Efficiency phosphorescent OLEDs with a low roll-off based on a hetero-triplet iridium complex

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In order to explore the triplet–triplet annihilation in cyclometalated iridium complexes, a hetero-triplet iridium complex [Ir(ppy)2pbi] employing two 2-phenylpyridine (Hppy) ligands and one 1,2-diphenyl-1H-benzo[d]-imidazole (Hpbi) ligand with similar triplet energies was synthesized. A device based on [Ir(ppy)2pbi] exhibited high current efficiency 26.7 cd/A at high doping concentration 12 wt%. More interestingly, the current efficiency was still maintained at 25.8 cd/A when the current density was above 253.2 mA/cm². The efficiency roll-off was only about 3.4%, much lower than that of traditional cyclometalated iridium complexes. It is proposed that the complicated energy level and unsymmetrical ligand in Ir(ppy)2pbi may help to suppress the triplet–triplet annihilation.

1. Introduction

Organic light-emitting devices (OLEDs) are currently an active research area due to their potential applications in flat-panel displays and solid state lighting [1–5]. Octahedral 4d⁶ and 5d⁶ metal complexes based phosphorescent materials, especially the iridium complexes, have attracted much attention for improving OLED efficiency because of the close-lying π–π* and metal to ligand charge transfer (MLCT) states in these complexes together with the heavy atom effect enhance the spin-orbit coupling, which results in utilization of both singlet and triplet excitons, causing nearly unity of internal quantum efficiency [5–9]. However, triplet–triplet annihilation (TTA) exists in phosphorescent OLEDs because of the long lifetime of triplet exciton and high triplet exciton concentration in the emitting layer [10–13]. Tris[2-phenylpyridine]iridium [Ir(ppy)3], one of the most studied phosphorescent dyes frequently shows efficiency roll-off when used in phosphorescent OLEDs [14–16]. Though the TTA can be suppressed to a certain extent by optimized device structure, the triplet lifetime 1.6 μs of Ir(ppy)3 may be too long to avoid the TTA. Therefore, developing short lifetime triplet exciton phosphorescent materials will be an effective strategy to suppress the TTA. Shu et al. [17] developed a cyclometalated osmium complex with short triplet lifetime 96 ns, which exhibited a less-pronounced efficiency roll-off at high current densities. We also developed a novel phosphor with triplet lifetime of 3.92 ns, and the efficiency roll-off was only 28.2% at 100 mA/cm² with low doping concentration 2 wt% [18]. Although developing short lifetime phosphors can effectively suppress the TTA, however, materials can only be designed by serendipity. Taking into account the chemical structure of cyclometalated iridium complexes, three homo-cyclometalated ligands are always employed like Ir(ppy)3 and tris[1-phenylisoquinoline]iridium [Ir(piq)3], commercialized materials for green and red phosphorescent OLEDs. Lee [19] has reported a novel red phosphorescent iridium complex Ir(ppy)2pic by intramolecular energy transfer from the MLCT of Ir-ppy to Ir-piq to improve the efficiency by 20%, however, there was no improvement of the TTA. Thus, here we design a new hetero-triplet iridium complex Ir(ppy)2pbi employing ppy and pbpi with similar triplet energy. Because of the different triplet energies existed in Ir(ppy)2pbi, we thought the TTA in the emitting layer will be different from homo-triplet exciton complexes.

The emitting mechanisms of Ir(ppy)3, Ir(ppy)2pic and Ir(ppy)2pbi were shown in Fig. 1. For Ir(ppy)3, the green phosphorescence emitted from the decay of degenerate 3MLCT energy level between iridium atom and ppy ligand, TTA became more serious as the triplet exciton density increased. For Ir(ppy)2pic, there was still no improvement about the TTA because of high exciton concentration of Ir-piq caused by the intramolecular energy transfer from Ir-ppy to Ir-piq which resulted in a pure red

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phosphorescence. For Ir(ppy)2pbi, the triplet energy levels of Ir-ppy and Ir-pbi were similar, both Ir-ppy and Ir-pbi contribute to the phosphorescence without intramolecular energy transfer. Experiments show that Ir(ppy)2pbi exhibits low photo-luminescence quantum yield of 0.21 which may be caused by the low triplet density in the emitting layer. Theoretical calculations show that the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels of Ir(ppy)2pbi were more complicated than that of Ir(ppy)3 because the introduction of different cyclometalated ligands destroys the high symmetry of cyclometalated complex. It supposed that the complicated energy level and unsymmetrical ligand play an important role in suppression TTA. As a result, efficient green phosphorescent OLEDs are obtained with efficiency roll-off of 3.4% at high doping concentration 12 wt%.

