Highly efficient blue and all-phosphorescent white polymer light-emitting devices based on polyfluorene host

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\textbf{A B S T R A C T}

We report efficient blue electrophosphorescent polymer light emitting devices with polyfluorene (PFO) as the host and iridium bis[2-(4,6-difluorophenyl)-pyridinato-N,C\textsubscript{2}] picolinate (FIrpic) as the dopant. Despite the low-lying triplet energy level of the polyfluorene polymer host, phosphorescent quenching can be suppressed by using poly(N-vinylcarbazole) (PVK) as anode buffer layer, resulting in a high luminous efficiency of 26.4 cd A\textsuperscript{-1}, which is one of the best results in the literature based on conjugated polymer reported to date. The reduced phosphorescent quenching is found to be associated with the exciton formation and charge carrier recombination within the PVK layer and the PVK/PFO interface due to the accumulation of holes. As compared with the devices based on non-conjugated host polymer PVK, the devices based on PFO showed a lower turn-on voltage (3.6 V vs. 4.4 V) and higher power efficiency (17 lm W\textsuperscript{-1} vs. 8.3 lm W\textsuperscript{-1}) due to the higher mobility of PFO. When doubly doped with a newly synthesized yellow-emitting metallophosphor, white polymer light-emitting devices with superior device performance (a peak device efficiency of 40.9 cd A\textsuperscript{-1}, a CIE coordinates of (0.32, 0.48), and a power efficiency of 31.4 lm W\textsuperscript{-1}) was achieved. These findings can broaden our selection in polymer hosts for highly efficient phosphorescent blue emitting devices and can find potential applications in full color displays and solid-state lighting applications in the future.

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\textbf{1. Introduction}

White polymer light-emitting devices (WPLEDs) have attracted broad research interest due to their potential applications in full-color display panels, flexible displays and solid-state lighting sources \cite{1,2}. In the past decade, the performance of WPLEDs has been improved significantly, in terms of efficiency and stability, due to the advance of novel materials and device configuration.

Among all kinds of WPLEDs, the polymer host–all phosphorescent dopants system is of particular interest, since it can allow for a conversion of up to 100% of injected charges (both singlet and triplet excitons can be harvested) into emitted photons \cite{3–6}, while it can be fabricated via solution-processed technology.

However, high-efficiency blue-emitting electrophosphorescent PLEDs represents a big challenge along because high-energy triplet excitons tend to flow back to low-energy sites \cite{7–9}, and the species of stable deep blue phosphorescence emitter are very rare. Alternatively, sky-blue-emitting triplet emitters, in combination with non-conjugated polymer, such as poly(N-vinylcarbazole) (PVK), which has relatively high triplet level (3.0 eV) \cite{10,11}, were commonly used to achieve blue-emitting electrophosphorescent...
PLEDs. Yang et al. reported efficient blue phosphorescent polymer light-emitting devices with iridium bis[2-(4,6-difluorophenyl)-pyridinato-N,C2] picolinate (Flrpic) as dopant, while PVK and electron-transporting 1,3-bis[(4-tert-butylphenyl)-1,3,4-oxadiazolyl] phenylene (OXD-7) as the host. The obtained devices showed a maximal luminous efficiency (LE) of 18.2 cd A\(^{-1}\) and power efficiency (PE) of 8.8 lm W\(^{-1}\), respectively [12]. Huang et al. reported that by using Li\(_2\)CO\(_3\)-doped poly[9,9-bis(2-(2-diethanol-aminoethoxy) ethoxy) ethyl] fluorene-alt-4, 4'-phenylether] (PDFPE) as the electron transporting layer and p-doped poly(3,4-ethylenedioxythiophene):poly(styrenesulfonic acid) (PEDOT:PSS) as hole transporting layer, blue-emitting phosphorescent PLEDs based on PVK: FIrpic exhibited a maximal LE of 20.3 cd A\(^{-1}\) and PE of 9.2 lm W\(^{-1}\) [13]. With similar strategy, the efficiency of the blue-emitting phosphorescent PLEDs from PVK: Flrpic have been improved to 22–28 cd A\(^{-1}\), via doping the active layer with electron transporting molecules or incorporation of small-molecule based electron-transport layer [14–17]. Despite the progress in the LE of these devices, their power efficiency are relatively low (i.e. 9–15 lm W\(^{-1}\)), mainly due to the non-conjugated nature of the PVK (low hole transport mobility of \(10^{-5}\) cm\(^2\)/V s), and its unmatched energy level (due to the very deep HOMO energy level of \(-5.8\) eV). On the other side, we found recently that despite the presence of the low-lying triplet states [18], conjugated polyfluorenes and their derivatives can be utilized as the host for green phosphorescent complexes, so long as there is a thin layer of PVK layer incorporated as the anode buffer interlayer [19]. More recently, we demonstrated highly efficient hybrid WPLEDs in which PFOs play the roles of a fluorescent blue emitter and a host material for the emitters, with the presence of PVK as the key anode interfacial layer [20,21]. Due to the broad emission covering the entire visible light spectrum from 400 to 780 nm, the resulting devices show a nearly pure white color with Commission Internationale d’Enclairage coordinates of (0.356,0.334), with a maximal LE reaching 21.4 cd A\(^{-1}\) [21].

