Organic Electronics 39 (2016) 91-99



Contents lists available at ScienceDirect

## **Organic Electronics**



journal homepage: www.elsevier.com/locate/orgel

## Synthesis and characterization of highly efficient blue Ir(III) complexes by tailoring $\beta$ -diketonate ancillary ligand for highly efficient PhOLED applications



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### ARTICLE INFO

Article history: Received 23 May 2016 Received in revised form 16 August 2016 Accepted 25 September 2016

Keywords: Blue PhOLEDs β-diketonate ancillary ligands Low efficiency roll-off High photoluminescence quantum yields

### ABSTRACT

We synthesized two new heteroleptic blue-emitting Ir(III) complexes tBuCN-FIrmMes and tBuCN-FIrdMes by using systematically tailored ancillary ligands 1-mesitylbutane-1,3-dione (mMes) and 1,3-dimesitylpropane-1,3-dione (dMes), respectively. Near-unity photoluminescence quantum yield (PLQY:  $96 \pm 3\%$ ) was achieved for tBuCN-FIrmMes in doped films with short phosphorescence lifetime and high horizontal dipole ratio ( $\Theta$ : 76%) than the di-mesityl complex, tBuCN-FIrdMes (PLQY: 75  $\pm$  3%,  $\Theta$ : 71%). Here, introduction of mMes reduces the singlet-triplet splitting energy ( $\Delta E_{ST}$ ), permanent dipole moment ( $\mu$ ), and the symmetry of tBuCN-FIrmMes as compared with tBuCN-FIrdMes, these parameters can highly affect the PLQY and  $\Theta$  values. As a result, the blue phosphorescent organic light-emitting diode (PhOLED) of tBuCN-FIrmMes exhibits high external quantum efficiency (EQE) of  $\geq$  20% throughout a wide luminance range 1000–10000 cd/m<sup>2</sup> with a very low efficiency roll-off, which is crucial for solid-state lighting applications.

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#### 1. Introduction

The performance of blue phosphorescent organic light-emitting diodes (PhOLEDs) is still a bottleneck though high efficiencies and long operating lifetimes have been realized in green and red emitting PhOLEDs [1–4]. In most of the applications, OLEDs are usually needed to operate at a luminance higher than 1000 cd/m<sup>2</sup>, especially 5000–10000 cd/m<sup>2</sup> for solid-state lighting [5,6]. Efficiency roll-off is a usual problem in PhOLEDs at such a high luminance level, particularly for blue PhOLEDs. The external quantum efficiency (EQE) value drops substantially when the luminance crosses 1000 cd/m<sup>2</sup>, although EQE more than 20% can be accomplished at a low luminance [7–11]. The use of a mixed-host system signifies a promising technique to realize a low efficiency roll-off and low driving voltages [12]. Besides, triplet exciton lifetime of

<sup>1</sup> G. Sarada and B. Sim made equal contribution for this article.

the phosphorescent emitter can play an important role in minimizing triplet-triplet annihilation (TTA), which is the main reason for efficiency roll-off in PhOLEDs [13–15]. Sometimes, the low thermal stability of the materials (host/emitter) used in device fabrication may also initiate the efficiency roll-off [4].

Bis[2-(4,6-difluorophenyl)pyridinato-  $C^2$ ,N](picolinato)iridium(III) (FIrpic) has been widely used as emitter for blue PhOLEDs, but it is limited to sky blue color with y-coordinate > 0.3 [16–18]. Therefore, development of blue PhOLEDs possessing high color purity with at least y-coordinate <0.2, along with high EQE and low roll-off in EQE at high luminance (>1000 cd/m<sup>2</sup>) remains a great challenge [19,20]. This requires the design of new blue emitting Ir(III) complexes with narrow spectral width and/or reduced longer wavelength shoulder peaks, high photoluminescence quantum yields (PLQYs) and short phosphorescence lifetimes ( $\tau$ ). Recently, several reports reveal that emitters possessing preferential horizontal emitting dipoles are beneficial to optical out-coupling or light extraction of OLEDs without further out-coupling techniques while extraction of the internally generated light in OLEDs has been a critical issue for achieving high EQEs [21–29]. In this regard,

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heteroleptic Ir(III) complexes are one of the most prominent phosphorescent emitters to have preferential horizontal dipole orientation. Interestingly, the emitting dipole orientation and the PLQY were largely affected by the substituents on the main ligands and the molecular structure of the ancillary ligand [30,31].

