Phosphorescence of red Os(fptz)$_2$(PPh$_2$Me)$_2$ doped organic light-emitting devices with n and p hosts

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We have applied a sterically hindered red phosphorescent dopant Os(fptz)$_2$(PPh$_2$Me)$_2$ [fptz=3-trifluoromethyl-1,2,4-triazole, PPh$_2$Me=phosphine ligand] in p-type 4,4'-N,N'-dicarbazole-biphenyl or n-type bis(2-methyl-8-quinolinolato)(p-phenylphenolato) aluminum host and found that the latter produced higher luminance efficiency at lower doping concentration. We present a model to rationalize this phenomenon in which the n-type host impedes hole transport, which leads to narrower recombination zone near the hole transport layer/emission layer interface than the p-type host, hence, more effective recombination. © 2006 American Institute of Physics. [DOI: 10.1063/1.2172405]

One of the key developments in the advance of modern organic light-emitting devices (OLEDs) technology is the discovery of electrophosphorescence which lifts the upper limit of the internal quantum efficiency of the usual fluorescent dopant-based devices from 25% to nearly 100%. 1, 2 To ensure effective proximity for complete energy transfer, the dopant concentration in phosphorescent OLEDs is always higher than that of the fluorescent OLEDs. 3–5 A short-distance Dexter Energy transfer (~10 Å) between the phosphorescent host and dopant has been often utilized to rationalize this phenomenon. 6 Nevertheless, a high doping concentration of phosphorescent dopants can also provide better overlap of ligand π orbitals, which will promote the direct recombination of electron-hole pairs on dopants. 7 In this case, the role of the host will not be the dominant excitation energy source as in the energy transfer model, rather a mere medium for carrier transport.

In this study, we used a highly sterically hindered red phosphorescent dye Os(fptz)$_2$(PPh$_2$Me)$_2$ [fptz=3-trifluoromethyl-1,2,4-triazole, PPh$_2$Me=phosphine ligand] as the dopant together with a p-type host 4,4'-N,N'-Dicarbazole-biphenyl (CBP) or n-type host bis(2-methyl-8-quinolinolato) (p-phenylphenolato) aluminum (BAIq) for our emission layer. By studying the electroluminescence (EL) characteristics of the dopant in the hosts of different charge transport natures, we expect to provide more insights about the relationship between phosphorescent dopant and host and attempt to elucidate the emissive mechanism.

The structure, purity, chemical, energy levels, and optical properties of Os(fptz)$_2$(PPh$_2$Me)$_2$ has been verified and disclosed in other publication. 8 Figure 1 depicts the absorption and luminescence spectrum of Os(fptz)$_2$(PPh$_2$Me)$_2$ in CH$_2$Cl$_2$. The strong absorption in the UV region are assigned to the spin-allowed \( ^1\pi\pi^* \) transition of fptz ligands, owing to their spectral similarity to the free fptz anion. The next lower energy absorption can be ascribed to a typical spin-allowed metal to ligand charge transfer \( (1MLCT) \) transition, while two absorption bands extending into visible region are associated with the spin-orbit coupling enhanced \( ^3\pi\pi^* \) and \( ^3MLCT \) transitions. Further luminescence properties \( (\text{vide infra}) \) support \(^3MLCT\) to be in the lowest triplet state with peak wavelength at 540 nm.

Figure 2 shows our experimental results of the device structure: indium tin oxide (75 nm)/copper phthalocyanine (CuPc) (15 nm)/1,4-bis[N-(1-naphthyl)-N'-phenylamino]biphenyl-4,4' diamine (NPB) (60 nm)/host: x% Os(fptz)$_2$(PPh$_2$Me)$_2$ (40 nm)/BAIq (15 nm)/tris(8-hydroxyquinolino)aluminum (Alq3), (20 nm)/LiF (1 nm)/Al(200 nm). The CuPc, NPB, BAIq, and Alq3 were used as the hole injection, hole transport, hole blocking material, and electron transport material, respect-

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FIG. 1. UV-visible absorption (■) and normalized emission spectrum (○) of Os(fptz)$_2$(PPh$_2$Me)$_2$ in CH$_2$Cl$_2$ at room temperature. Inset: molecular structure of Os(fptz)$_2$(PPh$_2$Me)$_2$.
In terms of color and operation voltage, both devices show a using BAlq as the host as compared to that of 30% in CBP.quired for reaching the maximum luminance efficiency when more, a much lowered doping concentration of 15% is re-
tation from 20% to 35%. However, when doped in Os

temperature at 430–580 nm which is the triplet energy peak of
ing at Fig. 3, there appears a small shoulder under low tem-

