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

Liangliang Han ^a, Dongyu Zhang ^{b,*}, Jun Wang ^a, Zhenggang Lan ^a, Renqiang Yang ^{a,*}

^a CAS Key Laboratory of Bio-based Materials, Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, Qingdao 266101, China

^b Suzhou Institute of Nano-Tech and Nano-Bionics, Chinese Academy of Sciences, Suzhou 215123, China

ARTICLE INFO

Article history:

Received 4 June 2014

Received in revised form

29 September 2014

Accepted 2 October 2014

Available online 12 October 2014

Keywords:

Heterocyclometalated iridium complex

Hetero-triplet iridium complex

Triples–triples annihilation

Efficiency roll-off

Exciton density

OLED

ABSTRACT

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-1*H*-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.

© 2014 Elsevier Ltd. All rights reserved.

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 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 μ s 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 homocyclometalated 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)₂piq 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 pbi 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)₂piq 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)₂piq, 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

* Corresponding authors.

E-mail addresses: dyzhang2010@sinano.ac.cn (D. Zhang), yangrq@qibebt.ac.cn (R. Yang).

Fig. 1. The emitting mechanism schematic diagrams of Ir(ppy)₃, Ir(ppy)₂piq and Ir(ppy)₂pbi. Ir(ppy)₃: Irradiative decay from degenerated Ir-ppy; Ir(ppy)₂piq: Irradiative decay from Ir-piq because of the intramolecular energy transfer; Ir(ppy)₂pbi: Irradiative decay from both Ir-ppy and Ir-pbi.

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 photoluminescence 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-*d*₆) 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 hexafluorophosphate (*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(*N*-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(9*H*-carbazol-9-yl)biphenyl (CBP) host was prepared via thermal codeposition. Next, a 30-nm-thick 1,3,5-tri(1-phenyl-1*H*-benzo[*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-1*H*-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 IrCl₃·3H₂O (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-μ-chloro-bridged dimer. The dimer complex, Hpbi (0.27 g, 1.0 mmol), Na₂CO₃ (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 (CDCl₃, 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), 6.63 (d, *J* = 7.8 Hz, 1H), 6.53 (t, *J* = 7.8 Hz, 1H), 6.05 (d, *J* = 8.4 Hz, 1H); ¹³CNMR (CDCl₃, 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, 130.13, 129.89, 129.78, 129.74, 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 C₄₁H₂₉IrN₄: 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 IrCl₃·3H₂O to give cyclometalated Ir-μ-chloro-bridged dimer, which could react with Hpbi to afford heterocyclometalated Ir(p-ppy)₂pbi, in the presence of Na₂CO₃. 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(p-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-1*H*-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 Δ*G* between the MLCT of acceptor and donor 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.

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.

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 0.61 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 ferrocene 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 (λ_{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 benzoimidazole compared to pyridine. The photophysics and electrochemistry characteristics of complexes Ir(ppy)₃ and Ir(ppy)₂pbi were summarized in Table 1.

Fig. 3. Cyclic voltammetry curves of Ir(ppy)₃ and Ir(ppy)₂pbi in dichloromethane solution.

Table 1

Photophysics and electrochemistry characteristics of complexes Ir(ppy)₃ and Ir(ppy)₂pbi in dichloromethane solution.

Complexes	Abs (nm)	PL (nm)	ϕ	E_g^a (eV)	E_{ox} (V)	HOMO ^b (eV)	LUMO ^c (eV)
Ir(ppy) ₃	345.8, 378.7, 405.7, 453.2, 485.4	514	0.40	2.08	0.64	−4.92	−2.84
Ir(ppy) ₂ pbi	374.8, 408.4, 454.5, 488.1	517	0.21	2.07	0.61	−4.89	−2.82

^a $E_g = 1240/\lambda_{edge}$.

^b $E_{HOMO} = -e(E_{ox} + 4.8 - E_{1/2}^{(Fc/Fc+)}).$

^c $E_{LUMO} = E_{HOMO} + E_g$.

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_c) 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_c 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_c and brightness were improved greatly to 24.1 cd/A and 58,170 cd/m², respectively. Interestingly, the η_c 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_c 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 ¹HNMR 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

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.

