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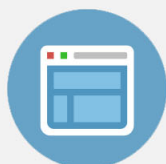
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# Organic light-emitting devices based on a highly robust osmium(II) complex

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An osmium(II) complex,  $\text{Os}(\text{fptz})_2(\text{PPh}_2\text{Me})_2$  [fptz=3-trifluoromethyl-5-(2-pyridyl)-1,2,4-triazole,  $\text{PPh}_2\text{Me}$ =methyl-diphenyl-phosphan], when doped in a 4,4'-*N,N'*-dicarbazolebiphenyl host as a phosphorescent red emitter in organic light-emitting devices, has the unusual property of resisting concentration quenching and sustaining its external quantum efficiency (EQE) (8%–9%) over a wide range of doping concentration (20%–40%). Single-crystal x-ray diffraction evidence is presented that the difference in doping behaviors can be linked to the octahedral configuration of  $\text{Os}(\text{fptz})_2(\text{PPh}_2\text{Me})_2$ , which could prevent the undesirable molecular aggregation from occurring at high concentration, thus delaying the onset of quenching. Accordingly, the high doping concentration of  $\text{Os}(\text{fptz})_2(\text{PPh}_2\text{Me})_2$  leads to a significant suppression of luminescence quenching at high brightness/current and achieves a “flat” EQE versus brightness response owing to the increase in the emission sites in the emission layer. © 2006 American Institute of Physics.

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## I. INTRODUCTION

One of the key developments in the advance of modern organic light-emitting device (OLED) 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%.<sup>1</sup> Phosphorescence is inherently a slower and less efficient process than singlet transitions responsible for fluorescence due to the fact that the emission from a triplet state does not conserve spin. But triplet states constitute the majority of electrogenerated excited states (~75%), so the successful utilization of the triplet manifold to produce light should undoubtedly increase the overall luminance. In compounds containing heavy-metal complexes, the decay of a triplet state becomes weakly allowed due to strong spin-orbit coupling that leads to singlet-triplet state mixing which removes the spin-forbidden nature of the radiative relaxation of the triplet state. In such cases, the decay of the triplet state may still be very slow, but phosphorescence is generated.

The utilization of phosphorescent materials in OLEDs is found by doping the phosphorescent material into a charge transport host material.<sup>2</sup> However, one of the significant issues in current doped phosphorescent light-emitting devices (PHOLEDs) is the decrease of quantum efficiency with increasing current. Since the total spin is conserved, two excited triplet excitons may combine to form an excited singlet exciton and a ground-state singlet exciton. Consequently, the process would destroy at least one triplet exciton, which is known as the triplet-triplet annihilation.<sup>3</sup> In general, the current-induced efficiency drop in PHOLEDs occurs owing to the long phosphorescent exciton lifetime of phosphores-

cent materials that causes saturation of emission sites. The triplet-triplet annihilation then happens between triplet excitons of hosts, which results in significant electroluminescent energy loss. This phenomenon will tend to be more serious when more current is injected and more triplet excitons of hosts are generated.

Triplet-triplet saturation and annihilation can be minimized if the phosphorescent lifetime of dopants is short enough. It would be even better if the dopants possess large steric hindrance to suppress concentration quenching owing to aggregation of dye molecules. As a result, a larger amount of dopant could exist in the luminescent matrix. If both conditions mentioned above were met, then the sufficient triplet excitons of the host could effectively transfer their excited energy to light via fast relaxation process instead of going through the nonradiation pathways. Based on these two concerns, most phosphorescent dopants of commercial importance are designed not only to be ligand-chelated heavy-metal complexes to increase spin state mixing, but also possess large steric hindrance to minimum bimolecular interaction. For example, it was found that the red triplet phosphor, bis(2-(2'-benzo[4,5-*a*] thienyl)pyridinato-*N*,*C*3') iridium(acetylacetonate) ( $\text{Btp}_2\text{Ir}(\text{acac})$ ) (Ref. 4) with a short phosphorescence lifetime (~4  $\mu\text{s}$ ) and a spherical structure leads to a significant improvement in external quantum efficiency (EQE) reaching 2.5% at high current density of 100  $\text{mA}/\text{cm}^2$  as the doping concentration was ~7%.

