Efficient carrier- and exciton-confining device structure that enhances blue PhOLED efficiency and reduces efficiency roll-off

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Abstract

In this study we used a known host material diphenylbis[4-(9-carbazoyl)phenyl]silane (SiCa) to realize a highly efficient bis[4,6-(difluorophenyl)-pyridinato-N,C20]picolinate (Firpic)–based blue phosphorescent device exhibiting high efficiencies of up to 18.3%, 41.5 cd/A, and 31 lm/W in a carrier- and exciton-confined device structure. At a practical brightness of 1000 cd/m2, the device performance ($\eta_{ext}$) remained as high as 16.7%. The enhanced efficiency and reduced roll-off resulted mainly from the introduction of (a) DTAF as an HTL that efficiently blocked and confined excitons within the Firpic-doped emissive layer, and (b) a thin layer of DPPS between the EML and TAZ, serving as an exciton- and hole-blocking layer to suppress exciton quenching by Firpic at the EML–ETL interface. In addition, we incorporated a red phosphorescent dopant (Mpq2Iracac) into the blue device to fabricate a white phosphorescent organic light-emitting device, which exhibited satisfactory efficiencies (11.6%, 21.2 cd/A, 14.2 lm/W) with the Commission Internationale de L’éclairage (CIE) coordinates of (0.35, 0.38).

1. Introduction

Phosphorescent organic light-emitting devices (PhOLEDs) featuring emissive layers comprising transition metal–centered dyes doped into appropriate host materials are attracting much research attention because they can achieve internal efficiencies as high as 100% [1]. Unlike the reported efficient green- and red-PhOLEDs, the realization of highly efficient blue PhOLEDs remains a great challenge because the triplet energy ($E_T$) of host molecules must be sufficiently high (i.e., $E_T \geq 2.7$ eV) to confine the triplet excitons within the emitting layer [2–5]. In addition, the tendency of triplet excitons to diffuse into the non-radiative levels of the neighboring hole transport layer (HTL) and/or electron transport layer (ETL) must also be avoided. In this regard, Zheng et al. demonstrated highly efficient blue PhOLEDs using 1,1-bis[(di-4-tolylamino)phenyl]cyclohexane (TAPC) as the HTL, obtaining a maximum external quantum efficiency ($\eta_{ext}$) of 18.1%, which is approximately 50% higher than the value obtained (12%) for a previously reported device featuring bis[N-(1-naphthyl)-N-phenylamino]biphenyl (NPB) as the HTL [6]. The Kido group recently reported several ETLs exhibiting hole-blocking ability that improve the performance of bis[4,6-(difluorophenyl)-pyridinato-N,C20]picolinate (Firpic)–based blue PhOLEDs [7–9]. For example, a device incorporating diphenylbis[4-(pyridin-3-yl)phenyl]silane (DPSS) as the ETL provided a maximum value of $\eta_{ext}$ of 22%, which is much higher than the value obtained (15.3%) when using 3-(4-biphenylyl)-4-phenyl-5-(4-tert-butylphenyl)-1,2,4-triazole (TAZ) as the ETL [9]. It appears that achieving highly efficient blue PhOLEDs requires improvements in the charge recombination efficiency by...
using efficient charge-transporting materials to maintain the charge balance as well as to confine the generated triplet excitons within the emissive layer. The neighboring hole- and electron-transport materials (HTMs and ETMs) require: (a) the higher triplet energy than that of blue dye to suppress the triplet exciton quenching of the emitter, (b) the carrier blocking ability to confine the carriers within EML and (c) the high carrier transport/injection property to reduce the driving voltage of devices.