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. 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 phosphorescent OLEDs were obtained based on the hetero-cyclometalated iridium complex Ir(ppy)₂pbi. The maximum η_c 26.7 cd/A was obtained and the η_c was still maintained at 25.8 cd/A when the current 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 phosphorescence because of the complicated energy level and unsymmetrical 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.

Acknowledgments

The work was supported by National Natural Science Foundation of China (21103213, 21274161, 51173199, 91233106 and 91123034), Outstanding Young Scientists Research Award Fund of Shandong Province (BS2010NJ021), Shandong Provincial Natural Science Foundation (ZR2011BZ007), Strategic Priority Research Program of the Chinese Academy of Sciences (XDA09020201), and National Science and Technology Ministry (2012BAF13B05-402).

References

- [1] Ho PKH, Kim JS, Burroughes JH, Becker H, Li SFY, Brown TM, et al. Molecular-scale interface engineering for polymer light-emitting diodes. *Nature* 2000;404:481–4.
- [2] Gu G, Parthasarathy G, Forrest SR. A metal-free, full-color stacked organic light-emitting device. *Appl Phys Lett* 1999;74:305–7.
- [3] Wu CC, Chen CW, Cho TY. Three-color reconfigurable organic light-emitting devices. *Appl Phys Lett* 2003;83:611–3.
- [4] Baldo MA, O'Brien DF, You Y, Shoustikov A, Sibley S, Thompson ME, et al. Highly efficient phosphorescent emission from organic electroluminescent devices. *Nature* 1998;395:151–4.
- [5] Adachi C, Baldo MA, Thompson ME, Forrest SR. Nearly 100% internal phosphorescence efficiency in an organic light-emitting device. *J Appl Phys* 2001;90:5048–51.
- [6] Ikai M, Tokito S, Sakamoto Y, Suzuki T, Taga Y. Highly efficient phosphorescence from organic light-emitting devices with an exciton-block layer. *Appl Phys Lett* 2001;79:156.
- [7] Lamansky S, Djurovich P, Murphy D, Razaq FA, Lee HE, Adachi C, et al. Highly phosphorescent bis-cyclometalated iridium complexes: synthesis, photophysical characterization, and use in organic light emitting diodes. *J Am Chem Soc* 2001;123:4304–12.
- [8] Wang Q, Chen YH, Chen JS, Ma DG. White top-emitting organic light-emitting diodes employing tandem structure. *Appl Phys Lett* 2012;101:133302.
- [9] Baldo MA, Lamansky S, Burrows PE, Thompson ME, Forrest SR. Very high-efficiency green organic light-emitting devices based on electrophosphorescence. *Appl Phys Lett* 1999;75:4.
- [10] Baldo MA, Adachi C, Forrest SR. Transient analysis of organic electrophosphorescence. II. Transient analysis of triplet-triplet annihilation. *Phys Rev B* 2000;62:10967–77.
- [11] Fukagawa H, Shimizu T, Ohbe N, Tokito S, Tokumaru K, Fujikake H. Anthracene derivatives as efficient emitting hosts for blue organic light-emitting diodes utilizing triplet-triplet annihilation. *Org Electron* 2012;13:1197–203.
- [12] Wu C, Tao SL, Chen MM, Wong FL, Yang QD, Mo HW. Highly efficient blue and white phosphorescent OLEDs based on an iridium complex. *Dyes Pigments* 2013;96:237–41.
- [13] Yang W, Chen YS, Jiang W, Ban XX, Huang B, Dai YQ, et al. A carbazole-based dendritic host material for efficient solution-processed blue phosphorescent OLEDs. *Dyes Pigments* 2013;97:286–90.
- [14] Kajii H, Takahota N, Wang YD, Ohmori Y. Current-density dependence of transient properties in green phosphorescent organic light-emitting diodes. *Jpn J Appl Phys* 2011;50: 04DK05.
- [15] Yang XH, Jabbour GE. Efficient light emitting devices based on phosphorescent partially doped emissive layers. *J Mater Chem C* 2013;1:4663–6.