With the aim to develop ideal blue emitters for display and solid-state lighting applications, we designed and synthesized two heteroleptic Ir(III) complexes with a new class of ancillary ligands. 1-mesitylbutane-1,3-dione (mMes) or 1,3-dimesitylpropane-1,3dione (dMes), consisting of bulky mesityl ring(s). Here, alteration of the ancillary ligand with a mesityl and a methyl group (mMes) rather than two symmetrically placed mesityl groups (dMes) at the peripheries of the  $\beta$ -diketonate framework results; i) high PLQY, ii) short  $\tau$ , thus, high radiative decay rate constant (K<sub>r</sub>), iii) high color purity, and iv) high horizontal dipole ratio ( $\Theta$ ) for the mMes based complex (tBuCN-FIrmMes) relative to the dMes based analogue (tBuCN-FIrdMes). As a result, the blue PhOLED of tBuCN-FIrmMes exhibited one of the best performances up to a very high luminance range of 1000–10000 cd/m<sup>2</sup> with EQEs of 22.4% and 19.8% at 1000 cd/m<sup>2</sup> and 10000 cd/m<sup>2</sup>, respectively, representing a remarkably low roll-off, which is crucial for practical display/solidstate lighting applications [32,33].

### 2. Experimental section

#### 2.1. General information

Synthetic route of the Ir(III) complexes, tBuCN-FIrmMes and tBuCN-FIrdMes, is provided in Scheme 1. The cyclometalating ligand and its dimer were synthesized using the procedure we have

developed previously [30]. Ancillary ligand, mMes, was purchased from TCI Co., LTD. The other ancillary ligand, dMes, was synthesized as per the literature procedure [34]. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Varian Mercury Plus 300 MHz spectrometer in CDCl<sub>3</sub> using tetramethylsilane as an internal reference. The chemical shifts were reported in ppm relative to the singlet of CDCl<sub>3</sub> at 7.26 and 77 ppm for the <sup>1</sup>H and <sup>13</sup>C NMR, respectively. UV-visible and the emission spectra were recorded with a IASCO V-570 and Hitachi F-4500 fluorescence spectrophotometers at room temperature. Transient PL measurements were carried out using compact fluorescence lifetime spectrometer C11367 at room temperature. Thermal analyses were carried out on a Mettler Toledo TGA/SDTA 851eanalyzer under N<sub>2</sub> atmosphere at a heating rate of 10 °C min<sup>-1</sup>. Cyclic voltammetry (CV) studies were carried out with a CHI 600C potentiostat (CH Instruments) at a scan rate of 100 mV  $s^{-1}$  in anhydrous dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) solvent with 0.1 M TBAClO<sub>4</sub> as supporting electrolyte. A platinum wire was used as the counter electrode and an Ag/AgCl electrode was used as the reference electrode. The potentials were referenced to the ferrocene/ferrocenium redox couple (Fc/Fc<sup>+</sup>). Density functional theory (DFT) and time-dependent-DFT (TD-DFT) calculations were carried out using Gaussian09 program [35]. The geometrical features of the Ir(III) complexes in solid-state were characterized by single crystal X-ray analysis using Bruker SMART CCD area-detector diffractometer. The single crystals of tBuCN-FIrmMes and tBuCN-FIrdMes were grown in dimethylformamide (DMF) solvent by slow evaporation and the structures were solved using a PLATON (version release date 21/06/ 2015) and further refined by full-matrix least-squares calculations on F<sup>2</sup>. All hydrogen atoms were omitted to reduce complexity.



Scheme 1. Synthetic route of tBuCN-FIrmMes and tBuCN-FIrdMes.

2.2. Synthesis of bis{3-[4-(tert-butyl)pyridin-2-yl]-2,6difluorobenzonitrile}(4-mesitylbut-3-en-2-ketonate)iridium(III) [tBuCN-FIrmMes]