In this study we demonstrated that the application of polyfluorene as the host for electrophosphorescent PLEDs can be extended to sky-blue emitter Flrpic, despite their lower-lying triplet energy levels (\(-2.3\) eV) as compared to Flrpic (\(-2.64\) eV). Due to a suppressed phosphorescent quenching by using PVK as the anode buffer layer, a high LE of 26.4 cd A\(^{-1}\), which is one of the best results based on conjugated polymer reported to date [11–17] was achieved. More importantly, as compared with the devices based on the non-conjugated host polymer PVK, the devices based on polyfluorene host showed a lower turn-on voltage (3.6 V vs. 4.4 V) and higher PE (17 lm W\(^{-1}\) vs. 8.3 lm W\(^{-1}\)). To the best of our knowledge, this is one of the most efficient solution-processed blue-emitting PLEDs reported so far [15]. On the basis of the blue-emitting PLEDs, we further found that this strategy is applicable to achieve efficient all-phosphorescent WPLEDs [22,23]. In combination with a newly reported yellow-emitting iridium complex [24], the obtained WPLEDs showed a peak PE of 31.4 lm W\(^{-1}\), which is among the best efficiency for WPLEDs based on conjugated polymer [22,25,26]. It is worthy of note that the PE of the device can be retained as high as 28 lm W\(^{-1}\) and 23 lm W\(^{-1}\) at a luminance of 100 cd m\(^{-2}\) and 1000 cd m\(^{-2}\), respectively, mainly due to the low operation voltage and low turn-on voltage (\(-3.4\)–\(-3.6\) V).

2. Experimental

2.1. Materials

PVK was purchased from Aldrich while PFO-POSS, OXD-7, Flrpic were purchased from American Dyes Sources. The synthesis of the home-made phosphor 1

**Scheme 1.** Molecular structure of the polymer host PFO–POSS, and the phosphorescent dyes Flrpic and 1 [24] used in this study.
was described in our previous report [24]. The molecular structures of the host polymer, poly(9,9-dioctylfluorenyl-2,7-diyl) end capped with POSS (polyhedral oligomeric silsesquioxane) (PFO–POSS), phosphorescent sky-blue and home-made yellow-emitting iridium complex used in this study are illustrated in Scheme 1.

