Highly efficient homojunction organic light-emitting diodes†

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Highly efficient blue p-i-n homojunction phosphorescent top-emitting organic light emitting diodes (TOLEDs) and white homojunction bottom-emitting phosphorescent OLEDs based on two different bipolar host materials, 2,6-bis(3-(carbazol-9-yl)phenyl)pyridine (26DCzPPy) and [4-(diphenyl(4-(1-phenyl-1H-benzimidazol-2-yl)phenyl)silyl)phenyl]diphenylamine (p-BISiTPA), are reported. The pyridine-containing bipolar transport 26DCzPPy is used as the host material for blue TOLEDs in this study. By electrical doping, the carrier injection and transport characteristics are greatly improved. The optical structure is optimized for blue light emission to enhance the color purity and improve the view characteristics. As a result, the optimized blue p–i–n homojunction phosphorescent TOLED exhibits a maximum current efficiency of 36.5 cd A⁻¹, a maximum power efficiency of 28.0 lm W⁻¹, and an external quantum efficiency (EQE) of up to 16.3%. The device emits a saturated blue color with the full width at half maximum of 50 nm and the color shift with viewing angles is almost eliminated. In order to realize high performance homojunction white OLEDs (WOLEDs) and further simplify the device structure, the tetraarylsilane-based p-BISiTPA with a triplet energy value at 2.69 eV and superior bipolar charge transport properties is employed without p- and n-doping in the charge transport layers. The WOLED, based on three primary-color emitters, shows a peak power efficiency of 32.9 lm W⁻¹, EQE of up to 16.4%, and rather stable spectra with a color-rendering index at 76. The results from both TOLEDs and WOLEDs demonstrate that the homojunction structure works well and homojunction OLEDs with performances comparable to those of heterojunction devices can be achieved by structure optimization.

Introduction

Organic light emitting diodes (OLEDs) have been attracting increasing attention for applications in flat-panel displays and solid-state lighting since the first ultra-thin multi-layered electroluminescent (EL) device was reported by Tang et al. in 1987† due to the advantages of high EL efficiency, self-luminescence, low cost, ease of processing, light weight, and the ability to be manufactured on various substrates at moderate temperatures. To achieve high-efficiency OLEDs, phosphorescent organometallic materials that can utilize radiative transitions from the triplet state are employed because phosphorescent OLEDs (PHOLEDs) using triplet excitons for light emission can reach a theoretical maximum internal quantum efficiency of 100%. In order to obtain the maximum luminescence efficiency, considerable efforts have been made and PHOLED devices frequently have complicated structures consisting of multiple layers for balancing charge carriers and exciton confinement.2–5 A typical PHOLED has a heterojunction structure, in which the emission layers are sandwiched within various functional layers, such as the hole injection layer, hole transport layer, hole blocking layer, electron transport layer, exciton blocking layer, and electron injection layer. Synthesizing materials for each layer, accounting for the energy levels of all adjacent layers, and fabricating a multilayer device will inevitably increase the complexity of the production cycle and fabrication cost, generating new obstacles on the way to the commercialization of these OLEDs. In order to overcome such complex device architecture, all manner of approaches have been executed to date.6–13 A device containing only one single organic material as the host, namely, the homojunction architecture, is an attractive alternative because of its simplicity.14–28 However, due to the absence of efficient bipolar host materials with excellent charge transport properties, this simplification in device structure often leads to low device performance due to unbalanced electron and hole fluxes in emitter and perhaps high operational voltage. Electrical doping in charge transport layers has proven to be very

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effective for reducing the operating voltage and the fabricated p-i-n devices show high luminance and efficiency at extremely low operating voltages. The highly conductive p- and n-doped layers could enhance the charge injection from the electrodes and reduce ohmic losses in these layers. However, this method has been rarely adopted in single-host homojunction devices, particularly in PHOLEDs. In our previous work, we reported high-performance p-i-n homojunction top-emitting OLEDs (TOLEDs) by employing an excellent bipolar material, 2,5-bis(2-(9H-carbazol-9-yl)phenyl)-1,3,4-oxadiazole (o-CzOXD), as host and molybdenum trioxide (MoO₃) and lithium carbonate (Li₂CO₃) as the p- and n-dopants, respectively. TOLEDs are attracting considerable scientific and industrial interest since light outcoupling from the top facilitates the fabrication of TOLEDs on more complicated thin film transistor circuits, providing not only a higher aperture ratio than the conventional bottom-emitting OLEDs (BOLEDs) but also a higher display image quality when used for high-resolution and high information content active matrix (AM) displays. In our report, high efficiency green, orange, and red p-i-n homojunction TOLEDs with saturated intrinsic emission of the emitting materials and angular independence of the emission have been realized. Even so, there is still a lack of efforts to develop blue homojunction TOLEDs, which are essential for full-color displays and solid-state lighting. In addition, homojunction white OLEDs (WOLEDs) are really worth studying because WOLEDs are promising devices for application as efficient solid-state lighting sources and AM displays. Unfortunately, there are very few reports on homojunction WOLEDs thus far.