Dimer (0.8 g, 0.52 mmol), ancillary ligand-mMes (1.06 g, 5.2 mmol), and anhydrous K<sub>2</sub>CO<sub>3</sub> (0.72 g, 5.2 mmol) were taken in 1,4-dioxane (25 mL) and refluxed under N<sub>2</sub> atmosphere over 6 h period. After that, HCl (1 N. 15 mL) was added to the reaction mixture and extracted using CH<sub>2</sub>Cl<sub>2</sub>. Organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under vacuum to get the crude product, which was purified by column chromatography on silica gel (EtOAc:Hexane, 2:8 v/v as eluent) to obtain the blue lightemitting yellow solid tBuCN-FIrmMes (0.15 g, yield 30%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 8.49 (d, J = 6 Hz, 1H, Ar H), 8.40–8.33 (m, 2H, Ar H), 8.30–8.26 (s, 1H, Ar H), 7.39 (d, J = 4.5 Hz, 1H, Ar H), 7.30 (d, J = 7.5 Hz, 1H, Ar H), 6.70 (s, 2H, mes-Ar H), 6.03 (d, *J* = 8.1 Hz, 1H, Ar H), 5.76 (d, *J* = 8.7 Hz, 1H, Ar H), 5.37 (s, 1H, acacH), 2.18 (s, 3H, CH<sub>3</sub>), 1.90–1.75 (m, 9H, mes-CH<sub>3</sub>), 1.47 (d, J = 7.2 Hz, 18H, *tert*-butyl); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ (ppm) 186.80, 184.42, 164.32, 164.06, 163.12, 162.86, 161.30, 161.04, 159.72, 157.84, 147.94, 147.47, 138.45, 137.74, 133.02, 130.07, 128.30, 120.95, 120.69, 120.49, 116.59, 111.04, 103.581, 35.54, 30.60, 29.0, 18.64. Calcd for C<sub>45</sub>H<sub>41</sub>F<sub>4</sub>IrN<sub>4</sub>O<sub>2</sub>: C, 57.62; H, 4.41; N, 5.97. Found: C, 57.94; H, 4.56; N, 5.68.

## 2.3. Synthesis of bis{3-[4-(tert-butyl)pyridin-2-yl]-2,6difluorobenzonitrile}(1,3-dimesitylpropane-1,3-diketonate) iridium(III) [tBuCN-FIrdMes]

Same procedure was followed using the ancillary ligand-dMes and obtained the titled product as yellow solid tBuCN-FIrdMes (0.21 g, yield 39%). <sup>1</sup>H NMR (300 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 8.65 (d,

*J* = 6.3 Hz, 2H, Ar H), 8.35 (s, 2H, Ar H), 7.35 (d, *J* = 5.4 Hz, 2H, Ar H), 6.70 (s, 4H, mes-Ar H), 6.00 (d, *J* = 9 Hz, 2H, Ar H), 5.49 (s, 1H, acacH), 2.18−1.88 (m, 18H, mes-CH<sub>3</sub>), 1.50 (s, 18H, *tert*-butyl); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ (ppm) 185.56, 164.61, 163.123, 161.51, 161.04, 159.78, 157.93, 147.96, 138.43, 137.95, 132.90, 130.14, 128.43, 120.60, 120.14, 116.91, 111.06, 106.14, 85.23, 35.63, 30.62, 21.0, 18.75. Calcd for C<sub>53</sub>H<sub>49</sub>F<sub>4</sub>IrN<sub>4</sub>O<sub>2</sub>: C, 61.08; H, 4.74; N, 5.38. Found: C, 61.32; H, 4.58; N, 5.54. Finally, both the Ir(III) complexes were purified by train sublimation technique, after the column purifications, to obtain highly pure materials.

#### 3. Results and discussion

The new Ir(III) complexes were thoroughly characterized by <sup>1</sup>H, <sup>13</sup>C NMR spectroscopy (Figs. S1 and S2), and the single crystal XRD analysis (Table S1). Fig. 1 shows the chemical structures and crystal ORTEP diagrams of tBuCN-FIrmMes (CCDC 1419975) and tBuCN-FIrdMes (CCDC 1419976). tBuCN-FIrdMes consists of two-fold rotational symmetry e.g. passing through the Ir and C17 atoms (Fig. 1) and the asymmetric unit contains only half a molecule indicating its symmetry, whereas, the asymmetric unit of tBuCN-FIrmMes contains three molecules by representing no such symmetry (Fig. S3) [36]. From the thermogravimetric analysis shown in Fig. 2a, both the Ir(III) complexes exhibit excellent thermal stabilities possessing the high decomposition temperatures (T<sub>d</sub>, at 5% weight loss) of 411 °C for tBuCN-FIrmMes and 416 °C for tBuCN-FIrdMes, pertaining to the bulky nature of the mesityl group(s) (T<sub>d</sub> of the standard sky-blue emitter, FIrpic: 356 °C).

Fig. 2b represents the UV–visible absorption and the photoluminescence (PL) spectra measured in chloroform (CHCl<sub>3</sub>) solution  $(1 \times 10^{-5} \text{ M})$ , and the PL spectra measured for the neat films, spincoated using chlorobenzene solution (10 mg of Ir(III) complex in



Fig. 1. Chemical structures and the crystal ORTEP diagrams of tBuCN-FIrmMes and tBuCN-FIrdMes. [Hydrogen atoms are omitted for clarity].