2. Experimental

2.1. Reagents and measurements

Hppy was purchased from Aldrich, all reactions were performed under argon. Solvents were carefully dried and distilled from appropriate drying agents prior to use. Commercially available reagents were used without further purification unless otherwise stated. All reactions were monitored by using thin-layer chromatography (TLC) with Merck precoated glass plates. Compounds were visualized with UV-light irradiation at 254 and 365 nm. High resolution mass spectra (HRMS) were obtained using a Bruker Maxis UHR-TOF, Ion Source: APCI system. Nuclear magnetic resonance (NMR) spectra were measured in appropriate deuterated solvents (CDCl3 or DMSO-d6) on a Bruker AVANCE 600 MHz Fourier transform NMR spectrometer; chemical shifts were quoted relative to the internal standard tetramethylsilane for 1H NMR data. Absorption and photoluminescence spectra were measured with a Hitachi U-4100 UV–Vis–NIR scanning spectrophotometer and HORIBA JOBIN YVON FluoroMax-4 spectrophotometer, respectively. The electrochemistry characteristics of the two complexes were investigated using a cyclic voltammetry employing a glass carbon electrode as working electrode, a platinum wire as counter electrode and an Ag/AgCl (3.0 M KCl) electrode as reference electrode. The cyclic voltammograms were obtained from a one-compartment glass cell in dichloromethane containing 10−3 M iridium complexes and 0.1 M tetra(n-butyl)ammonium hexa-fluorophosphate (n-Bu4NPF6) as a supporting electrolyte, where the scan rate was 100 mV/s, the HOMO and LUMO energy level was calculated as the reference method [20].

2.2. Device fabrication and measurements

OLEDs were prepared on a glass substrate pre-coated with a ~130-nm-thick indium–tin-oxide (ITO) layer with a sheet resistance of ~20 Ω/sq. Prior to organic layer deposition, the substrate was degreased with solvents and cleaned for 5 min by exposure to a UV-ozone ambient, then it was immediately loaded into the evaporation system. With a base pressure of ~3 × 10−4 Pa, the organic and metal cathode layers were grown successively by using an in vacuo mask exchange mechanism without breaking the vacuum. Firstly, a 10-nm-thick 4,4′,4″-tris(3-methylphenyl-N-phenylamino)triphenylamine (m-MTDATA) hole injection layer (HIL) was deposited, followed by a 20-nm-thick 4,4′-bis[N-(1-naphthyl)-N-phenylamino]biphenyl (NPB) hole transporting layer (HTL). Then a 30-nm-thick light-emitting layer (EML) consisting of various weight ratio iridium complexes doped into a 4,4′-bis[9H-carbazol-9-yl]biphenyl (CBP) host was prepared via thermal codeposition. Next, a 30-nm-thick 1,3,5-tri(1-phenyl-1H-benzol[d]imidazol-2-yl)phenyl (TPBi) layer was used to block hole and transport electron. A shadow mask with rectangular 2 mm × 2 mm openings was used to define the cathode consisting of a 1-nm-thick LiF layer, followed by a 100-nm-thick Al layer. The electroluminescence spectra were recorded with a PR655 spectrophotometer. The brightness-current-voltage (B–I–V) characteristics of OLEDs were measured with Keithley 2400. All the measurements were carried out at room temperature under ambient conditions.

2.3. Theoretical calculations

The molecular structures and corresponding molecular orbital were obtained at the B3LYP [21,22]/def2-SVP [23] level. All the calculations were performed using ORCA [24] program.
2.4. The general procedure for the synthesis of Ir(ppy)_2pbi