In this study, we report highly efficient blue p-i-n homojunction phosphorescent TOLEDs and white homojunction PHOLEDs based on two different bipolar host materials. The pyridine-containing bipolar transport material with a high triplet energy (Eₜ) of 2.71 eV, 2,6-bis(3-(carbazol-9-yl)phenyl)-pyridine (26DCzPPy), which was proven to be able to produce blue PHOLEDs with extremely high efficiencies, is used as the host material for blue TOLEDs in this study. By electrical doping, the carrier injection and transport characteristics are greatly improved. The optical structure is optimized for blue light emission to enhance the color purity and improve the view characteristics. As a result, the optimized blue p-i-n homojunction phosphorescent TOLED exhibits a maximum current efficiency of 36.5 cd A⁻¹, a maximum power efficiency of 28.0 lm W⁻¹, and external quantum efficiency (EQE) of up to 16.3%. The device emits a saturated color with the full width at half maximum (FWHM) of 50 nm and color shift with viewing angle is almost eliminated. In order to further simplify the device structure, we employ another tetraarylsilane-based host material, 4-(diphenyl(4-(1-phenyl-1H-benzimidazol-2-yl)phenyl)silyl)phenyl)diphenylamine (p-BISITPA), which has a Eₜ value at 2.69 eV and superior bipolar charge transport properties, as host for homojunction bottom-emitting WOLEDs without p- and n-doping in the charge transport layers. The WOLED based on three primary-color emitters shows a peak power efficiency of 32.9 lm W⁻¹, EQE of up to 16.4%, and rather stable spectra with a color-rendering index (CRI) at 76. The results of both TOLEDs and WOLEDs demonstrate that the homojunction structure works well and homojunction OLEDs with performances comparable to those of heterojunction devices can be achieved by structure optimization.

**Results and discussion**

**Blue homojunction TOLEDs**

A typical TOLED consists of a reflective bottom anode, a semi-transparent top cathode, and organic layers sandwiched in between. With this optical architecture, TOLEDs show quite strong microcavity effects, which bring various merits for display applications, such as color saturation and efficiency enhancement, and results in large color variation with viewing angle. In our previous reports, we demonstrated a joint theoretical and experimental analysis on the emission characteristics of TOLEDs as a function of the device structure and device performance of the optimized TOLEDs were, simultaneously, fully enhanced in terms of efficiency, color saturation, and color stability with viewing angles. Herein, we adopt this strategy to optimize the structure of the blue homojunction TOLEDs. Fig. 1 shows...
the device structure used in this study. The bipolar transport, 26DCzPPy, with a high $E_T$ at 2.71 eV is used as the host material doped with a conventional blue triplet emitter, bis(4,6-(difluorophenyl)pyridinato-N,C$_2^0$)iridium(picolinate) (FIrpic).

To enhance the conductivity of the 26DCzPPy-based charge carrier transport layers, molybdenum trioxide (MoO$_3$) and lithium carbonate (Li$_2$CO$_3$) are employed as the p- and n-dopants, respectively, both of which have proven effective in achieving high conductivity and efficient carrier injection upon doping with charge transport materials. To study the influence of electrical doping on the carrier injection and transport properties of 26DCzPPy, the following carrier-only devices were fabricated. The electron-only device structure is ITO/Li$_2$CO$_3$ (1 nm)/26DCzPPy:Li$_2$CO$_3$ (100 nm)/Li$_2$CO$_3$ (1 nm)/Ag (100 nm), with the doping concentration varying from 0 to 5 wt%. The hole-only device structure is ITO/MoO$_3$ (5 nm)/26DCzPPy:MoO$_3$ (100 nm)/MoO$_3$ (5 nm)/Ag (100 nm), with the doping concentration varying from 0 to 35 wt%. Fig. 2(a) shows the current density–voltage ($J$–$V$) characteristics of the electron-only devices in a log–log plot as a function of doping concentration of Li$_2$CO$_3$ in 26DCzPPy. It is clear that the current density increases with Li$_2$CO$_3$ doping level, reaching a maximum at a doping concentration of 3 wt%. In the hole-only devices, current density reaches a maximum at a doping concentration of 30 wt%, indicating that the transport capability of the doped films increases with doping level until this point, as shown in Fig. 2(b).

