo¨rster transfer from singlets of PVK to the MLCT bands of $btp_2Ir(acac)$ not only takes place but also increases with the doping concentration.

Similar to $btp_2Ir(acac)$-doped PVK system, the PL of $btp_2Ir(acac)$-doped PA system shows that the blue emission at 452nm from PA also reduces with raising the dopant concentration from 5 to 15 wt % (Fig. 3B). On the other hand, the system exhibits less host emission at the same doping concentration, implying better energy transfer between PA and $btp_2Ir(acac)$, which is consistent with previous predictions from the overlap analysis in Fig. 2.

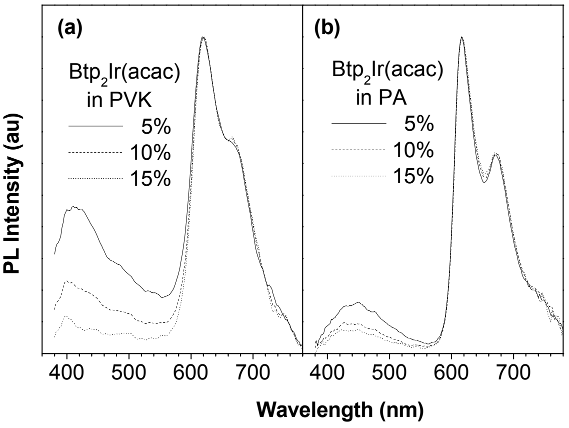

Fig. 3. PL spectra of (a) PVK and (b) PA doped with various concentrations of Btp$_2$Ir(acac).

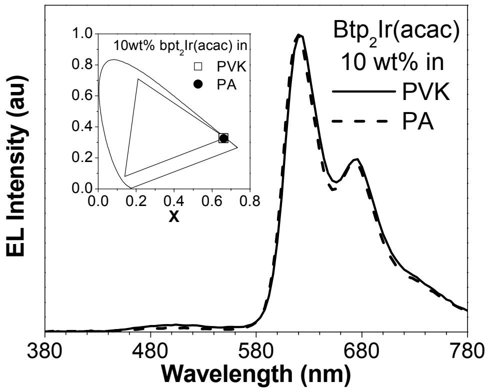

Fig. 5. EL Spectra of the devices A with PVK (or PA) doping 10 wt% Btp$_2$Ir(acac). Inset: CIE 1931 coordinates of the two devices.

In order to investigate their EL properties, we constructed EL devices as shown in Fig. 4 with a multilayer configuration of ITO/PEDOT:PSS/ PVK(or PA):btp$_2$Ir(acac)/BCP/Alq$_3$/LiF/Al (Type A), and ITO/PEDOT:PSS/PA:btp$_2$Ir(acac)/BAlq/LiF/Al (Type B).

We first measured the EL properties in device Type A. Fig. 5 shows the EL spectra of PVK and PA doped with 10 wt% btp$_2$Ir(acac). The CIE coordinates of the EL spectra were also plotted in the same figure. All the EL spectra were peaked at 620nm with a shoulder at 674nm, resembling to the PL spectrum of pure btp$_2$Ir(acac). The saturated CIE coordinates were at x = 0.66 and y = 0.33 (Insert), which are the NTSC standard red emissions for red subpixels of CRT displays. Their most distinguishing feature in the EL spectra of 10 wt% btp$_2$Ir(acac)-doped PVK or PA, compared with their PL spectra in Figure 3, is the absence of any a PVK- or a PA-induced emission at 408 or 452nm. This absence implies that besides an exciton transfer mechanism there is an additional charge trapping [6]. No blue emission was observed even at a high current density of 450 A/m^2, indicating that there is a complete energy transfer from host to btp$_2$Ir(acac) under electrical excitation.

Figure 6 shows the comparison of the EL efficiencies between PVK- and PA-host systems in the device Type A configuration. Clearly, The maximum external quantum efficiency was dependent on the polymer host. The maximum efficiency attained by PVK-host and PA-host system was 0.65 and 0.91% ph/el respectively, suggesting that the EL efficiency of the device Type A could be 1.4-fold improved by using PA as host instead of PVK.