Although most of the high efficiency phosphorescent materials under development were focused on Ir(III) central metal, other complexes based on Os(II) central metal were also considered potential candidates, which, in general, possess a shorter triplet-state exciton lifetime ( $\leq a$  few microseconds) due to the enhancement of the heavy-metal atom participating in the lowest excited triplet manifolds.<sup>5-7</sup> More-

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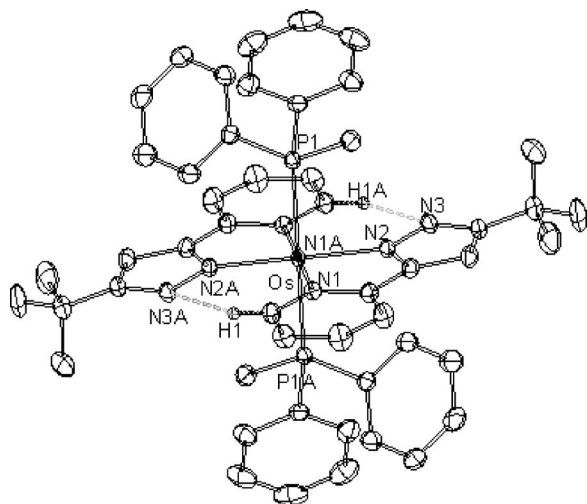


FIG. 1. Oak Ridge Thermal Ellipsoid Plot Program (ORTEP) diagram of the Os(II) complex with a special emphasis on the intramolecular hydrogen bonding. N(3) and N(3A) formed intramolecular hydrogen bonds with H(1A) and H(1), respectively, that establishes a planar six-ringed basal arrangement, together with two PPh<sub>2</sub>Me ligands located at the axial positions to construct an octahedral configuration.

over, in terms of molecular design, the phosphorescent dopant based on Os(II) central metal has the merit of larger steric hindrance, which allows higher dopant concentration to be used in the emission layer. In this study, we conducted the fabrication of OLEDs that contain an Os(II) complex, Os(fptz)<sub>2</sub>(PPh<sub>2</sub>Me)<sub>2</sub> [fptz=3-trifluoromethyl-5-(2-pyridyl)-1,2,4-triazole, PPh<sub>2</sub>Me=methyl-diphenyl-phosphane], with an octahedral configuration as the emitting material. A device based on the red Os(fptz)<sub>2</sub>(PPh<sub>2</sub>Me)<sub>2</sub> is expected to alleviate the triplet-triplet annihilation often encountered in PHOLEDs, which greatly improves the luminance efficiency over a wide range of drive current conditions.

## II. RESULTS AND DISCUSSION

### A. Structure analysis of Os(fptz)<sub>2</sub>(PPh<sub>2</sub>Me)<sub>2</sub>

The synthesis, structure, purity, and chemical properties of the red dopant used in this study has been verified and disclosed in other publication.<sup>8</sup> As depicted in Fig. 1, the molecular frame reveals an octahedral configuration where two chelating fptz ligands establish a nearly planar OsN<sub>4</sub> basal arrangement, together with two PPh<sub>2</sub>Me ligands located at the axial positions. The Os atom is located at a crystallographic center of inversion, which constructs a C<sub>2</sub> symmetry. On the other hand, the observed exciton lifetimes of Os(fptz)<sub>2</sub>(PPh<sub>2</sub>Me)<sub>2</sub> are 0.96 μs in degassed CH<sub>2</sub>Cl<sub>2</sub> and 0.18 μs in solid state.<sup>8</sup> It is notable that the radiative lifetimes of Os(fptz)<sub>2</sub>(PPh<sub>2</sub>Me)<sub>2</sub> are considerably shorter than those of most reported red emitting Ir(III) complexes, implying that the OLED devices fabricated using Os(fptz)<sub>2</sub>(PPh<sub>2</sub>Me)<sub>2</sub> should be beneficial in reducing triplet-triplet annihilation at high current/brightness and increasing quantum efficiency.