The improvement of carrier injection and transport in 26DCzPPy by p- and n-doping makes p–i–n blue homojunction TOLEDs feasible. Using the optimizing strategy developed previously, the device structure was finally determined as Al (120 nm)/26DCzPy:MoO$_3$ (30 wt%, 30 nm)/26DCzPPy (5 nm)/26DCzPPy:Flrpic (8 wt%, 20 nm)/26DCzPPy (5 nm)/26DCzPPy:Li$_2$CO$_3$ (3 wt%, 15 nm)/Ag (18 nm)/26DCzPPy (60 nm) (Fig. 1). The 60 nm 26DCzPPy on top of the Ag cathode was introduced as the capping layer to improve the outcoupling efficiency and angular emission characteristics. The two undoped 26DCzPPy layers between the emission layer (EML) and the p- and n-doped transport layers were employed to avoid direct contact between the highly doped transport layers and the EML, which could block the diffusion of the dopants and prevent the quenching of the emission by dopants in the emitting zone. Fig. 3(a) displays the current density–voltage–luminance ($J$–$V$–$L$) characteristics of such a p–i–n homojunction TOLED. The blue TOLED has a moderate turn-on voltage of 4.1 V and reaches a peak brightness of 48 300 cd m$^{-2}$. A maximum EQE of 16.3%, a maximum current efficiency of 36.5 cd A$^{-1}$ (Fig. S1, ESI$^+$), and a maximum power efficiency of 28.0 lm W$^{-1}$ are achieved using Flrpic as the blue emitter, as shown in Fig. 3(b). The EL spectra of the blue TOLED at different viewing angles, plotted in the inset of Fig. 3(b), are normalized to the 0° intensity. Due to microcavity effects, the top-emitting device exhibits a saturated EL spectrum with a full width at half maximum (FWHM) of 50 nm in normal direction with the Commission Internationale de L’Eclairage (CIE) coordinates of (0.14, 0.38). More importantly, based on the optimum optical structure, the color variation is almost eliminated in the present TOLED where the CIE coordinates slightly shift to (0.16, 0.34) at 70°. As a result, a blue TOLED showing comparable performance to a conventional multilayer device is achieved using a simpler p–i–n homojunction device structure.
Homojunction WOLEDs

Encouraged by the impressive results obtained from the green, orange, and red p–i–n homojunction TOLEDs in our previous reports and the blue p–i–n homojunction TOLEDs in this work, we have good reason to expect high performance WOLEDs through the same strategy. Because the requirements for realizing white TOLEDs are high, we adopt the bottom-emitting structure to study the homojunction WOLEDs. In order to further simplify the device structure, the electrical doping method was abandoned in both hole and electron transport layers, placing greater demands on the charge transport ability of the host material. The tetraarylsilane-based host material, p-BISiTPA, with an $E_T$ value of 2.69 eV and superior bipolar charge transport properties, was chosen as host for homojunction bottom-emitting WOLEDs without p- and n-doping in the charge transport layers.

As shown in Fig. 4, the homojunction WOLEDs were fabricated with the device configuration of ITO/MoO$_3$ (5 nm)/p-BISiTPA (X nm)/p-BISiTPA:(ppy)$_2$Ir(acac):(PPQ)$_2$Ir(acac) (15 nm)/p-BISiTPA:FIrpic (10 nm)/p-BISiTPA (Y nm)/LiF (1 nm)/Al (120 nm). Fig. 4 displays the relative energy levels and molecular structures of the materials adopted in these devices. The LUMO and HOMO levels of all materials used were taken from the literature. The dopants (ppy)$_2$Ir(acac) and (PPQ)$_2$Ir(acac), which stand for bis(2-phenylpyridinato-κN$_2$C$^{2+}$)iridium(acetylacetonate) and bis(2,4-diphenylquinolyl-κN$_2$C$^{2+}$)iridium(acetylacetonate), were used for green and red phosphorescent emission, respectively. The RG-B (where R is red, G is green, and B is blue) type of EML based on three primary-color emitters for WOLEDs was employed, in which p-BISiTPA was doped with 8 wt% (ppy)$_2$Ir(acac), 1 wt% (PPQ)$_2$Ir(acac), and 8 wt% FIrpic. The device structure was optimized by changing the thicknesses of the hole (X) and electron (Y) transport layers. Fig. 5 shows the EL spectra of the homojunction WOLEDs using three different groups of X/Y values. It can be seen that the thicker hole transport layer results in more blue emission and there is hardly any emission from (ppy)$_2$Ir(acac) in all the three devices. The X/Y = 20/40 device has the highest current density at a particular voltage but the lowest current efficiency at a particular current density (Fig. S2, ESI†). This suggests that the charge fluxes are not balanced in the X/Y = 20/40 device, which leads to high current leakage, particularly at low bias voltage. The extremely low current efficiency of the X/Y = 20/40 device at low bias voltage justifies our conclusion, as shown in Fig. S2(b) (ESI†). The more balanced charge fluxes in the X/Y = 50/30 device enable higher current efficiency and more blue emission. The absence of emission from (ppy)$_2$Ir(acac) can be attributed to the different emission mechanisms of (ppy)$_2$Ir(acac) and (PPQ)$_2$Ir(acac). It is reported that a self-charge-trapping effect dominates the (PPQ)$_2$Ir(acac) emission in the RG-B WOLED. Therefore, strong emission from (PPQ)$_2$Ir(acac) can be detected in all the three devices, despite the rather low doping concentration. However, (ppy)$_2$Ir(acac) emission is mainly attributed to the sequential host-FIrpic-(ppy)$_2$Ir(acac) energy transfer in the RG-B device. The unbalanced charge fluxes and 10 nm thick FIrpic-based layer may hamper the triplet energy transfer from FIrpic to (ppy)$_2$Ir(acac). Consequently, in order to optimize the device structure for higher efficiency and improved EL spectra, we need to reduce the thicknesses of both the RG emission layer to limit (PPQ)$_2$Ir(acac) emission, and the B emission layer to facilitate the FIrpic-(ppy)$_2$Ir(acac) energy transfer.