8.5 cd/A has the property of resistance to concen-


tering at Fig. 3, there appears a small shoulder under low tem-

the operation voltage of the CBP-based

doped in n-type

The photoluminescence spectra of BAlq and CBP under room and low temperatures are illustrated in Fig. 3. By looking at Fig. 3, there appears a small shoulder under low temperature at 430–580 nm which is the triplet energy peak of CBP in addition to the singlet energy peak at ~360 nm which will blue shift under low temperature. Moreover, the

fluorescent spectrum of CBP overlaps with the two spin-

allowed absorption transitions of Os(fptz)2(PPh2Me)2 at 290 and 400 nm. According to the energy transfer model, the 25% singlet energy of CBPs excitons could effectively transform into the singlet energy of Os(fptz)2(PPh2Me)2, which then generates phosphorescence via internal system crossing process. Not only that, the triplet energy of CBPs excitons is higher than the transition energy due to 3MLCT in Os(fptz)2(PPh2Me)2. Therefore, the triplet energy of CBPs excitons can successfully transform into that of Os(fptz)2(PPh2Me)2 as well. On the other hand, the situation is totally different in the case of BAlq. First, the fluorescent spectrum of BAlq at 490 nm has shown poor overlap with the spin-allowed singlet transition of Os(fptz)2(PPh2Me)2. Second, the photoluminescent spectra of BAlq under room and low temperatures seem to be identical (even at 22 K). We believe this is attributed to the very weak triplet energy of BAlq, which gives signal that is undetectable by the instrument. If this is the case, the energy transfer from the host to dopant mentioned previously will not be applicable to explain the observation depicted in Fig. 2 since CBP obviously has higher probability to undergo energy transfer but consequently has lower luminance efficiency.

In order to clarify the emission mechanism of doped OLEDs, we have designed the devices without hole blocking layer (devices C and D). The hole-blocking layer of 15 nm BAlq was removed and replaced by Alq3 of the same thickness. The doping concentrations for both devices are optimized for achieving the highest luminance efficiency. The EL spectra and detailed EL performance of the devices are shown in Fig. 4 and Table I, respectively.

From Fig. 4, the Alq3 emission at ~520 nm can be observed besides the Os(fptz)2(PPh2Me)2 emission at 624 nm for the CBP-based device without hole-blocking layer, therefore, the CIE coordinates of device C were blueshifted to (0.63, 0.36). Significant drop in luminance efficiency to 2.4 cd/A can be seen as well from Table I for the CBP-based device without hole-blocking layer and the operation voltage is ~2 V lower than that of the device with hole-blocking layer. But these phenomena do not exist in the case of BAlq-based devices. The luminance efficiency of device D is well above 12 cd/A at 20 mA/cm2 and the color saturation remains unchanged at CIE=(0.65,0.34) due to no Alq3 emission was observed. The operation voltages of the BAlq-based devices are very similar. Based on these evidences, it is clearly shown that the removal of the hole-blocking layer

FIG. 2. Efficiency dependency on Os(fptz)2(PPh2Me)2 concentration in CBP (□) and BAlq (○) hosts.

FIG. 3. The photoluminescent spectra of CBP (top figure) and BAlq (bottom figure) under room and low temperatures. CBP: 293 K (■), 77 K (○), amplified phosphorescent signals at 77 K (△); BAlq: 293 K (■), 77 K (○), 22 K (△).

FIG. 4. EL spectra of Os(fptz)2(PPh2Me)2 doped devices driven at 20 mA/cm2. The spectrum of CBP-based device without hole-blocking layer (device D) reveals Alq3 emission at ~520 nm.
will cause the holes to diffuse/drift into Alq3/cathode without recombining radiatively in the emission layer and the formed triplet excitons also have a chance to diffuse into Alq3 layer, which will then transfer to the irradiative Alq3 triplet energy level. On the contrary, the removal of the hole-blocking layer did not have much impact on the efficiency of the BAlq-based device since the recombination zone is narrower and near the hole transport/emission layer interface.

We conclude that the direct recombination of electron-hole pairs on dopants may be the dominate electroluminescent mechanism in red Os(fptz)2(PPh2Me)2 doped devices. Our rationalization is that the n-type host will impede hole transport, which leads to a narrow recombination zone near the hole transport layer/emission layer interface. The confinement of the holes leads to narrow recombination zone, hence, more effective recombination. On the contrary, the p-type host will assist holes to transport deeper in the emission layer, which makes less restrain for carrier recombination. As the result, reactivity of recombination is reduced in the emission layer, hence lower efficiency.

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Table I. EL performance of Os(fptz)2(PPh2Me)2 doped devices driven at 20 mA/cm2.

<table>
<thead>
<tr>
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<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
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<tr>
<td>Host</td>
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<td>BAlq</td>
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<td>BAlq</td>
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<td>BAlq</td>
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<tr>
<td></td>
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