2.2. Device fabrication

Device fabrication followed the well-established standard processes described elsewhere [22]. The ITO glass substrate was cleaned in ultrasonic bath sequentially in acetone, detergent, deionized water and isopropanol, and backed at 80 °C for 12 h. A 40-nm thick layer of PEDOT:PSS (Baytron P4083 Bayer AG, H.C. Stack, Inc.) was spin-coated onto the precleaned ITO-glass substrates after O2 plasma treatment, and dried at 120 °C for 30 min. Then, if necessary, a 40 nm thick layer of PVK was spin-coated on the top of PEDOT and baked at 120 °C for 10 min. A mixture of FIrpic or (Fi rpic, phosphor 1) with PFO–POSS and OXD-7 were spin-coated from the solution in p-xylene and chlorobenzene blend (~7:3) was spin-coated on the top of PVK with a thick of 40 nm. After baked at 120 °C for 20 min, a thin layer of CsF (1 nm) with about 120 nm thick Al capping layer was deposited through a shadow mask at a vacuum chamber with a base pressure of ~10^-4 Pa. Profilometer (Veeco Dektak 150) was used to measure the thickness of the films. CsF and Al layer thickness was monitored upon deposition by using a crystal thickness monitor (Sycon). Except the fabrication of PEDOT:PSS layer, all the device fabrication procedures were carried out in a controlled atmosphere dry-box (Vacuum Atmosphere Co.) in N2 atmosphere. The J–V–L data were collected using a Keithley 236 Source meter and a silicon photodiode. The luminance was calibrated by a PR-705 Spectra Scan Spectrophotometer (Photo Research) with simultaneous acquisitions of the EL spectra and the CIE coordinates. Time-resolved spectra were measured by fluorescence lifetime spectrometer (FLS-920, Edinburgh Instrument Ltd.).

3. Results and discussion

In light of the fact that efficient green electrophosphorescence can be realized by using conjugated polymer PFO–POSS as the host [19], the deep-blue-emitting properties of PFO–POSS (with CIE coordinates of (0.18,0.14) for
the EL) and the relatively high EL efficiency for a PFO–POSS based PLEDs (with a maximal external quantum efficiency (EQE) of 2.0% and a maximal LE of 2.4 cd A\(^{-1}\), Fig. 1), we extended PFO–POSS as the host material for sky-blue emitter, Flrpic.

Sky-blue-emitting devices with a device structure of ITO/PEDOT:PSS (40 nm)/PVK(40 nm)/PFO–POSS(100 wt.%)/OXD-7(40 wt.%): Flrpic(10 wt.%):CsF(1 nm)/Al were fabricated (Device A). Control devices without the presence of the PVK hole transporting layer (Device B) and devices based on PVK host (Device C) were also fabricated for comparison. The electroluminescent (EL) spectra, current density–luminance–voltage characteristics (\(J–V–L\)) and luminous efficiency–power efficiency–luminance characteristics (\(LE–PE–L\)) of all devices are shown in Fig. 2.

As can be seen clearly in Fig. 2a, upon the incorporation of a thin layer of PVK, nearly pure emission from Flrpic was observed in Device A, which resembles that of Device C. In other words, phosphorescent quenching by the lower-lying triplet energy (\(E_T\)) of PFO–POSS can be effectively avoided [19], despite the fact that PFO–POSS possesses a lower \(E_T\) level (\(-2.3\) eV) as compared to Flrpic (\(-2.64\) eV) [21]. In contrast, the EL emission from Flrpic is thoroughly quenched in the control Device B in which PVK is absent, resulting in a pure EL emission from PFO–POSS with low LE of 0.3 cd A\(^{-1}\). Moreover, the devices based on PFO–POSS exhibited a lower turn-on voltage (3.6 V vs. 4.4 V, see Fig. 2b) and more steeper current increase after turn-on as compared with PVK based devices, which can be attributed to a reduced charge carrier injection barrier height (see Fig. 3a, PFO–POSS can form ohmic contact with the CsF/Al cathode while there exists a barrier height of 0.6 eV for electron injection for PVK devices) and more balanced charge transport properties between hole and electron in the active layer. More importantly, Device A displayed a high LE of 26.4 cd A\(^{-1}\) at a luminance of 660 cd m\(^{-2}\) (Fig. 2c), which is one of the best results for blue electrophosphorescent PLEDs reported to date, while the Device C based on PVK host showed a LE of 18.2 cd A\(^{-1}\) (see Fig. 2b), consistent with some previous reports [14–
It is also important to note that Device A showed a higher maximal PE as compared with Device C (17.0 lm W\(^{-1}\) at 4.6 V vs. 8.3 lm W\(^{-1}\) at 6.4 V, Fig. 2b), mainly due to its lower turn-on voltage and operation voltage.