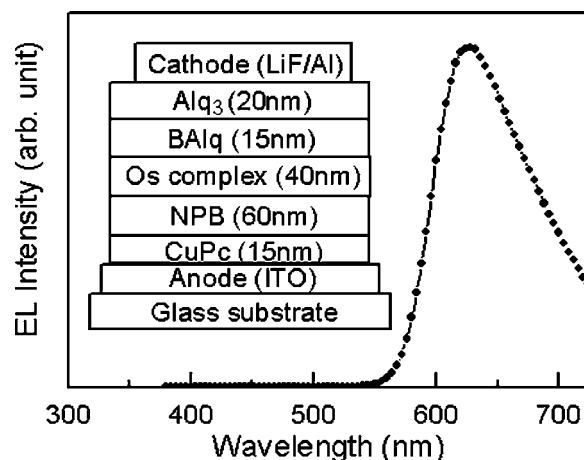


FIG. 2. Electroluminescence spectrum of the OLED device without doping Os(fptz)<sub>2</sub>(PPh<sub>2</sub>Me)<sub>2</sub> in host. Inset: multilayer configuration of the device.

### B. OLED performance with neat Os(fptz)<sub>2</sub>(PPh<sub>2</sub>Me)<sub>2</sub> as the emission layer

The essential electroluminescent (EL) properties of Os(fptz)<sub>2</sub>(PPh<sub>2</sub>Me)<sub>2</sub> were investigated in the device fabricated with the structure shown in the inset of Fig. 2: Indium tin oxide (ITO) (75 nm)/copper phthalocyanine (CuPc) (15 nm)/1,4-bis[*N*-(1-naphthyl)-*N'*-phenylamino]biphenyl-4,4' diamine (NPB) (60 nm)/Os(fppz)<sub>2</sub>(PPh<sub>2</sub>Me)<sub>2</sub> (40 nm)/aluminum(III)bis(2-methyl-8-quinolinolato)-4-phenylphenolato (BALq) (15 nm)/aluminum(III)tris-8-hydroxyquinolinolato (Alq<sub>3</sub>) (20 nm)/LiF (1 nm)/Al (200 nm). This device was fabricated using conventional vacuum deposition in a 5.0 × 10<sup>-5</sup> Pa vacuum on a pre-cleaned glass substrate coated with ITO. ITO was used as the transparent anode with a sheet resistance of 10 Ω/square. The CuPc, NPB, BALq, and Alq<sub>3</sub> were used as the hole injection, hole transport, hole blocking material, and electron transport material, respectively.

The device exhibited red emission with the Commission Internationale d'Eclairage (CIE) coordinates of *x*=0.65 and *y*=0.34. A maximum luminous efficiency of 3.1 cd/A and an external quantum efficiency (EQE) of 3.4% were obtained at 1 mA/cm<sup>2</sup> (4.3 V) while the emission layer was composed of pure Os(fptz)<sub>2</sub>(PPh<sub>2</sub>Me)<sub>2</sub>. The emission color and the EL spectrum did not change as the applied voltage was varied. As shown in Fig. 2, the EL spectrum of the device (λ<sub>max</sub> = 628 nm) is in agreement with that observed for the photoluminescence of Os(fptz)<sub>2</sub>(PPh<sub>2</sub>Me)<sub>2</sub> in solution.<sup>8</sup>

The current-voltage-luminance characteristics of the device are shown in Fig. 3 and the plot of EQE versus brightness is shown in the inset. It is noteworthy that luminance loss due to triplet-triplet annihilation in PHOLEDs has been suppressed apparently in this device. Up to 6000 nits (~200 mA/cm<sup>2</sup>), the EQE drop is less than 5%, which is rarely seen in conventional phosphorescent devices. Although the mechanism behind the "flat" EQE response is not fully understood, it is clear that the capability in allowing high phosphorescent dopant concentration as well as short triplet radiative lifetime owing to the proper molecular de-