Among the many silicone-based wide-bandgap host materials that have been developed, tetraphenylsilane-functionalized ultrahigh-energy-gap hosts (UGHs) are particularly useful for fabricating deep blue PhOLEDs [3,10,11]. Unfortunately, tetraphenylsilane has an undesirably low glass transition temperature \( T_g \), which limits its practical applicability. To solve this problem, Kim et al. developed a new host material, diphenylbis[4-(9-carbazoyl)phenyl]silane (SiCa) [12], by appending carbazole moieties through their 9-positions (i.e., the nitrogen atom) to a tetraphenylsilane core. The design of SiCa was based on the fact that both tetraphenylsilane and carbazole possess large triplet energy gaps (3.5 and 3.0 eV, respectively) [10,13]. The tetrahedral Si center serves as an effective spacer that blocks the \( \pi \)-conjugation of the carbazole substituents, thereby maintaining a high triplet energy \( (E_T = 3.0 \text{ eV}) \) and enhancing the thermal stability \( (T_g = 109^\circ \text{C}) \). These values suggest that SiCa might be a promising host material for blue electrophosphorescent devices. Unfortunately, the use of SiCa as a host for tris[3,5-difluoro-4-cyanophenyl]iridium (FCNIr) [12,14] resulted in a low quantum efficiency (4.9% at 300 cd/m\(^2\)), presumably because of poor energy transfer in the host/guest system, poor triplet exciton confinement, and/or unbalanced charge recombination in the emitting layer.

In this report, we demonstrate that high efficiency can be achieved in a carrier- and exciton-confined device structure. Indeed, we achieved a maximum value of \( \eta_{\text{ext}} \) of 18.3% when using the well-established blue phosphorescent iridium complex FIrpic as the dopant dispersed in SiCa by using efficient charge-transporting materials (DTAF and DPPS) to maintain the charge balance as well as to confine the generated triplet excitons within the emissive layer. These results can provide the basic guidelines for the device design of FIrpic-based OLEDs. We have also used SiCa in conjunction with a red phosphorescent dopant (MpqIracac) [15] to fabricate a white PhOLED that exhibited satisfactory efficiency (11.6%, 21.2 cd/A, 14.2 lm/W) with the Commission Internationale de L’éclairage (CIE) coordinates of \((0.35, 0.38)\).

2. Results and discussion

We adopted two approaches to improve the performance of the previously reported device incorporating SiCa as the blue host: (1) employing a dopant material having a lower triplet energy and (2) optimizing the device structure so that it featured charge transport layers with high triplet energies [16]. Because the triplet energy of SiCa \( (E_T = 3.0 \text{ eV}) \) is 0.2 eV higher than that of FCNIr \( (E_T = 2.8 \text{ eV}) \), it should serve as a host for FCNIr, except that the neighboring charge transport layers – bis[N-(1-naphthyl)-N-phenylamino]biphenyl (NPB) and 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) with low triplet energies are strong quenchers of the blue phosphorescence of FCNIr. We anticipated that selecting the popular blue emitter FIrpic, which has a lower triplet energy \( (E_T = 2.62 \text{ eV}) \) [2], as the dopant would prevent back energy transfer from the dopant to the adjacent functional layers. Therefore, we employed the phosphor FIrpic to replace FCNIr in the emitting layer having the original structure reported by Kim [12]. By changing the doping concentration of FIrpic, we prepared three devices (A1–3) having the following configuration: indium tin oxide (ITO)/ \( N,N’-\text{diphenyl-N,N’-bis-[4-(phenyl-m-tolyl-amo)}\)-phenyl]-biphenyl-4,4’-diamine (DNTPD, 60 nm)/NPB (30 nm)/SiCa:FIrpic (A1: 5%; A2: 10%; A3: 15%) (30 nm)/BCP (5 nm)/tris[8-hydroxyquinoline] aluminum \((\text{Alq}_3, 20 \text{ nm})/\text{LiF} (1 \text{ nm})/\text{Al} (200 \text{ nm})\). Fig. 1 presents the current

![Fig. 1. (a) Current density–voltage–luminance \((I–V–L)\) characteristics, (b) external quantum \((\eta_{\text{ext}})\) and power \((\eta_p)\) efficiencies plotted as a function of brightness, and (c) EL spectra of devices A1–3.](image-url)
density–voltage–luminance (I–V–L) characteristics and EL efficiencies of devices A1–3. Notably, the brightnesses (39,400–43,100 cd/m²) and current densities (1880–2380 mA/cm²) of our devices were significantly higher than those reported previously [12], suggesting that SiCa is capable of effectively confining the triplet energy of FIrpic. Nevertheless, the EL efficiencies (3.6–2.3% or 4.3–1.7 lm/W) of devices A1–3 were low relative to those reported previously, presumably because we used NPB, which has a low triplet energy (E_T = 2.3 eV), as the HTL [17], which could not efficiently prevent exciton diffusion.

