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1. Introduction

Over the last decade, phosphorescent materials,^{1–5} in particular blue-emitting Ir(\mathfrak{m}) complexes,^{6–10} have garnered significant attention for the construction of highly efficient organic lightemitting diodes (OLEDs). Recently, control of the molecular orientation by the transition dipole moments in the emissive layer has been considered as a way to improve the external quantum efficiency of the OLED device.^{11–13} Heteroleptic Ir(\mathfrak{m}) complexes have a horizontal dipole alignment relative to the substrate, resulting in higher external quantum efficiencies (EQEs), whereas homoleptic Ir(\mathfrak{m}) complexes tend to have an isotropic orientation in films.^{12,14,15} The development of new heteroleptic blue phosphorescent Ir(\mathfrak{m}) complexes, which are important components for efficient device performance, is therefore desirable.

New blue phosphorescent heteroleptic Ir(III) complexes with imidazole- and *N*-methylimidazole carboxylates as ancillary ligands[†]

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Imidazole- and *N*-methylimidazole carboxylate have been introduced to serve as ancillary ligands in heteroleptic Ir(m) complexes containing 2-phenylpyridine-based main ligands, with consideration of the frontier orbital energy levels. Complexes Ir1-Ir4 were synthesized and found to have LUMO levels higher than that of the corresponding Ir(m) complex containing pyridyl carboxylate. All the synthesized Ir(m) complexes exhibited blue phosphorescence emission maxima in the region of 465–467 nm at room temperature. Phosphorescent quantum efficiencies were increased by a factor of 1.8-6.7 by blocking the intermolecular hydrogen bonding between the imidazole carboxylate ligands of neighboring Ir(m) complexes, which was achieved by *N*-methylation of the imidazole carboxylate ancillary ligand. The organic light-emitting diodes fabricated using Ir3 and Ir4 as dopant materials in the emissive layers were found to emit blue emission with peaks at 469 and 471 nm and maximum external quantum efficiencies of 20.0 and 22.4%, respectively. Moreover, all the fabricated devices with Ir3 and Ir4 exhibited low efficiency roll-off, indicating excellent stability of the materials.

Designing 2-phenylpyridine-based heteroleptic blue phosphorescent Ir(III) complexes by introducing electron-donating and electron-withdrawing substituents at appropriate positions on the ligands appeared to be a promising way to achieve a large HOMO-LUMO energy band gap.16-18 Earlier molecular orbital calculations¹⁹ of the HOMO and LUMO of the tris- $(2-\text{phenylpyridinato-N,C}^{2\prime})$ iridium(III) (Ir(ppy)₃) showed that a d-orbital of Ir(III) metal makes a large contribution (52.8%) to the HOMO. In the ligand, the phenyl ring makes a larger contribution (38.9%) than the pyridine ring (8.2%) to the HOMO of the complex. In contrast to the HOMO, contributions to the LUMO come exclusively from the π -ligand, 2-phenylpyridine, with an orbital from pyridine ring contributing the major portion, 73.5%, and the phenyl ring contributing only 25.9%. Earlier calculations of the HOMO and LUMO energies of some selected heteroaromatic rings by Tamao²⁰ indicate that imidazole has a higher LUMO level (5.35 eV) than pyridine (3.45 eV) (Fig. 1). Based on energy-level calculations and our observations,^{21,22} we have designed blue phosphorescent heteroleptic Ir(III) complexes, Ir1-Ir4, utilizing imidazole- and N-methylimidazole carboxylates with high LUMO levels as ancillary ligands, instead of picolinate ((dfpmpy)₂Ir(pic)) (Fig. 2). In addition, an electrondonating methyl group was substituted on the nitrogen atom of the imidazole moiety to investigate the effect on the emission wavelength and phosphorescence efficiency.



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Fig. 1 Calculated HOMO and LUMO energies of pyridine and imidazole heteroaromatic rings. $^{\rm 20}$



Fig. 2 Molecular structures of (dfpmpy)₂Ir(pic) and new phosphorescent Ir(III) complexes, Ir1–Ir4.

2. Experimental

Chemicals and instruments

Chemical reagents were purchased from Sigma Aldrich or TCI and used without further purification. 2-Imidazolecarboxylic acid was prepared by the following literature²³ and 4-imidazole-carboxylic acid, 1-methyl-1*H*-imidazole-2-carboxylic acid, and 1-methyl-1*H*-imidazole-4-carboxylic acid as ancillary ligands were purchased from Sigma Aldrich. Phenylpyridine derivatives as main ligands and μ -chloro bridged Ir(III) dimers were synthesized as previously reported.^{21,22,24}

Column chromatography was done with silica gel 60G (particle size 40 ~ 63 µm, Merck Co.). ¹H-, ¹³C-, and ¹⁹F-NMR spectra were recorded on CDCl₃, DMSO-d₆, and CD₃OD solutions and chemical shifts were reported in parts per million relative to CHCl₃ (7.26 ppm for ¹H-NMR and 77.0 ppm for ¹³C-NMR), DMSO (2.52 ppm for ¹H-NMR), and CH₃OH (4.78 and 3.31 ppm for ¹H-NMR and 49.3 ppm for ¹³C-NMR) as internal standards. The absorption and photoluminescence (PL) spectra were measured using a Jasco V-570 UV-vis spectrometer and a Hitachi F-4500 fluorescence spectrometer in dichloromethane at room temperature. Phosphorescence quantum yields (Φ_p) were estimated using a dichloromethane solution of FIrpic as a standard with known value of $\Phi_p = 0.42.^{25}$

Synthetic procedures

N-(2,2-Dimethoxyethyl)trichloroacetamidine (3)²³. Aminoacetaldehyde dimethyl acetal (2) (10.9 mL, 10.5 g, 100 mmol) was added to a solution of trichloroacetonitrile (1) (14.4 g, 100 mmol) in THF (25 mL) at -35 to -40 °C (Ar atmosphere). The cooling bath was removed when the temperature reached ambient and the reaction mixture was diluted with ethyl acetate. The organic layer was washed with water and dried

over anhydrous sodium sulfate. Removal of the solvent *in vacuo* gave **3** as an oil (90%). ¹H-NMR (CDCl₃, 300 MHz) δ (ppm) 3.42 (s, 6H), 3.47 (d, 2H, *J* = 5.4 Hz), 4.55 (t, 1H, *J* = 5.4 Hz, 5.4 Hz).