Bis[1,2-diphenyl-1H-benzo[d]-imidazole][2-phenylpyridine]iridium(III) [Ir(ppy)_2pbi]: Hppy (0.31 g, 2.0 mmol) was dissolved into a mixed solution of 2-ethoxyethanol (12 mL) and water (4 mL) in a 25 mL round bottomed flask, and then IrCl_3·3H_2O (0.28 g, 0.8 mmol) was added. The mixture was stirred under nitrogen at 120 °C for 12 h. The mixture was cooled to room temperature and the precipitate was collected and washed with water, ethanol, and acetone, then dried in vacuum to give a cyclometalated Ir-m-chloro-bridged dimer. The dimer complex, Hpbi (0.27 g, 1.0 mmol), Na_2CO_3 (0.34 g, 3.2 mmol) and 5 mL glycerol were charged into a round bottomed flask, the mixture was then heated to 240 °C under an argon atmosphere for another 12 h. After cooling to room temperature, the mixture was poured into 100 mL water, yellow precipitate was filtered off and washed with water, ethanol and ether. The crude product was purified by silica column chromatography with dichloromethane/petroleum ether (1:2, v/v) as the eluent to give 0.29 g Ir(ppy)_2pbi as a yellow powder. Yield: 47.5%, 0.14 g.

Ir(ppy)_3 can also be obtained as a byproduct, yield: 27.5%. 1HNMR (CDCl_3, 600 MHz): 7.90 (t, J = 6.4 Hz, 2H), 7.85 (d, J = 4.8 Hz, 1H), 7.77 (d, J = 5.4 Hz, 1H), 7.69–7.59 (m, 7H), 7.50–7.47 (m, 2H), 7.06 (t, J = 7.8 Hz, 1H), 6.97 (d, J = 7.8 Hz, 1H), 6.92–6.78 (m, 10H), 6.72 (t, J = 7.8 Hz, 1H), 6.53 (t, J = 7.8 Hz, 1H), 6.05 (d, J = 8.4 Hz, 1H). 13CNMR (CDCl_3, 150 MHz): 167.65, 166.68, 163.39, 162.61, 161.33, 148.06, 144.33, 143.92, 140.86, 137.90, 137.85, 136.91, 136.87, 136.32, 135.90, 135.80, 134.10, 130.38, 129.89, 129.78, 128.53, 128.17, 125.25, 123.94, 123.72, 123.23, 122.38, 122.00, 121.29, 119.66, 119.52, 119.09, 118.66, 118.54, 115.23, 110.53; HRMS (APCI): m/z calcd for C_{41}H_{29}IrN_4: 770.2021; found: 771.2094 (M+H)^+.  

3. Results and discussion

3.1. Synthesis

The cyclometalated ligand Hpbi was synthesized by condensation of N-phenyl-o-phenylenediamine and benzaldehyde in 2-ethoxyethanol as described in literature [25], after purified by column chromatography using petroleum ether and ethyl acetate as eluent, off white powder was obtained in 72% yield. The synthesis of Ir(ppy)_2pbi was carried out according to the reference method [26,27] as shown in Scheme 1. Hppy was used to react with IrCl_3·3H_2O to give cyclometalated Ir-m-chloro-bridged dimer, which could react with Hpbi to afford heterocyclometalated Ir(ppy)_2pbi, in the presence of Na_2CO_3. More interestingly, Ir(ppy)_3 can also be obtained as a byproduct when we attempted to purify Ir(ppy)_2pbi on a silica gel column with dichloromethane and hexane as eluent, which was used for device fabrication directly. Both the complexes show strong phosphorescence on silica gel plates under the excitation of 365 nm.

3.2. Photophysics characteristics

The UV–vis absorption and photoluminescence spectra of complexes Ir(ppy)_3 and Ir(ppy)_2pbi in dichloromethane solutions were shown in Fig. 2. Both the complexes show similar absorption between 375 and 525 nm, however, a difference was obvious in the region 325–375 nm because of the introduction of the pbi ligand, from which we can conclude both the MLCT of ppy and pbi were excited according to literature [19]. Ir(ppy)_3 and Ir(ppy)_2pbi show strong green phosphorescence with a peak maximum wavelength at 514 and 517 nm with photoluminescence quantum yield (φ) of 0.40 and 0.21, respectively, calculated based on our previous report [28]. In the heterocyclometalated complex Ir(ppy)_2pbi, the triplet MLCT state of Ir-ppy and Ir-pbi were 2.41 and 2.37 eV, respectively, estimated from the emission of Ir(ppy)_3 [14] and tris(1,2-diphenyl-1H-benzimidazol)iridium [Ir(pbi)_3] [29]. Therefore the 0.04 eV difference between the triplet MLCT state of Ir-ppy and Ir-pbi was too small for the occurrence of efficient intramolecular energy transfer [30]. That is, the ΔG between the MLCT state of Ir-ppy and Ir-pbi was << 0 eV, so inefficient energy transfer should be existed in Ir(ppy)_2pbi molecule. As shown in Fig. 1, both the triplet of Ir-ppy and Ir-pbi contribute to the phosphorescence.