The observed reduced phosphorescent quenching in Device A is consistent with the discovery by Wang [27] and more recent report by Swensen et al. that triplet energy of the charge transport layer has a more significant impact on the quenching of triplet emission and the subsequent device performance than the triplet energy of the host material [28], although the exact reason was not very clear to date.

Here we tentatively attribute the reduced phosphorescent quenching in this PVK/PFO–POSS:Flrpic system to the exciton confinement within the PVK layer and the PVK/PFO–POSS interface [4], which can be explained as follows. As shown in Fig. 3a, the energy band diagram of the devices suggests that hole injection from the Fermi level of ITO/PEDOT (\(-5.2\) eV) into the HOMO of PVK (\(-5.6\) eV) and PFO–POSS (\(-5.8\) eV) is not very energetically favorable, while the cathode can form ohmic contact for highly efficient electron injection. Therefore, exciton formation and charge carrier recombination are forced to take place within the PVK layer and the PVK/PFO–POSS interface due to the accumulated holes [4]. This analysis can be further verified by the OXD-7 concentration dependence of EL spectra, in a series of devices with varied OXD-7 (x = 5, 10, 20, and 40, respectively. As can be clearly seen in Fig. 3b, as the content of OXD-7 relative to PFO–POSS decreased from 40 wt.%, to 5 wt.%, the deep blue emission located at around 430 nm, which can be attributed to the emission from PFO–POSS, is seen to increase gradually. In consideration of the electron transport properties of OXD-7, Fig. 3b suggests that with the absence of adequate amount of OXD-7, exciton formation zone are slightly shifted away from the PVK/PFO–POSS interface; while for the device with 40 wt.% of OXD-7 in the EML (Device A), exciton formation and recombination region are mainly formed and confined within PVK or the PVK/PFO–POSS interface, followed by energy transfer to the triplet emitter which can lead to highly efficient blue electroluminescence. On the other hand, given the very high LE in Device A (even higher than that of the control Device C based on PVK(40 nm)/PFO–POSS(100 wt.%): OXD-7(40 wt.%)/CsF(1 nm)/Al, where x = 2, 1.25, 1, and 0.5, corresponding to the blend ratios of 5:1, 8:1,10:1 to 20:1 between Flrpic and phosphor 1, respectively, and the devices are denoted as Devices D–G.

The role of the PVK layer and the proposed efficient interfacial energy transfer between PVK/Flrpic can be further clarified by the transient PL spectra of a thin film of PFO–POSS–Flrpic (10 wt.%)(40 nm) on top of PVK layer (40 nm). When the sample is excited at the absorption peak of PVK (~300 nm), and the probe is fixed at the emission peak of Flrpic (~470 nm), a single exponential decay with a lifetime of 714 ns was observed (Fig. 4), consistent with what was reported in the literature [29]. The result also indicates efficient energy transfer occurs from PVK to Flrpic and phosphorescent quenching by the lower-lying triplet energy lying of PFO–POSS is effectively avoided. In contrast, when the same sample is excited at the absorption peak of PFO–POSS (~375 nm), the photoluminescence of Flrpic is severely quenched, due to the low-lying triplet energy level of PFO–POSS.