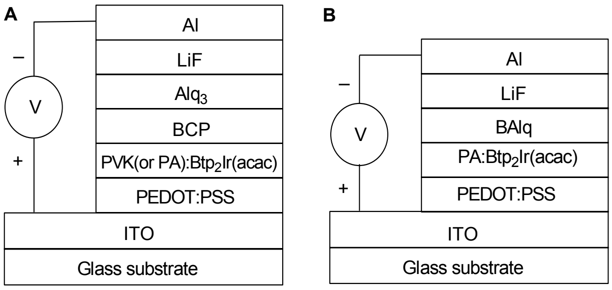

Fig. 4. Configurations of the EL devices Type A and Tape B.

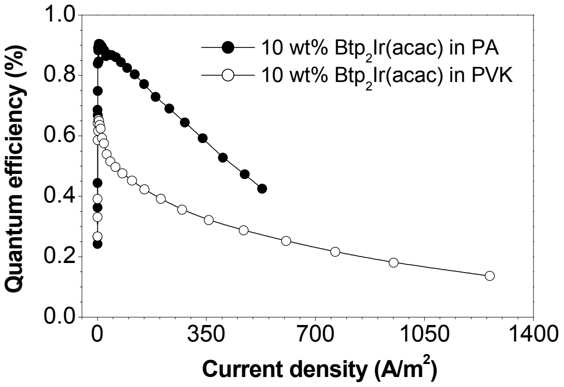

Fig. 6. The dependence of the quantum efficiency on current density for EL devices A with 10 wt% Btp$_2$Ir(acac) doped in host PVK or PA.

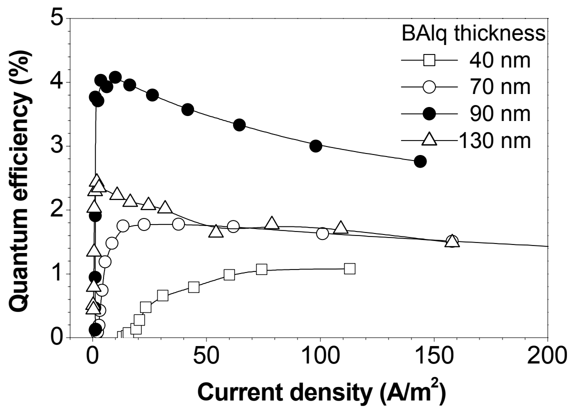

Fig. 7. The dependence of the quantum efficiency on current density for various thickness of BAlq in EL devices B.

In our previous study, we found that BAlq can serve as an electron transport layer as well as a hole blocking layer to enhance EL efficiency several times in green-emission phosphorescent polymer LED.[6] Thus we used BAlq layer instead of BCP/Alq_3 layers to construct EL device Type B (Figure 4). As shown in Figure 7, the peak efficiency of the device B is much sensitive to the thickness of the BAlq layer. Obviously, the optimal thickness is 90nm, at which a peak external quantum efficiency of 4.1% ph/el can be achieved, leading to a 4.5 fold enhancement in EL efficiency compared with that obtained in device A.

CONCLUSION

A carbazole-containing polyacetylene (PA) was first used as a host material in red-emission phosphorescent polymer LEDs. Compared with a well known polymer host PVK, The new PA as a host can enhanced the quantum efficiency up to 1.4 fold in the same device with configuration of ITO/PEDOT:PSS/host:$btp_2Ir(acac)$/BCP/Alq_3/LiF/Al. By using a BAlq layer instead of BCP/Alq_3 layers, the efficiency of the device can be further improved 4.5 fold and external quantum efficiency of 4.1% photons/electron has been achieved. Thus, our findings suggest that this new PA is a promising candidate of polymer hosts for red phosphorescent LEDs.

ACKNOWLEDGEMENT

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