After optimization, the homojunction WOLED with the best performance had a structure of ITO/MoO$_3$ (5 nm)/p-BISiTPA (50 nm)/p-BISiTPA:(ppy)$_2$Ir(acac):(PPQ)$_2$Ir(acac) (10 nm)/p-BISiTPA:FIrpic (5 nm)/p-BISiTPA (30 nm)/LiF (1 nm)/Al (120 nm). Fig. 6(a) shows the EQE and power efficiency characteristics of the WOLED. The device exhibits a peak current efficiency of 36.6 cd A$^{-1}$ (Fig. S3, ESI†), power efficiency of 32.9 lm W$^{-1}$, and EQE of up to 16.4%. The greatly improved device performance confirms the correctness of the above-mentioned analysis. More importantly, the EL spectra depicted in Fig. 6(b) indicate that the FIrpic-(ppy)$_2$Ir(acac) energy transfer becomes efficient in the present device.

Fig. 4 Proposed energy level diagrams and molecular structures of the materials for the homojunction WOLEDs.

Fig. 5 EL spectra of the homojunction WOLEDs with different thicknesses of the hole/electron transport layers.
The spectra cover all wavelengths from 450 to 750 nm and the CRI is calculated to reach as high as 76. Notably, this WOLED possesses high color stability. When the applied voltage changes from 5 to 14 V, the CIE coordinates vary slightly from (0.44, 0.45) to (0.42, 0.46). Thus, a high performance homo-junction WOLED has been achieved by employing a superior bipolar host and optimizing the device structure.

Conclusions

We have reported two types of homojunction OLEDs: the blue p-i-n TOLEDs and bottom-emitting WOLEDs. The 26DCzPPy-based blue p-i-n TOLED exhibits a maximum current efficiency of 36.5 cd A$^{-1}$, a maximum power efficiency of 28.0 lm W$^{-1}$, and an EQE of up to 16.3% by electrical doping in the charge transport layers. The optimized device emits a saturated blue color with the FWHM of 50 nm and a rather small color shift. Adopting a simpler device structure without p- and n-doping in the charge transport layers, high performance homojunction bottom-emitting WOLEDs have been achieved by employing the tetraarylsilane-based host, p-BISiTPA. The device structure has been optimized through changing the thicknesses of both transport layers and the EML. A peak power efficiency of 32.9 lm W$^{-1}$, EQE of up to 16.4%, and rather stable EL spectra with a CRI at 76 have been obtained from the homojunction WOLED based on three primary-color emitters. The results from both TOLEDs and WOLEDs demonstrate that the homojunction structure works well and homojunction OLEDs with performances comparable to those of heterojunction devices can be achieved by structure optimization. It should be noted that, compared to the conventional OLEDs with heterojunctions, the concept of homojunction OLEDs holds promise for long-lived PHOLEDs by eliminating redundant interfaces and avoiding exciton quenching at interfaces.

Experimental

Top-emitting devices were grown on clean glass substrates. Bottom-emitting devices were grown on glass substrates pre-coated with a 180 nm thick layer of indium tin oxide (ITO). The substrates were thoroughly cleaned before use. All layers were grown in succession by thermal evaporation without breaking the vacuum (5 × 10$^{-4}$ Pa). Current–brightness–voltage characteristics were measured using Keithley source measurement units (Keithley 2400 and Keithley 2000) with a calibrated silicon photodiode. The EL spectra were measured using a spectrascan PR650 spectrophotometer. All the measurements were carried out in an ambient atmosphere.

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