**Fig. 2.** (a) TGA curves and (b) UV–visible absorption and PL spectra in CHCl<sub>3</sub> ( $1 \times 10^{-5}$  M), and PL spectra of the neat films of the Ir(III) complexes measured at room temperature. [Here, s = solution and f = film].

0.5 mL solvent), of tBuCN-FIrmMes and tBuCN-FIrdMes at room temperature. The structural variation of the ancillary ligands has not affected the peak positions of the absorption and the PL spectra of tBuCN-FIrmMes and tBuCN-FIrdMes due to the restricted  $\pi$ -

conjugation by the twisted orientation of the mesityl group(s) as shown by the dihedral angles C3-C4-C5-C6 (102.81°) and C17-C18-C-19-C20 (96.74°), respectively. However, the vibronic shoulder peak and the PL spectral width are notably reduced for tBuCN-FIrmMes relative to tBuCN-FIrdMes in both solution and neat film state, as tBuCN-FIrdMes exhibits multiple intermolecular  $\pi$  ...,  $\pi$ stacking (parallel-offset) interactions between the mesityl and the functionalized phenyl ring (C<sup>N</sup> ligand) [Fig. S4]. tBuCN-FIrmMes displayed intense blue light in CHCl<sub>3</sub> solution with the maximum PL intensity (PLmax) at 462 nm and an unresolved vibronic peak at 489 nm with a full width at half maximum (FWHM) of  $2 \times 10^5$  cm<sup>-1</sup>, whereas, tBuCN-FIrdMes emitted blue light with PLmax at 460 nm and a well resolved vibronic peak at 489 nm with a FWHM of  $1.85 \times 10^5$  cm<sup>-1</sup>. Interestingly, tBuCN-FIrmMes maintained high color purity even in the neat film showing completely suppressed shoulder peak with FWHM of  $1.69 \times 10^5$  cm<sup>-1</sup>, although tBuCN-FIrdMes exhibited high intensity shoulder peak with FWHM of  $1.33 \times 10^5 \text{ cm}^{-1}$ , (Fig. 2b).

The relative PLQYs of tBuCN-FIrmMes and tBuCN-FIrdMes measured in CH<sub>2</sub>Cl<sub>2</sub> solution (1  $\times$  10<sup>-5</sup> M) using FIrpic (=42% in CHCl<sub>3</sub>) [37] as standard are 89% and 71% (±5%), respectively (Table 1). The relative PLOYs were also measured for the thin films prepared by spin-coating a CHCl<sub>3</sub> solution of poly (methyl methacrylate) [PMMA] and the target Ir(III) complex (10% w/w relative to PMMA) using Coumarin-102 (=46% in PMMA film) [38,39] as standard. The results follow the trend of the absolute PLOYs of the deposited films, discussed below (see Tables 1 and 2). Moreover, the  $\tau$  of tBuCN-FIrmMes measured in both CH<sub>2</sub>Cl<sub>2</sub> solution and the doped PMMA film are lower than the corresponding  $\tau$  of tBuCN-FIrdMes, as shown by the decay profiles (Fig. S5), this gives high K<sub>r</sub> for tBuCN-FIrmMes (Table 1). The absolute PLQYs were measured for the films of 9-(4-(9H-pyrido [2,3-b]indol-9-yl) phenyl)-9H-3,9'-bicarbazole (pBCb2Cz):diphenylphosphine oxide-4-(triphenylsilyl)phenyl (TSPO1):10% Ir(III) complexes, the same host-guest combination was used for the emitting layer (EML) of the PhOLEDs, using an integrating sphere. The PLQYs of tBuCN-FIrmMes and tBuCN-FIrdMes were found to be 96  $\pm$  3% and  $75 \pm 3\%$ , respectively (Table 2). Here, the substitution of one mesityl ring with a methyl group in the ancillary ligand, mMes, resulted in 22% increment in PLQY of tBuCN-FIrmMes as compared with tBuCN-FIrdMes. Because both the Ir(III) complexes exhibit same lowest triplet (T<sub>1</sub>) energy of 2.72 eV, measured from PL analysis at 77 K (Fig. S6), that is lower than the mixed-host materials; the low PLQY of tBuCN-FIrdMes in the doped film is due to the complex itself. When both the mesityl rings are replaced with methyl groups

Table 1				
Thermal,	photophysical,	and	electronic	properties.