To improve the EL efficiencies of devices A1–3, we used 1,1-bis[(di-4-tolylamino)phenyl]-9,9'-fluorene (DTAF) to replace NPB as the HTL [18,19]. The molecular design of DTAF endows it with several advantageous properties: (1) high morphological and thermal stability (T_g = 124 °C); (2) an appropriate HOMO energy level (−5.22 eV) to provide a low hole injection barrier from the anode and a low-lying LUMO energy level (−1.75 eV) to block electrons injected from the cathode; (3) high hole transport properties (μ_h > 10^-3 cm²/Vs); and (4) a high triplet energy gap (E_T = 2.87 eV) relative to that of NPB, allowing triplet excitons to be confined in the EML. In addition, we adopted a 5-nm-thick layer of diphenylbis[4-(pyridin-3-yl)phenyl]silane (DPPS), inserted between the EML and the ETL (TAZ), to serve as an exciton-blocking layer (HBL) for suppressing the FIrpic exciton quenching at the EML–ETL interface. Chemical structures of related compounds and their energy levels are shown in Fig. 2, in which HOMO levels of compounds in films are determined here by Riken AC-2 photoemission spectrometer while the HOMO levels of DPPS and TAZ are taken from the literature [9]. The LUMO levels of all compounds are derived by subtracting the HOMO levels from the optical energy gaps.

To evaluate the feasibility of using DTAF as an HTL and DPPS as an HBL, we designed three different devices B1–3 having the following configuration: ITO/poly(3,4-ethylene dioxythiophene)/poly(styrenesulfonic acid) (PEDOT:PSS) (30 nm)/HTL (25 nm)/SiCa:12 wt% FIrpic (25 nm)/ETL (50 nm)/LiF (0.5 nm)/Al (100 nm). In device B1, NPB (20 nm)/TCTA (5 nm) was used as the HTL; in devices B2 and B3, DTAF (25 nm) was employed as the HTL. In addition, TAZ (50 nm) was adopted as the ETL in devices B1 and B2, whereas DPPS (5 nm)/TAZ (45 nm) was adopted in device B3 as the ETL. In device B1, we inserted a thin layer of 4,4',4''-tri(N-carbazolyl)triphenylamine (TCTA, 5 nm), which has a high triplet energy (E_T = 2.76 eV) [20], between NPB and the EML to act as the exciton-blocking layer. In device B3, we inserted a 5-nm-thick layer of DPPS, which has a HOMO energy level of 6.5 eV, between the EML and TAZ to serve as the exciton-blocking layer. In device B2, we inserted a 5-nm-thick layer of DPPS, which has a HOMO energy level of 6.5 eV, between the EML and TAZ to serve as the exciton-blocking layer.

Fig. 3 displays the electroluminescence (EL) characteristics of devices B1–3 featuring this new device structure;
exhibited similar turn-on voltages (ca. 3.5 V) and similar EL performances of devices.