Scheme 1. Synthetic route of Ir(ppy)_2pbi.
3.3. Electrochemistry characteristics

Fig. 3 depicts the cyclic voltammograms of both the complexes. The onset oxidation (E_{ox}) of Ir(ppy)_3 and Ir(ppy)_2pbi were 0.64 and 0.26 V, respectively, which were usually considered as the metal-centered couple, i.e., IrIII/IrIV of the complexes [31,32]. The oxidation and reduction onset of ferrocence were 0.78 and 0.26 V, respectively, then the HOMO of Ir(ppy)_3 and Ir(ppy)_2pbi were estimated to be −4.92 and −4.89 eV, respectively, according to the previously reported method [33]. The optical band gaps (E_g) of Ir(ppy)_3 and Ir(ppy)_2pbi were calculated about 2.08 and 2.07 eV, respectively, according to the absorption edge (E_{edge}) in their dichloromethane solutions (Fig. 2). As a result the LUMO were calculated from HOMO and the absorption edge (E_{edge}) in their dichloromethane solutions (Fig. 2). As a result the LUMO were calculated from HOMO and E_g, estimated to be −2.84 and −2.82 eV, respectively. By replacing ppy with pbi, the HOMO and LUMO changed slightly because of the similar electron deficient ability of benzimidazole compared to pyridine. The photophysics and electrochemistry characteristics of complexes Ir(ppy)_3 and Ir(ppy)_2pbi were summarized in Table 1.

![Fig. 2. UV–vis absorption and photoluminescence spectra of Ir(ppy)_3 and Ir(ppy)_2pbi in dichloromethane solution (excited at 300 nm) at room temperature.](image)

![Fig. 3. Cyclic voltagmmetry curves of (cyclopbi)Iracac and (cyclopbi)IrCF3 in dichloromethane solution.](image)

### Table 1

| Complexes   | Abs (nm) | PL (nm) | φ (eV) | E_g (eV) | E_m (V) | HOMO (eV) | LUMO (eV) |
|-------------|----------|---------|--------|----------|---------|-----------|-----------|
| Ir(ppy)_3   | 345.8    | 378.7   | 405.7  | 453.2    | 485.4   | 514       | 2.08      |
| Ir(ppy)_2pbi| 374.8    | 408.4   | 454.5  | 481.8    |         | 517       | 2.07      |

* E_g = 1240/λ_{max}
The oxidation and reduction onset of ferrocence were 0.78 and 0.26 V, respectively, then the HOMO of Ir(ppy)_3 and Ir(ppy)_2pbi were estimated to be −4.92 and −4.89 eV, respectively.

3.4. Electroluminescence characteristics

As is well known, the efficiency of phosphorescent OLEDs drops markedly as the doping concentration increased because of the strong concentration quenching, in addition, incomplete Dexter energy transfer will exit as the doping concentration decreased which cause strong NPB or CBP emission [18]. The electroluminescence characteristics of Ir(ppy)_3 and Ir(ppy)_2pbi are shown in Fig. 4. The optimized doping concentration of Ir(ppy)_3 was 6 wt%, and the device showed the maximum current efficiency (η_i) of 30.9 cd/A and maximum brightness of 50,340 cd/m², however, because of the strong TTA, efficiency dropped badly to 23.4 cd/A at 215.3 mA/cm² with an efficiency roll-off of 24.3%. Same phenomenon was obtained for Ir(ppy)_2pbi, at doping concentration 6 wt%, the maximum η_i was only about 19.5 cd/A, much lower than that of Ir(ppy)_3, may be because of the lower ϕ of Ir(ppy)_2pbi than Ir(ppy)_3, and the efficiency roll-off was obviously as the current increased. However, when the doping concentration was increased to 10 wt%, both the maximum η_i and brightness were improved greatly to 24.1 cd/A and 58,170 cd/m², respectively. Interestingly, the η_i is higher than that of Ir(ppy)_3 when the current density increased to 195.8 mA/cm². The reason was ascribed to the lower efficiency in the Ir(ppy)_2pbi device than the Ir(ppy)_3 one caused by the low exciton density, which was identical to the lower photoluminescence quantum yield of Ir(ppy)_2pbi than Ir(ppy)_3. In order to further investigate the TTA in this hetero-cyclometalated complex, the doping concentration was increased to 12 wt%, as shown in Fig. 4a, the efficiency was extremely stable from 3.5 mA/cm² to 253.2 mA/cm², and the efficiency roll-off was only about 3.4% from the maximum η_i 26.7 cd/A to 25.8 cd/A at 253.2 mA/cm². At 103.1 mA/cm² and above, this device was more efficient than that of Ir(ppy)_3 and the brightness was as high as 27,000 cd/m². We infer that the suppressed TTA was ascribed to more complicated excited states and the unsymmetrical ligand in Ir(ppy)_2pbi which lead to low exciton density unlike Ir(ppy)_3 or Ir(ppy)_2piq in which the phosphorescence radiatively decayed only from the triplet exciton of Ir-ppy or Ir-piq.