Complex	$T_d$ (°C)	PL <sub>max</sub> (nm) <sup>a</sup>	$T_1 (eV)^b$	Measured in CH <sub>2</sub> Cl <sub>2</sub>			Measured in PMMA films			HOMO, LUMO (eV) <sup>k</sup>
				PLQY (%) <sup>c,d</sup>	τ (μs) <sup>e</sup>	$K_{r,} K_{nr} (10^5 \text{ s}^{-1})^{f,g}$	PLQY (%) <sup>c,h</sup>	$\tau  (\mu s)^i$	$K_{r,} K_{nr} (10^5 \text{ s}^{-1})^{f,j}$	
tBuCN-FIrmMes tBuCN-FIrdMes	411 416	462, 488 460, 489	2.72 2.72	89 71	0.240 0.392	37.1, 4.58 18.1, 7.40	94 80	0.93 1.15	10.1, 0.645 6.96, 1.74	-5.86, -3.1 -5.88, -3.14

 $^a\,$  Measured in CHCl\_3 solution at room temperature (1  $\times$  10  $^{-5}$  M).

<sup>b</sup> Measured at 77 K in CHCl<sub>3</sub>.

<sup>c</sup> Relative PLQY.

<sup>d</sup> Measured in CH<sub>2</sub>Cl<sub>2</sub> solution (1  $\times$  10<sup>-5</sup> M) using Flrpic (=42% in CHCl<sub>3</sub>) as standard (error ±5%).

<sup>e</sup> Phosphorescence lifetimes measured in  $CH_2Cl_2$  solution (1  $\times$  10<sup>-3</sup> M) after N<sub>2</sub> purging.

 $^{\rm f}~K_r=PLQY/\tau$  ,  $K_{nr}=(1{-}PLQY)/\tau$  .

<sup>g</sup> Calculated from the solution PLQY and phosphorescence lifetimes.

<sup>h</sup> Measured for the thin films by spin-coating a CHCl<sub>3</sub> solution of PMMA and the target Ir(III) complex (10% w/w relative to PMMA) using Couamrin-102 (PMMA film = 46%) as standard (error ±5%).

<sup>i</sup> Phosphorescence lifetimes measured for the above films (PMMA).

<sup>j</sup> Calculated from the film PLQY and phosphorescence lifetimes.

<sup>k</sup> HOMO is calculated from the onset oxidation potentials from CV,  $LUMO = E_g$  (optical) + HOMO.

### Table 2

Photophysical prope	rties of the Ir(III) cor	nplexes in mixed-host films	(deposited)	). and the DFT & TD-DFT data.
			· · · · · · · · · · · · · · · · · · ·	

Complex	PLQY (%) <sup>a,b</sup>	τ (μs) <sup>b,c</sup>	$K_{r}$ , $K_{nr} (10^5 \text{ s}^{-1})^{d,e}$	Θ (%) <sup>b,f</sup>	μ (D) <sup>g</sup>	$S_1 (eV)^h$	$T_1 (eV)^i$	$\Delta E_{ST}  (eV)^j$	HOMO, LUMO (eV) <sup>k</sup>
tBuCN-FIrmMes	96 ± 3	1.1	8.73, 0.36	76	11.25	2.95	2.64	0.31	-5.79, -1.87
tBuCN-FIrdMes	75 ± 3	1.35	5.55, 1.85	71	13.17	2.83	2.45	0.38	-5.30, -2.19

<sup>a</sup> Absolute PLQY.

b Measured for the thin films of pBCb2Cz:TSPO1:10 wt% Ir(III) complexes.

с

d

Phosphorescence lifetimes.  $K_r = PLQY/\tau$ ,  $K_{nr} = (1-PLQY)/\tau$ . Calculated using the PLQY and lifetimes of the films [pBCb2Cz:TSPO1:10 wt% Ir(III) complexes]. e

f Horizontal dipole ratio.

<sup>a</sup> Permanent dipole ratio.
 <sup>b</sup> Lowest singlet excited state energy obtained from TD-DFT.
 <sup>i</sup> Lowest triplet excited state energy obtained from TD-DFT.

<sup>j</sup> Singlet-triplet splitting energy,  $\Delta E_{ST} = S_1 - T_1$ . <sup>k</sup> HOMO and LUMO energy calculated from DFT.