Table 1 summarizes the data. Although devices B1–3 exhibited similar turn-on voltages (ca. 3.5 V) and similar brightnesses (37,300–40,900 cd/m²) relative to those of devices A1–3, the current densities (360–450 mA/cm²) had obviously decreased. The J–V characteristics revealed that the device B2 incorporating DTAF as HTL exhibited a slightly lower current density at high voltage relative to device B1 incorporating NPB/TCTA as HTLs. The lower current density may be due to a large barrier of 0.5 eV between DTAF/CaSi. (see the schematic energy level diagram in Fig. 2). The large energy mismatch should enable a lot of holes accumulate at the HTL/EML interface and lead to a direct trap of charge carriers by FIrpic. In addition, the high triplet energy of DTAF (E_T = 2.87 eV) also enables the efficient confinement of excitons within the EML. Combining these effects together, the DTAF-based device B2 exhibited efficiencies [a maximum η_ext of 18.9% (41.7 cd/A) and a value of η_p of 30 lm/W] that were much higher than those of the traditional NPB/TCTA-based device B1 (14.2%, 31 cd/A, and 20.6 lm/W, respectively; Fig. 3b). These results indicate that the exciton-confined ability is more crucial than hole injection, because of the greater number of holes than electrons in the OLED. Therefore, the charge balance in the DTAF-based device B2 might be better than that of the NPB/TCTA-based device B1, and results in a higher charge-recombination efficiency.

Careful analysis of the electroluminescence (EL) spectra of devices B1 and B2 revealed the presence of short wavelength (λ = 360–410 nm) emissions (Fig. 3c), which presumably arose from a portion of the holes that overcame the barrier at the EML–TAZ interface recombining with electrons in TAZ. Thus, we inserted a 5-nm-thick layer of DPPS between the EML and TAZ in device B3 to serve as the exciton–hole-blocking layer to prevent exciton quenching and hole leakage into the TAZ. Obviously, the emission of device B3 occurred only from FIrpic, without any other emission from its neighboring materials. The quantum efficiency roll-off of device B3 might be due to a large barrier of 0.5 eV between DTAF/CaSi. (see the schematic energy level diagram in Fig. 2). The large energy mismatch should enable a lot of holes accumulate at the HTL/EML interface and lead to a direct trap of charge carriers by FIrpic. In addition, the high triplet energy of DTAF (E_T = 2.87 eV) also enables the efficient confinement of excitons within the EML. Combining these effects together, the DTAF-based device B2 exhibited efficiencies [a maximum η_ext of 18.9% (41.7 cd/A) and a value of η_p of 30 lm/W] that were much higher than those of the traditional NPB/TCTA-based device B1 (14.2%, 31 cd/A, and 20.6 lm/W, respectively; Fig. 3b). These results indicate that the exciton-confined ability is more crucial than hole injection, because of the greater number of holes than electrons in the OLED. Therefore, the charge balance in the DTAF-based device B2 might be better than that of the NPB/TCTA-based device B1, and results in a higher charge-recombination efficiency.

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<table>
<thead>
<tr>
<th>Device</th>
<th>V_on [V]</th>
<th>L_max [cd/m²]</th>
<th>J_max [mA/cm²]</th>
<th>η_ext [%]</th>
<th>η_p [cd/A]</th>
<th>η_p [lm/W]</th>
<th>L = 1000 nit [%]</th>
<th>CIE [x, y]</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>3.5</td>
<td>39,400 (15 V)</td>
<td>1880</td>
<td>3.6</td>
<td>7.2</td>
<td>4.3</td>
<td>3.21</td>
<td>0.16, 0.32</td>
</tr>
<tr>
<td>A2</td>
<td>3.5</td>
<td>40,400 (15 V)</td>
<td>2030</td>
<td>2.7</td>
<td>5.3</td>
<td>2.6</td>
<td>2.6, 1.8</td>
<td>0.16, 0.32</td>
</tr>
<tr>
<td>A3</td>
<td>3.5</td>
<td>43,100 (16 V)</td>
<td>2380</td>
<td>2.3</td>
<td>4.5</td>
<td>1.7</td>
<td>2.3, 1.5</td>
<td>0.16, 0.33</td>
</tr>
<tr>
<td>B1</td>
<td>3.5</td>
<td>37,300 (15 V)</td>
<td>450</td>
<td>14.2</td>
<td>31</td>
<td>20.6</td>
<td>11.5, 9.5</td>
<td>0.18, 0.37</td>
</tr>
<tr>
<td>B2</td>
<td>3.5</td>
<td>40,900 (16 V)</td>
<td>420</td>
<td>18.9</td>
<td>41.7</td>
<td>30</td>
<td>13.8, 10.6</td>
<td>0.18, 0.38</td>
</tr>
<tr>
<td>B3</td>
<td>3.5</td>
<td>36,400 (16.5 V)</td>
<td>360</td>
<td>18.3</td>
<td>41.5</td>
<td>31</td>
<td>16.7, 13.2</td>
<td>0.18, 0.38</td>
</tr>
<tr>
<td>C1</td>
<td>3</td>
<td>18,200 (13 V)</td>
<td>1070</td>
<td>7.3</td>
<td>7.3</td>
<td>4.2</td>
<td>6.3, 2.5</td>
<td>0.66, 0.34</td>
</tr>
<tr>
<td>D1</td>
<td>3</td>
<td>21,600 (14 V)</td>
<td>520</td>
<td>11.6</td>
<td>21.2</td>
<td>14.2</td>
<td>9.5, 6.8</td>
<td>0.37, 0.38</td>
</tr>
</tbody>
</table>

