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FEATURE ARTICLE

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Amidinate-ligated iridium(III) bis(2-pyridyl)phenyl complex as an excellent phosphorescent material for electroluminescence devices[†]

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Highly efficient, low driving-voltage, and emitter concentration insensitive phosphorescent EL devices are established for the first time by using an amidinate-ligated iridium(III) complex as an emitting component.

Organic light-emitting devices (OLEDs) using phosphorescent metal complexes as emitting materials have received much current interest, because their emission efficiency is higher than that of the fluorescent counterparts.^{1,2} Unfortunately, however, high-performance phosphorescent OLEDs are usually fabricated by doping the emitters into a charge-transporting host matrix in a rather low and narrow concentration range, because of the poor carrier mobility or luminescence self-quenching of the neat phosphorescent dopants. Consistent control of the doping process to keep a constant, low dopant concentration (less than 10%) is a challenging task for the reproducibility of mass production. Recently, considerable efforts have been devoted to the development of phosphorescent OLEDs with a non-doped emitting layer or with higher dopant concentrations.³ However, the emitting materials reported so far usually required complicated synthetic processes and the resulting EL devices generally showed rather high turn-on voltages (>4 V) and moderate efficiency (<7 lm W^{-1}). The search for new emitting materials suitable for low driving-voltage, high performance OLEDs with a non-doped emitting layer or that are insensitive to dopant concentration is, therefore, of much importance and interest.

Amidinates [R'NC(R)NR'] have been widely used as ancillary ligands for various transition metal complexes in coordination chemistry.⁴ However, the use of an amidinate ligand for a phosphorescent metal complex has not been reported previously. We envisioned that a sterically hindered chelating amidinate ligand might help to solve the self-quenching problems encountered previously with phosphorescent metal complexes and thus lead to formation of more efficient phosphorescent OLEDs. To examine the usefulness of an amidinate unit as an ancillary ligand for phosphorescent metal complexes, we chose N,N'-diisopropylbenzamidinate (dipba) as an ancillary ligand to combine with the well-known phosphorescent "(ppy)₂Ir" species (ppy = o-(2-pyridyl)phenyl). We report here the synthesis and novel luminescence properties of the iridium(III) bis(pyridylphenyl)/amidinate complex (**ppy**)₂**Ir(dipba**). This new complex showed highly efficient electroluminescence not only in a non-doped device but also in doped devices in a wide range of doping concentrations.

Scheme 1 illustrates the chemical structure and synthetic route of the amidinate-ligated iridium complex (**ppy**)₂**Ir**(**dipba**). The one-pot reaction of bromobenzene with "BuLi and N,N'-diisopropylcarbodiimide, followed by refluxing with $[(ppy)_2Ir(\mu-Cl)]_2^5$ in hexane afforded (**ppy**)_2**Ir**(**dipba**) in 74% isolated yield.

An X-ray diffraction study[‡] revealed that the distance between two nearest parallel ppy planes is as long as 3.9 Å and there is no overlap between these two planes in (ppy)₂Ir(dipba) (Fig. 1 (left)). These results suggest that no significant intermolecular $\pi - \pi$ interaction between the ppy groups could be present, which could help prevent undesired self-quenching problems in the solid state of this compound. In agreement with this structure feature, (ppv)₂Ir(dipba) displayed brilliant yellowish-green photoluminescence in both neat thin film and powder even in the air (Fig. 1 (right)). The emission maxima of (ppy)₂Ir(dipba) in neat thin film appeared at 553 nm, which was blue-shifted in dichloromethane to 543 nm (see ESI[†]). Its phosphorescence quantum yield (Φ_p) in solution is 0.30, which is comparable to that of the well-known $Ir(ppy)_3$ complex (0.4).^{3b} The phosphorescence lifetime of (ppy)2Ir(dipba) under ambient temperature conditions was found to be 0.35 µs.

To ascertain the influence of the amidinate ligand on the luminescence properties of the iridium complex, DFT calculations on (**ppy**)₂**Ir**(**dipba**) were carried out. The LUMO of (**ppy**)₂**Ir**(**dipba**) is located largely on the ppy ligand (Fig. 2), which is similar to those of the well-known, analogous Ir complexes $Ir(ppy)_3$ and $(ppy)_2Ir(acac)$.⁶ However, the HOMO of (**ppy**)₂**Ir**(**dipba**) consists principally of a mixture of the N atoms of the dipba ligand (49.1%) and the *d*-orbitals of the Ir



Scheme 1 Synthetic route for the Ir complex (ppy)₂Ir(dipba).

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⁴ Electronic supplementary information (ESI) available: Experimental details. CCDC 714889. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b902807b



Fig. 1 Crystal packing diagrams (left) and fluorescence images (right) of solid film and powder of (**ppy**)₂**Ir(dipba**).