Fig. 3. (a) HOMO/LUMO distributions obtained by DFT and (b) Spin density distribution of T<sub>1</sub> state using TD-DFT (UB3LYP) for tBuCN-FIrmMes and tBuCN-FIrdMes.

in the ancillary ligand, acetylacetonate (acac) [30], the PLQY is reduced (90 ± 3%) relative to tBuCN-FIrmMes. The beneficial effects of mesityl group attached to phenylpyridine backbone on PLQY of the blue heteroleptic Ir(III) complexes and on performance of the PhOLEDs were demonstrated in literature reports [40,41]. The  $\tau$  measured by the transient PL for the same doped film (pBCb2Cz:TSPO1:10 wt% Ir(III) complex) containing tBuCN-FIrmMes (1.1  $\mu$ s) is shorter than tBuCN-FIrdMes (1.35  $\mu$ s) resulting in enhanced  $K_r$  for tBuCN-FIrmMes. For instance,  $K_r = 8.73 \times 10^5 \ s^{-1}$  and non-radiative decay rate constant ( $K_{nr}$ ) = 0.36  $\times 10^5 \ s^{-1}$  for tBuCN-FIrmMes, and  $K_r = 5.55 \times 10^5 \ s^{-1}$  and  $K_{nr} = 1.85 \times 10^5 \ s^{-1}$  for tBuCN-FIrdMes. Hence, it is worth highlighting that simple tailoring of the ancillary ligand structure significantly improved the emission properties (PLQY,  $K_{\rm p}$   $\tau$ , and FWHM) of tBuCN-FIrmMes relative to tBuCN-FIrdMes.

Fig. 3a shows the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) distributions of tBuCN-FIrmMes and tBuCN-FIrdMes, calculated from DFT using Gaussian09 program. Ground state geometry optimization for the two molecules was performed using B3LYP exchange-correlation functional, LANL2DZ basis set for Ir atom, and 6-31G(d) basis set for all other atoms. For tBuCN-FIrmMes, the HOMO is located mostly on Ir atom and functionalized phenyl moiety and slightly on pyridyl rings; whereas LUMO is mainly located on pyridyl rings and a phenyl group. In case of tBuCN-FIrdMes, the HOMO is located on Ir atom and phenylpyridine part; whereas LUMO is located on pyridyl and mesityl rings. The calculated HOMO, LUMO and the T<sub>1</sub> energies are given in Table 2. Spin density distributions of the Ir(III)

complexes in T<sub>1</sub> state were obtained from TD-DFT and the results (Fig. 3b) show that the T<sub>1</sub> states of tBuCN-FIrmMes and tBuCN-FIrdMes are entirely contributed by the ancillary ligand and the Ir atom. In addition, from the TD-DFT calculations, the lowest singlet (S<sub>1</sub>) and T<sub>1</sub> states are found to be dominated by the HOMO to LUMO transition for the two Ir(III) complexes. To understand the basis for the superior photophysical properties of tBuCN-FIrmMes as compared with tBuCN-FIrdMes, we calculated the permanent dipole moment ( $\mu$ ) and the singlet-triplet splitting energy ( $\Delta E_{ST}$ ) using DFT and the TD-DFT. The resultant  $\Delta E_{ST}$  and the  $\mu$  values are 0.31 eV and 11.253 D for tBuCN-FIrmMes and 0.38 eV and 13.166 D for tBuCN-FIrdMes, respectively. In general, a minimal  $\Delta E_{ST}$  is beneficial for increasing the ISC rates [42-45], resulting to an enhanced K<sub>r</sub> (theoretically, K<sub>r</sub> is inversely proportional to  $\Delta E_{ST}$ ) [45]. Here, the calculated  $\Delta E_{ST}$  of tBuCN-FIrmMes is less than tBuCN-FIrdMes and many other reported heteroleptic Ir(III) complexes [42,43]. Thus, the high K<sub>r</sub> and PLQY of tBuCN-FIrmMes were closely related to its small  $\Delta E_{ST}$ . Hence, it is rational to conclude that the structural variation between tBuCN-FIrmMes and tBuCN-FIrdMes (mesityl-methyl instead of mesityl-mesityl) is the reason for their distinct photophysical properties. The higher  $\mu$  value of tBuCN-FIrdMes as compared with tBuCN-FIrmMes is the evidence for its broadening of PL spectral width [21,22].