3.5. Theoretical calculations

To obtain a qualitative picture on the electronic property of Ir(ppy)_3 and Ir(ppy)_2pbi, theoretical calculations were carried out and the results were shown in Fig. 5. The optimized structures of Ir(ppy)_3 and Ir(ppy)_2pbi were consistent with the experimental results. For complex Ir(ppy)_3, because of the symmetrical structure (which was also proved by the ^1^H NMR data), a few HOMO (HOMO-2, HOMO-1, HOMO) and LUMO (LUMO, LUMO + 1, LUMO + 2) were evenly distributed throughout the iridium atom and the three ppy ligands. Moreover, due to high symmetry, three HOMOs become degenerate and their energies are −4.30 eV. For LUMOs, their energies are closed, namely −1.96 eV (LUMO) and −1.88 eV (LUMO + 1, LUMO + 2). However, for complex Ir(ppy)_2pbi, the
energy levels were more complicated compared to Ir(ppy)₃, the HOMO was concentrated in the metal and the electron-rich groups of ppy and pbi with −3.97 eV, and the HOMO-1 and HOMO-2 were mainly in the ppy and pbi ligand with different energy levels −4.19 eV and −4.28 eV, respectively. The LUMO, LUMO + 1 and LUMO + 2 also show different energy levels −1.85 eV, −1.77 eV and −1.74 eV, respectively. The calculations indicate more complicated electron transitions may exist in the complex Ir(ppy)₂pbi because the introduction of different cyclometalated ligands destroys the high symmetry of cyclometalated complexes. As the result of the loss of electronic-state degeneracy, different types of triplet excitons may be generated when Ir(ppy)₂pbi is excited. Thus in the visible absorption range the distance between the same kind of exciton becomes large, which results in

**Fig. 4.** Electroluminescence characteristics of Ir(ppy)₃ and Ir(ppy)₂pbi. a: Current efficiency and current density relationships of 6 wt% doped Ir(ppy)₃ and 6 wt%, 10 wt% and 12 wt% doped Ir(ppy)₂pbi; b: Brightness and current density relationships of 6 wt% doped Ir(ppy)₃ and 6 wt%, 10 wt% and 12 wt% doped Ir(ppy)₂pbi.

**Fig. 5.** Optimized structures and plots of molecular orbital of Ir(ppy)₃ and Ir(ppy)₂pbi with corresponding energies in Hartree unit.
suppressed TTA. More detailed dynamic processes are still under-
way and the result will be published in due course.

4. Conclusion

In conclusion, high efficiency and efficiency-stable phos-
phorescent OLEDs were obtained based on the hetero-cyclometalated
iridium complex Ir(ppy)2pbi. The maximum $\eta_E$ 26.7 cd/A was ob-
tained and the $\eta_E$ was still maintained at 25.8 cd/A when the cur-
crent density was above 253.2 mA/cm², only 3.4% efficiency roll-off. Both
the triplet state of Ir-ppy and Ir-pbi contributed to the phospho-
rescence because of the complicated energy level and unsymmet-
ical ligand in Ir(ppy)2pbi, which was qualitatively proved by
theoretical calculations. This result could be very interesting and
useful when designing efficiency phosphorescent materials with
lower efficiency decay.

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