The success in fabrication of highly efficient blue-emitting phosphorescent polymer light-emitting devices (WPLEDs) can be extended to all-phosphorescent white-emitting PLEDs. A series of single emission layer WPLEDs were fabricated by double doping of the blue-emitting Flrpic and yellow-emitting phosphor 1 (Scheme 1) with different ratios into the PFO–POSS host, in the presence of PVK as the anode buffer layer and OXD-7 as the electron transport materials. The typical device configuration of the white-emitting devices is ITO/PEDOT:PSS (40 nm)/PVK(40 nm)/PFO–POSS(100 wt.%): Flrpic(10 wt.%): phosphor 1 (x wt.%)/CsF(1 nm)/Al, where x = 2, 1.25, 1, and 0.5 corresponding to the blend ratios of 5:1, 8:1,10:1 to 20:1 between Flrpic and phosphor 1, respectively, and the devices are denoted as Devices D–G.

Fig. 5a shows the electroluminescence (EL) spectra of the resulting WPLEDs obtained at a current density of 10 mA cm\(^{-2}\). While tuning the blend ratio between Flrpic and phosphor 1 from 5:1, 8:1,10:1 to 20:1, the CIE coordinates of the white color shift from (0.35,0.51), (0.33,0.48), (0.30,0.47) to (0.27,0.45). The maximal forward-viewing L\(_E\) values of Devices D–G were found to be 45.6, 40.9, 40.5, and 30.8 cd A\(^{-1}\), respectively. Among all of the devices, Device E possessed both appropriate emission color for solid-state lighting and high LE, mainly due to its high luminous efficacy [24]. As can be clearly seen in the J–L–V characteristics (Fig. 5b), the Device E displayed a low turn-on voltage of 3.4 V, resulting in a maximal PE of 31.4 lm W\(^{-1}\) at the voltage 3.8 V. It is worthy of note that at a luminance of 100 cd m\(^{-2}\) and 1000 cd m\(^{-2}\), the PE was kept at 28 lm W\(^{-1}\) and 23 lm W\(^{-1}\), respectively (Fig. 5c). As compared with our previous report on WPLEDs based on PVK:Flrpic:yel-
low phosphor [23], the WPLEDs in this study displayed a much higher PE (30 lm W\(^{-1}\) vs. 20 lm W\(^{-1}\)), despite the fact that both showed comparable LE of around \(~40\ cd\ A^{-1}\).

In addition, our devices showed a minor current-dependent emission color. Taking Device D as an example, when the applied current density increased from 1 mA cm\(^{-2}\) to 10, 20, 40, and 80 mA cm\(^{-2}\), the CIE coordinates undergo minor color shift from (0.333,0.488) to (0.328,0.484), (0.323,0.480), (0.317,0.478) and (0.318,0.476), respectively (Fig. 5d).

4. Conclusions

In summary, we report efficient blue phosphorescent polymer light-emitting devices using polyfluorene (PFO–POSS) doped with OXD-7 as the host and PVK as the anode buffer layer. Suppressed triplet energy transfer from Flrpic to PFO–POSS is achieved upon the incorporation of PVK layer, mainly because the exciton formation and charge carrier recombination take place within the PVK layer and the PVK/PFO–POSS interface. Owing to the higher charge mobility of the host used in this study, the blue-emitting phosphorescent device show a reduced turn-on voltage of 3.6 V, a higher peak luminous efficiency of 26.4 cd A\(^{-1}\) and a doubled peak power efficiency of 17 lm W\(^{-1}\). When doubly doped with a newly synthesized yellow-emitting metallophosphor, white-emitting PLEDs with superior device performance (a peak device efficiency of 40.9 cd A\(^{-1}\), a CIE coordinates of (0.32,0.48), and a power efficiency of 31.4 lm W\(^{-1}\)) can be obtained, which is one of the best WPLEDs based on conjugated polymer reported to date.

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