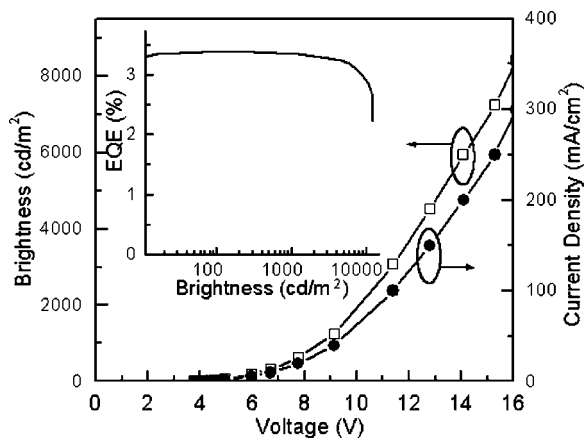


FIG. 3. Current-voltage-luminance characteristics of the device shown in the inset of Fig. 2. Inset: the plot of luminescence efficiency vs brightness for the device without doping in host.

sign would increase emission sites, which is expected to suppress the efficiency loss at high brightness/current in PHOLEDs.

### C. OLEDs performance with $\text{Os}(\text{fptz})_2(\text{PPh}_2\text{Me})_2$ as the dopant material

The EL properties of  $\text{Os}(\text{fptz})_2(\text{PPh}_2\text{Me})_2$ -doped devices were investigated in the devices: ITO (75 nm)/CuPc (15 nm)/NPB (60 nm)/CBP:  $x\%$   $\text{Os}(\text{fptz})_2(\text{PPh}_2\text{Me})_2$  (40 nm)/BAIq (15 nm)/Alq<sub>3</sub> (20 nm)/LiF (1 nm)/Al (200 nm). The doping concentration of  $\text{Os}(\text{fptz})_2(\text{PPh}_2\text{Me})_2$  ranges from 4% to 50%. It is apparent from Fig. 4 that when  $\text{Os}(\text{fptz})_2(\text{PPh}_2\text{Me})_2$  is doped in CBP, it resists concentration quenching as well as sustains its EQE over a wide range of doping concentrations. The device EQE is within 8%–9% when the doping concentration ranges from 20% to 40%, which indicates a broad doping concentration window. The subsequent decline of EQE is mild and reaches 6.7% under 50% doping concentration. Such high doping concentration in CBP without showing the concentration quenching effect is rarely seen. This has proved that the octahedral structure of  $\text{Os}(\text{fptz})_2(\text{PPh}_2\text{Me})_2$  works better than the ordinary spherical structure of phosphorescent dopant in minimizing the dye-dye bimolecular interaction at high concentration that leads to quenching of the luminance.

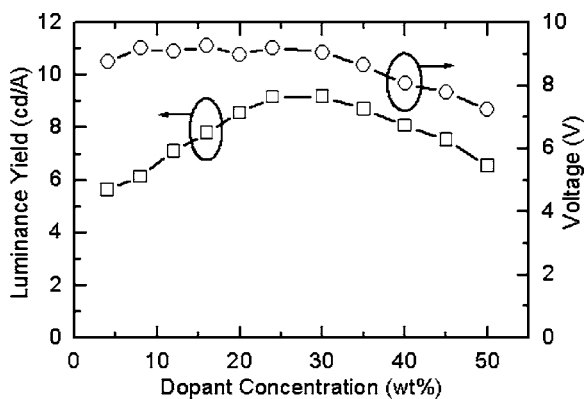


FIG. 4. External quantum efficiency and driving voltage dependency on  $\text{Os}(\text{fptz})_2(\text{PPh}_2\text{Me})_2$  concentration in CBP of the doped devices.

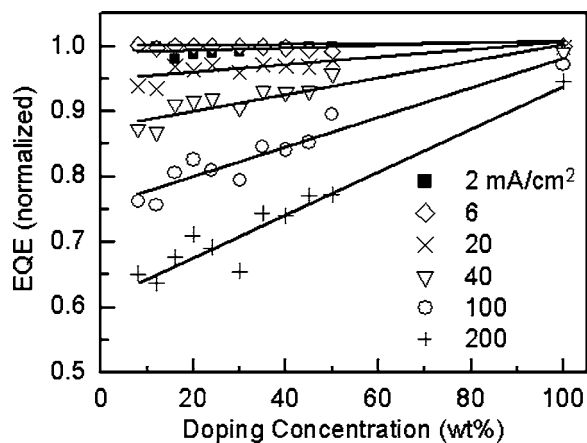


FIG. 5. External quantum efficiency decay with increasing injected current vs  $\text{Os}(\text{fptz})_2(\text{PPh}_2\text{Me})_2$  doping concentration.