*a* Defined as the voltage at which the EL is rapidly enhanced.
device B3c: doping 8 nm next to DPPS) were also fabricated and tested. Although all three devices showed emission dominantly from FIrpic, device B3b showed much lower quantum efficiency (4%) than devices B3a and B3c (7.8% and 8.7%, respectively). The results indicate that the emitting zone mainly takes place near the HTL/EML and EML/ETL interfaces. The holes accumulate at the HTL/EML interface due to a large barrier of 0.5 eV between DTAF/CaSi. FIrpic is an emitting ET material [21], therefore, localization of excitons on FIrpic can occur through direct charge trapping at the HTL/EML interface. The emitting zone also takes place near the EML/ETL interface, where electrons inject either onto CaSi or directly onto FIrpic.

We confirmed this hypothesis by exploring the carrier transport properties of SiCa, probed using time-of-flight (TOF) techniques [22]. The device used for TOF measurement was prepared through vacuum deposition with the structure ITO glass/SiCa (2.1 µm)/Ag (150 nm) and then it was placed inside a cryostat under vacuum. Fig. 4a display representative TOF transients for holes measured at ambient temperature under an applied field of 9.7 × 10⁴ V/cm. (b) Hole mobility plotted with respect to E¹/². The hole mobilities exist in the range from 1.2 × 10⁻⁴ to 5.4 × 10⁻⁴ cm²/Vs for fields varying from 9.7 × 10⁴ to 5.3 × 10⁵ V/cm. Conversely, the electron mobility of SiCa was too low to be measured. The preferential hole mobility of SiCa agrees with the results observed for devices.

In addition to acting as a blue host, SiCa can also be used as the host for red phosphorescent dopants. Using the structure of device B3, we introduced Mpq2Iracac [15] as a red phosphorescent emitter to obtain device C1, which exhibited a maximum brightness of 18,200 cd/m² at 1070 mA/cm² with CIE coordinates of (0.66, 0.34). The I–V characteristics of device C1 revealed a higher current density (1070 mA/cm² at 13 V) than that of device B3 (Fig. 3a). This result can be rationalized by considering that the HOMO energy level of Mpq2Iracac is close to that of DTAF, thereby reducing the hole injection barrier at the interface. Notably, however, device C1 provided relatively low values of ηext, ηl, and ηp (7.3%, 7.3 cd/A, and 4.2 lm/W, respectively), due to the intrinsic lower quantum yield of red triplet emitter.

To take advantage of the double confinement strategy used in device B3, we fabricated a white PhOLED (device D1) by doping the emitting layer in device B3 with the red phosphor Mpq2Iracac. The CIE coordinates of device D1 (Fig. 5a) reveal the complementary nature of these

\[ \mu = \frac{d}{E^{1/2}} \]

where \( d \) is the thickness of the organic film, \( V \) is the applied voltage, and \( t \) is the transit time. Fig. 4b plots the calculated field-dependent hole mobility of SiCa as a function of \( E^{1/2} \). The hole mobilities exist in the range from 1.2 × 10⁻⁴ to 5.4 × 10⁻⁴ cm²/Vs for fields varying from 9.7 × 10⁴ to 5.3 × 10⁵ V/cm. Conversely, the electron mobility of SiCa was too low to be measured. The preferential hole mobility of SiCa agrees with the results observed for devices.