The emitting dipole orientations of the thin films of pBCb2Cz:TSPO1:10% Ir(III) complexes deposited by thermal evaporation on fused silica substrate are preferentially horizontal with  $\Theta$  of 76% for tBuCN-FIrmMes and the  $\Theta$  of 71% for tBuCN-FIrdMes (Fig. 4). This high  $\Theta$  value of tBuCN-FIrmMes enhances optical out-coupling or light extraction of the PhOLEDs. The low  $\Theta$  of tBuCN-FIrdMes is tentatively correlated with its high molecular symmetry due to the two symmetrically placed mesityl groups [31],



**Fig. 4.** (a) Comparison of the experimentally measured angle-dependent p-polarized PL profiles at maxima of each dopants of the thin films composed of pBCb2Cz:TSPO1:10% Ir(III) complex on a fused silica substrate (open symbols) and simulated profiles (solid lines) and (b) Chemical structures of pBCb2Cz and TSPO1.



Fig. 5. (a) Energy-level diagram and (b) J-V-L characteristics of the optimized PhO-LEDs. [ETL = TSPO1: 1 wt% Rb<sub>2</sub>CO<sub>3</sub>].



Fig. 6. (a) EQE-L characteristics and (b) CIE coordinates at 10 mA/cm<sup>2</sup> of the optimized PhOLEDs. [ETL = TSPO1: 1 wt%  $Rb_2CO_3$ ].

as explained before. The HOMO energy levels were deduced from the onset oxidation potentials, obtained by CV analysis (Fig. S7), and were found to be -5.86 and -5.88 eV for tBuCN-FIrmMes and tBuCN-FIrdMes, respectively. The LUMO levels were calculated using the HOMO values and the optical band gaps, obtained from the absorption edges, and were found to be -3.10 and -3.14 eV for tBuCN-FIrmMes and tBuCN-FIrdMes, respectively. The HOMO/ LUMO of the two Ir(III) complexes were not varied as like the peak positions in the absorption and the PL spectra.

To evaluate the performance of tBuCN-FIrmMes and tBuCN-FIrdMes as dopants, we fabricated blue PhOLEDs with the following simple configuration: ITO (70 nm)/ReO<sub>3</sub> (1 nm)/pBCb2Cz (40 nm)/pBCb2Cz:TSPO1:10 wt% Ir(III) complex (30 nm)/TSPO1 (or)

TSPO1:1 wt% Rb<sub>2</sub>CO<sub>3</sub> (35 nm)/LiF(1 nm)/Al (100 nm). Before fabrication of OLEDs, device structure was optimized using the optical simulation based on classical dipole model to maximize the out-coupling efficiency [28]. The theoretically achievable maximum EQEs of the PhOLEDs with the measured  $\Theta$  and PLQYs of the Ir(III) complexes are 25.6% with tBuCN-FIrmMes and 19.1% with tBuCN-FIrdMes. Experimentally, we approached the theoretical maximum EQEs using the 1:1 M ratio of the mixed-host and 10 wt% of the dopant in the EML due to a good charge balance. Therefore, a 1:1 M ratio of pBCb2Cz:TSPO1 as the mixed-host and the 10 wt% Ir(III) complex as dopant were used as the EML. The pBCb2Cz and TSPO1 (or) TSPO1:1 wt% Rb<sub>2</sub>CO<sub>3</sub> were used as the hole transporting layer (HTL) and the electron transporting layer (ETL), respectively. Fig. 5a shows the energy level diagram of the blue PhOLEDs.

Figs. 5b and 6a show the current density-voltage-luminance (J-V-L) and the EQE-L characteristics of the PhOLEDs containing TSPO1:1 wt% Rb<sub>2</sub>CO<sub>3</sub> as ETL. The data of the PhOLEDs without electrical doping (Rb<sub>2</sub>CO<sub>3</sub>) in ETL were given in Fig. S8 and Table S2. Upon doping Rb<sub>2</sub>CO<sub>3</sub> (1 wt%) in ETL, the performance of the PhO-LEDs is improved representing the betterment in charge balance. In particular, the doped-ETL devices showed the maximum EQEs of 22.4% and 17.8% for tBuCN-FIrmMes and tBuCN-FIrdMes, respectively, with the turn on voltage (Von) of 3.0 V. Interestingly, the overall performance of tBuCN-FIrmMes based devices is highly superior to the ones with tBuCN-FIrdMes. For example, the PhOLED (doped-ETL) with tBuCN-FIrmMes showed an excellent maximum luminance  $(L_{max})$  of 26000 cd/m<sup>2</sup> at 7.8 V, whereas the one with tBuCN-FIrdMes showed 16000 cd/m<sup>2</sup> at 8 V. Similarly, the PhOLED of tBuCN-FIrmMes displayed one of the best stability with EOEs of 22.4% at 1000 cd/m<sup>2</sup>, 19.8% at 10000 cd/m<sup>2</sup>, and 16.5% at 20000 cd/ m<sup>2</sup> compared with the PhOLED of tBuCN-FIrdMes, where the EQEs are 17.8% at 1000 cd/m<sup>2</sup> and 14.9% at 10000 cd/m<sup>2</sup>. This represents that the maximum EQE has retained up to 88% at 10000  $cd/m^2$  and 74% at 20000 cd/m<sup>2</sup> for tBuCN-FIrmMes based device, which is very rare, but essential for solid-state lighting. Especially, the remarkably high L<sub>max</sub> and the low roll-off in EQE up to the high brightness level (10000 cd/m<sup>2</sup>) for tBuCN-FIrmMes are far better than the other reported blue Ir(III) complex dopants [7–11]. As discussed above, the structural modification i.e replacement of a mesityl ring with a methyl group brings about high PLQY and  $\Theta$  for tBuCN-FIrmMes, this is the main reason for its superior device performance than tBuCN-FIrdMes. The low roll-off in EQE is mainly attributed to the short  $\tau$  (1.1 µs) of tBuCN-FIrmMes as compared with tBuCN-FIrdMes (1.35 µs) and also credited to the mixed-host system [13–15].