From the direct photoionization measurements (Riken AC-2) and UV absorption measurement,<sup>9</sup> the highest occupied molecule orbital (HOMO)/lowest unoccupied molecule orbital (LUMO) of  $\text{Os}(\text{fptz})_2(\text{PPh}_2\text{Me})_2$  is 5.3/3.3 eV which is in between that of CBP (5.5/2.0 eV). This suggests that  $\text{Os}(\text{fptz})_2(\text{PPh}_2\text{Me})_2$  molecules may act as carrier traps under low  $\text{Os}(\text{fptz})_2(\text{PPh}_2\text{Me})_2$  doping concentration. When an electric field is applied, the carriers will be driven forward and forced to undergo the trapping-detrapping mechanism, which is a power consuming behavior. As a result, the driving voltage is higher. However, as the doping concentration of  $\text{Os}(\text{fptz})_2(\text{PPh}_2\text{Me})_2$  is increased, the driving voltage declines (also see in Fig. 4), which indicates that the probability for undergoing the power consuming trapping-detrapping mechanism is reduced. We attribute this to the improved overlapping of  $\text{Os}(\text{fptz})_2(\text{PPh}_2\text{Me})_2$   $\pi$  orbitals, which allows the carriers to hop directly over  $\text{Os}(\text{fptz})_2(\text{PPh}_2\text{Me})_2$  molecules.

### D. Suppression of triplet-triplet annihilation

To further prove that the triplet-triplet annihilation phenomenon will be suppressed as the doping concentration (emission site) is increased, we compare the EQE of all devices driven from 2–200 mA/cm<sup>2</sup> with different doping concentrations and normalized by the EQE under 2 mA/cm<sup>2</sup>. In Fig. 5, it is obvious that the highest EQE of most devices occurred at the lowest current density of 2 mA/cm<sup>2</sup> and the EQE declined with the increase in current density. However, the decrease in EQE is suppressed by the increase of  $\text{Os}(\text{fptz})_2(\text{PPh}_2\text{Me})_2$  doping concentration. It is, therefore, clear that the capability in allowing high phosphorescent dopant concentration as well as short triplet radiative lifetime owing to the proper molecular design would increase emission sites, which is expected to suppress the efficiency loss at high brightness/current in phosphorescent OLEDs.

### III. SUMMARY

In this study, electroluminescent properties of an emissive Os(II) complex with an octahedral configuration have been studied. We fabricated OLEDs based on

$\text{Os}(\text{fptz})_2(\text{PPh}_2\text{Me})_2$  phosphor with a multilayer configuration of ITO/CuPc/NPB/CBP: $x\%$   $\text{Os}(\text{fptz})_2(\text{PPh}_2\text{Me})_2$ /BAIq/Alq<sub>3</sub>/LiF/Al demonstrated red emission with CIE coordinates of  $x=0.65$ ,  $y=0.34$ , a maximum external quantum efficiency of 9%. Owing to its sterically hindered structure,  $\text{Os}(\text{fptz})_2(\text{PPh}_2\text{Me})_2$  has the property of resistance to concentration quenching and the sustaining of its EQE over a wide range of doping concentration in CBP. The device also successfully suppressed the problem of luminescence quenching at high brightness/current and achieved a flat EQE versus brightness response while the emission layer was composed of neat  $\text{Os}(\text{fptz})_2(\text{PPh}_2\text{Me})_2$ .

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<sup>9</sup>We used AC2 to measure the HOMO of the organic materials first. Then we got the energy gap ( $E_g$ ) by UV absorption. The LUMO was obtained indirectly from the HOMO and the  $E_g$ .