Fig. 2 The contour plots of LUMO (left) and HOMO (right) in **(ppy)₂Ir(dipba)** from DFT calculations.

atom (29.6%). This is different from those of Ir(ppy)₃ and (ppy)₂Ir(acac) which are distributed on the π orbitals of the ppy ligands in addition to the Ir *d*-orbitals. These results can be ascribed in part to the π -bonding ability of the dipba ligand being stronger than that of the acac ligand or the ppy ligand,⁶ and are consistent with the fact that the HOMO energy level of (**ppy)**₂Ir(**dipba**) (-4.78 eV) is higher than those of Ir(ppy)₃ (-5.2 eV)^{7a} and (ppy)₂Ir(acac) (-5.0 eV)^{8c} and that the HOMO–LUMO energy gap of (**ppy)**₂Ir(**dipba**) (-2.29 eV) is significantly smaller than those of Ir(ppy)₃ (-2.4 eV) and (ppy)₂Ir(acac) (-2.4 eV). These data also suggest that the amidinate-ligated iridium complex should have hole-transporting ability better than those of Ir(ppy)₃ and (ppy)₂Ir(acac).⁹

To examine the electrophosphorescence properties of the present iridium complex, three devices (I, II and III) were fabricated with the same configuration of ITO/NPB (30 nm)/emitter (35 nm)/BCP (10 nm)/AlQ (25 nm)/LiF (0.5 nm)/Al (NPB = 4,4-bis(N-(1-naphthyl)-N-phenylamino)-biphenyl, BCP = 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline, AlQ = tris(8-hydroxyquinoline)aluminium). Device I used (**ppy**)₂Ir(dipba) as a non-doped emitter, while devices II and III employed (**ppy**)₂Ir(dipba) doped in CBP (4,4'-N,N'-dicarbazolylbiphenyl) with different doping levels (25 mol% in II and 7 mol% in III). Here, NPB, BCP and AlQ serve as hole-transporting, hole-blocking and electron-transporting layers, respectively, while CBP acts as a host material.

All devices fabricated above exhibited bright yellowish-green emission, independent of the applied voltages in the range of 3 V to 16 V. The electroluminescence (EL) spectra of devices I–III at a driving voltage of 6 V are shown in Fig. 3 (inset). The maximum EL emission of the non-doped device I appeared at 552 nm. It was blue-shifted to 544 nm in the doped device III



Fig. 3 Brightness–voltage curves of devices I–III. Inset: EL spectra of devices I–III at 6 V.

which has a low doping concentration (7 mol%). The maximum emission of device II, which has a higher dopant concentration (25 mol%), was almost the same as that of the non-doped device I.

The non-doped device I and the high-concentration doped device II exhibited rather low turn-on voltages (2.3 cd m^{-2} at 2.4 V and 1 cd m^{-2} at 2.5 V, respectively), which are even lower than that of the low-concentration doped device III (3.6 V) (Fig. 3). Moreover, devices I and II showed very low driving voltages at the practical brightness of 100 cd m⁻² and 1000 cd m⁻². In particular, the driving voltages for 100 cd m⁻² and 1000 cd m^{-2} in the non-doped device I are as low as 3.15 V and 4.30 V, respectively, which are near the best values reported for Ir(ppy)₃-doped devices which possessed further sophisticatedly modified device structures.⁷ The lowering of the driving voltages in devices I and II could result from the narrow HOMO-LUMO energy gap of (ppy)₂Ir(dipba). Moreover, because the HOMO level of (ppy)₂Ir(dipba) (-4.78 eV) is higher than that of CBP (-6.1 eV),^{8c} the direct injection of holes from NPB (HOMO: -5.4 eV)^{8c} into the Ir complex in the non-doped device I and the high-concentration doped device II should be energetically more favorable than that in low-concentration doped device III. These results suggest that the direct hole-transfer between the holetransporting layer and the triplet emitter is obviously important to guarantee an efficient carrier recombination on the phosphor.8

In addition to their better brightness/driving-voltage performance, devices I and II also exhibited power efficiency a little higher than that of device III in the whole current density range (Fig. 4). Device I showed the maximum power efficiency of 32.5 lm W⁻¹, which, as far as we are aware, represents the most efficient non-doped phosphorescent OLED ever reported.³ The maximum power efficiency of device II reached 29.5 lm W^{-1} , which is the highest ever reported for an OLED at a similar doping concentration level (ca. 25 mol%).^{3b,d,f} It is also noteworthy that at the practical brightness of 100 cd m^{-2} and 1000 cd m^{-2} , the power efficiencies of device I remained as high as 28 lm W⁻¹ and 22 lm W^{-1} , respectively, and those of device II as high as 28.5 lm W^{-1} and 23.5 lm W^{-1} , respectively. The pronounced EL performance enhancement could partly profit from the very low driving voltages, and on the other hand, may also suggest that the emitting iridium complex (ppy)₂Ir(dipba) can



Fig. 4 Power efficiency-current density curves of devices I-III.

efficiently transport charges without the need for a host. There should be a stable charge carrier balance and efficient confinement of the triplet excitons generated within the emitting layer in the non-doped device.^{7a}

In summary, we have demonstrated for the first time that the use of a sterically demanding amidinate group as an ancillary ligand for a bis-cyclometalated $(C^{\wedge}N)$ phosphorescent iridium species can lead to a significant reduction in self-quenching and a dramatic improvement in the electroluminescence properties of the complex, thus enabling the successful fabrication of high efficiency, low driving-voltage phosphorescent OLEDs in a wide range of doping concentrations or even without the requirement of doping the emitter into a host matrix. The insensitivity of EL properties to emitterdoping concentration would make a sophisticated control of the doping process unnecessary and thus lead to more efficient, reproducible fabrication of high performance EL devices. Because of the excellent performance and the ease of synthesis, amidinate-ligated phosphorescent metal complexes should have high potential in practical applications such as flat-panel displays and organic lighting. Further studies on other phosphorescent cyclometalated $(C^{\wedge}N)$ metal complexes bearing amidinate and related ancillary ligands are in progress.

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Notes and references

 \ddagger Single crystals suitable for X-ray structural analysis were obtained by vacuum sublimation. Diffraction data were collected on a Rigaku R-Axis Rapid diffractometer (Mo K α radiation, graphite monochromator) in

the ψ rotation scan mode. The structure determination was performed by direct methods using SHELXTL 5.01v and refinements with full-matrix least squares on F^2 .

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