- [16] Reineke S, Walzer K, Leo K. Triplet-exciton quenching in organic phosphorescent light-emitting diodes with Ir-based emitters. *Phys Rev B* 2007;75: 125328.
- [17] Wu CH, Shih PI, Shu CF, Chi Y. Highly efficient red organic light-emitting devices based on a fluorene-triphenylamine host doped with an Os(II) phosphor. *Appl Phys Lett* 2008;92:233303.
- [18] Han LL, Yang DF, Li WL, Chu B, Chen YR, Su ZS, et al. The reduced triplet-triplet annihilation of electrophosphorescent device doped by an iridium complex with active hydrogen. *Appl Phys Lett* 2008;93:153303.
- [19] Lee JY. Intramolecular energy transfer in heteroleptic red phosphorescent dopants. *Appl Phys Lett* 2006;89:223517.
- [20] Li YF, Cao Y, Gao J, Wang DL, Yu G, Heeger AJ. Electrochemical properties of luminescent polymers and polymer light-emitting electrochemical cells. *Synth Met* 1999;99:243–8.
- [21] Becke AD. Density-functional thermochemistry. III. The role of exact exchange. *J Chem Phys* 1993;98:5648.
- [22] Stephens PJ, Devlin FJ, Chabalowski CF, Frisch MJ. Ab initio calculation of vibrational absorption and circular dichroism spectra using density functional force fields. *J Phys Chem* 1994;98:11623–7.
- [23] Weigend F, Ahlrichs R. Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: design and assessment of accuracy. *Phys Chem Chem Phys* 2005;7:3297–305.
- [24] Neese F. ORCA – an ab initio, density functional and semi empirical program package V 2.9 development. D-45470 Muelheim/Ruhr, Germany: Max Planck Institute for Bioinorganic Chemistry; 2012.
- [25] Huang WS, Lin JT, Chien CH, Tao YT, Sun SS, Wen YS. Highly phosphorescent bis-cyclometalated iridium complexes containing benzoimidazole-based ligands. *Chem Mater* 2004;16:2480–8.
- [26] You Y, Park SY. Inter-Ligand energy transfer and related emission change in the cyclometalated heteroleptic iridium complex: facile and efficient color tuning over the whole visible range by the ancillary ligand structure. *J Am Chem Soc* 2005;127:12438–9.
- [27] Kwon TH, Cho HS, Kim MK, Kim JW, Kim JJ, Lee KH, et al. Color tuning of cyclometalated iridium complexes through modification of phenylpyrazole derivatives and ancillary ligand based on ab initio calculations. *Organometallics* 2005;24:1578–85.
- [28] Han LL, Yang DF, Li WL, Chu B, Chen YR, Su ZS, et al. Intramolecular energy transfer between the triplet of ancillary ligand and the metal to ligand charge transfer state existed in heterocyclometalated iridium (III) complexes. *Appl Phys Lett* 2009;94:163303.
- [29] Ding JQ, Gao J, Cheng YX, Xie ZY, Wang LX, Ma DG, et al. Highly efficient green-emitting phosphorescent iridium dendrimers based on carbazole dendrons. *Adv Funct Mater* 2006;16:575–81.
- [30] Baldo MA, Adachi C, Forrest SR. Transient analysis of organic electrophosphorescence. I. Transient analysis of triplet energy transfer. *Phys Rev B* 2000;62:10958–66.
- [31] Deng LJ, Zhang T, Wang RJ, Li JY. Diphenylphosphorylpyridine-functionalized iridium complexes for high-efficiency monochromatic and white organic light-emitting diodes. *J Mater Chem* 2012;22:15910–8.
- [32] Su HC, Fang FC, Hwu TY, Hsieh HH, Chen HF, Lee GH, et al. Highly efficient orange and green solid-state light-emitting electrochemical cells based on cationic Ir^{III} complexes with enhanced steric hindrance. *Adv Funct Mater* 2007;17:1019–27.
- [33] Han LL, Zhang DY, Zhou YH, Yang Y, Woo HY, Bai FL, et al. Greenish yellow organic light emitting devices based on novel iridium complexes containing 2-cyclohexenyl-1-phenyl-1H-benzo[d]imidazole. *Dyes Pigments* 2013;99: 1010–5.