The electroluminescence (EL) spectra do not change with increasing current density (Fig. S9), indicating that the exciton formation zone in the EML did not shift with the driving voltage. Although the maximum EL intensity ( $EL_{max}$ ) shows the same wavelength (464 nm) for the devices of both the Ir(III) complexes, the CIE coordinates (Fig. 6b) are slightly blue shifted for tBuCN-FIrmMes (0.140, 0.206) relative to tBuCN-FIrdMes (0.147, 0.215). The data of the PhOLEDs are listed in Table 3.

# Table 3 Data of the blue PhOLEDs (ETL = TSPO1: 1 wt% $Rb_2CO_3$ ) with the new Ir(III) complexes.

Dopant	$V_{on} (V)^{a}$	$L_{max}$ (cd/m <sup>2</sup> )	EQE (%) <sup>b</sup>	PE (lm/W) <sup>b</sup>	$EL_{max}/CIE (nm)/(x, y)^{c}$
tBuCN-FIrmMes	3.0	26000	22.4/22.4/19.8/16.5	31.9/24.9/15.3/11	464/(0.140, 0.206)
tBuCN-FIrdMes	3.0	16000	17.8/17.8/14.9/-	31.7/21.1/11.4/-	464/(0.147, 0.215)

<sup>a</sup> Turn on voltage (at 1  $cd/m^2$ ).

<sup>b</sup> In the order of maximum, then values at 1000, 10000, and 20000 cd/m<sup>2</sup>.

<sup>c</sup> Measured at 10 mA/cm<sup>2</sup>.

#### 4. Conclusion

In summary, two blue Ir(III) complexes, tBuCN-FIrmMes and tBuCN-FIrdMes, with the newly introduced ancillary ligands 1mesitylbutane-1,3-dione (mMes) and 1,3-dimesitylpropane-1,3dione (dMes), respectively, were synthesized. Here, we shown that the simple structural alteration of the ancillary ligand (mMes) viz. replacement of one of the mesityl rings by a methyl group brings high PLQY (96%) and short  $\tau$  (1.1 µs) for tBuCN-FIrmMes in doped films by minimization of  $\Delta E_{ST}$  and  $\mu$  as compared with tBuCN-FIrdMes (75%, 1.35  $\mu$ s). The high  $\Theta$  of tBuCN-FIrmMes is the further advantage for the light out-coupling of the PhOLEDs, accredited to the symmetry reduction of tBuCN-FIrmMes due to the structural alteration. Owing to these collective reasons, the blue PhOLED of tBuCN-FIrmMes showed the high  $L_{max}$  of 26000 cd/m<sup>2</sup>, and the EQEs of 22.4% (max.) at 1000 cd/m<sup>2</sup> and 19.8% at 10000 cd/  $m^2$ . To the best of our knowledge, the high  $L_{max}$  and the low EQE roll-off, up to a wide luminance range 1000–10000 cd  $m^{-2}, \mbox{ for }$ tBuCN-FIrmMes are among the best data for blue PhOLEDs that exhibit y-coordinate  $\leq$  0.21.

#### Acknowledgements

This work was supported by grant fund from the National Research Foundation (NRF) (2011–0028320, 2014R1A2A1A01002030) and the Pioneer Research Center Program through the NRF (2013M3C1A3065522) by the Ministry of Science, ICT & Future Planning (MSIP) of Korea.

### Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.orgel.2016.09.030.

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