Fig. 4. (a) Representative TOF transients for holes of SiCa (d = 2.1 µm) at a value of \( E \) of 9.4 × 10⁴ V/cm. (b) Hole mobility plotted with respect to \( E^{1/2} \) at ambient temperature.

Fig. 5. (a) Chromaticity diagram (CIE coordinates), and (b) EL spectra of devices B3 (blue), C1 (red), and D1 (white) at various luminance (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).
two phosphors for white light emission. White emission with CIE coordinates close to (0.33, 0.33) could be achieved if appropriate combinations were made [23–25]. For the two-dopant single-EML device, the EL was strongly influenced by the ratio of the two dopants. Through systematic tuning of the dopants' concentrations, we fabricated a white light-emitting device D1 incorporating 12 wt% of Flrpic and 0.2 wt% of Mpq4Iracac doped into the host SiCa. The proportion of red dopant required to produce balanced emission in this device is relatively low because the red emission occurred from the combined effects of efficient energy transfer from the blue phosphor and exciton formation by charge trapping on the red dopant. The maximum brightness of 21,600 cd/m² was achieved at 14 V, with maximum efficiencies ($\eta_{ext}$, $\eta_i$, and $\eta_p$) of 11.6%, 21.2 cd/A, and 14.2 lm/W. Fig. 5b displays the EL spectra of device D1 recorded at various brightnesses. The relative intensity of the red emission decreased slightly when the brightness increased, leading to a slight shift in the CIE coordinates from (0.38, 0.38) at a value of $L$ of 330 cd/m² to (0.35, 0.38) at 10,000 cd/m². This color shift originated from the shifting of the recombination zone upon increasing the applied voltage and from the easier formation of high-energy excitons at higher voltage [26]. Compared with multi-EML white organic light emitting diodes (WOLEDs) [27–29,24], our two-dopant single-EML device exhibits higher color stability, which we attribute to the more-uniform distribution of the two dopants in the EML [30].

3. Experimental

We study of carrier-transport properties in the organic materials by the time-of-flight (TOF) transient photocurrent technique. The samples for the TOF measurement were prepared by vacuum deposition using the structure: ITO glass/SiCa (2.1 μm)/Ag (150 nm), and then placed inside a cryostat and kept under vacuum. The thickness of organic film was monitored in situ with a quartz crystal microbalance a cryostat and kept under vacuum. The thickness of organic film was monitored in situ with a quartz crystal microbalance. By incorporating a red phosphorescent dopant (Mpq4Iracac) into the blue device, we fabricated a white PhOLED that exhibited satisfactory efficiencies (11.6%, 21.2 cd/A, 14.2 lm/W) with CIE coordinates of (0.35, 0.38).

4. Conclusion

We have fabricated a highly efficient Flrpic-based blue PhOLED, exhibiting a decreased efficiency roll-off that possesses a carrier-balanced and exciton-confined device structure. This device exhibited a maximum external quantum efficiency ($\eta_{ext}$) of 18.3% (41.5 cd/A) and a power efficiency of 31 lm/W. The enhanced efficiency and reduced roll-off resulted mainly from the introduction of (a) DTAf as an HTL that efficiently blocked the injected electrons and confine excitons within the Flrpic-doped emissive layer, and (b) a thin layer of DPPS between the EML and TAZ, serving as an exciton- and hole-blocking layer to suppress exciton quenching by Flrpic at the EML–ETL interface. By incorporating a red phosphorescent dopant (Mpq4Iracac) into the blue device, we fabricated a white PhOLED that exhibited satisfactory efficiencies (11.6%, 21.2 cd/A, 14.2 lm/W) with CIE coordinates of (0.35, 0.38).

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