2-Imidazole carboxylic acid (4)²³. *N*-(2,2-Dimethoxyethyl)trichloroacetamidine (3) (2.00 g, 8.0 mmol) was added to TFA (2 mL) at 0 °C. The solution was stirred at room temperature for 24 h. After the solvent was removed *in vacuo*, benzene was added to the residue and the mixture was evaporated to dryness *in vacuo* to give impure 2-(trichloromethyl)imidazole. ¹H-NMR (CD₃OD, 300 MHz) δ (ppm) 7.81 (s).

Water (5 mL) was added to a TFA solution of crude 2-(trichloromethyl)imidazole and the solution was heated at reflux temperature for 1 h. After the solvent was removed *in vacuo*, benzene was added to the residue and the mixture was evaporated to dryness *in vacuo* (repeated twice). The solid residue was crystallized from 2-propanol/THF to give pure 4 (50% yield). m.p. 162–164 °C. ¹H-NMR (DMSO-d₆, 300 MHz) δ (ppm) 7.42 (s, 1H), 7.66 (s, 1H), 9.07 (COOH).

Synthesis of Ir(m) complexes, Ir1-Ir4

General procedure. A mixture of μ -chloro-bridged Ir(m) dimmer complex, [(2-(2',4'-difluorophenyl)-4-methylpyridine)₂Ir(μ -Cl)]₂ (0.15 g, 0.12 mmol), 2-imidazolecarboxylic acid (39 mg, 0.35 mmol) as an ancillary ligand, and sodium carbonate (0.19 g, 1.77 mmol) was heated at 135 °C in 2-ethoxyethanol (7 mL) for 24 h under nitrogen. After cooling to room temperature, the solution was evaporated *in vacuo*, and water was added to the residue. The mixture was extracted with dichloromethane, the organic layer was dried over sodium sulfate, and the filtrate was evaporated *in vacuo*. The crude product was subjected to column chromatography on silica gel and finally purified by recrystallization from dichloromethane/hexane to give **Ir1** as a yellow solid (yield 70%). The other new heteroleptic Ir(m) complexes, **Ir2–Ir4**, were also prepared from μ -chloro-bridged iridium dimmer complex and the corresponding ancillary ligands by the similar procedure.

[(2-(2',4'-Difluorophenyl)-4-methylpyridine)]₂Ir(imidazole-2carboxylate) (Ir1) (70%). ¹H-NMR (CDCl₃, 300 MHz): δ (ppm) 8.46 (d, 1H, J = 5.7 Hz), 8.07 (s, 1H), 8.03 (s, 1H), 7.47 (d, 1H, J = 5.7 Hz), 7.10 (s, 1H), 6.98 (d, 1H, J = 5.7 Hz), 6.83 (d, 1H, J = 5.7 Hz), 6.52 (s, 1H), 6.32–6.45 (m, 2H), 5.79 (dd, 1H, J = 8.7 Hz, 1.8 Hz), 5.66 (dd, 1H, J = 8.7 Hz, 1.8 Hz), 2.55 (s, 3H), 2.54 (s, 3H). ¹³C-NMR (100 MHz, CDCl₃): δ (ppm) 166.36 (OC=O), 164.54 (d, ${}^{1}J_{CF}$ = 153 Hz), 164.48 (d, ${}^{1}J_{CF}$ = 153 Hz), 164.16 (d, ${}^{2}J_{CF} = 33$ Hz), 164.04 (d, ${}^{2}J_{CF} = 33$ Hz), 162.00, 161.63 (d, ${}^{2}J_{CF} = 33$ Hz), 161.50 (d, ${}^{2}J_{CF} = 33$ Hz), 159.66, 159.36, 154.26 (d, ${}^{3}J_{CF}$ = 6 Hz), 149.00 (d, ${}^{1}J_{CF}$ = 164 Hz), 148.82 (d, ${}^{1}J_{CF} = 164$ Hz), 147.34 (d, ${}^{3}J_{CF} = 6$ Hz), 143.15, 128.40, 126.07, 123.91, 123.72, 123.37, 123.19, 121.45, 114.68 (d, ${}^{3}J_{CF}$ = 4 Hz), 114.52 (d, ${}^{3}J_{CF}$ = 4 Hz), 97.85 (dd, ${}^{2}J_{CF}$ = 27 Hz, 27 Hz), 97.23 (dd, ${}^{2}J_{CF}$ = 27 Hz, 27 Hz), 21.53, 21.50. 19 F-NMR (564 MHz, $CDCl_3$): δ (ppm) -108.76 (dd, J = 17 Hz, 11 Hz, 1F), -109.03 (dd, J = 17 Hz, 11 Hz, 1F), -110.88 (m, 2F). HRMS (FAB) $[M + H]^+$, calcd for C₂₈H₂₀F₄IrN₄O₂ 713.1152, found 713.1147.

[(2-(2',4'-Difluorophenyl)-4-methylpyridine)]₂Ir(Imidazole-5carboxylate) (Ir2) (88%). ¹H-NMR (CD₃OD, 300 MHz): δ (ppm) 8.46 (d, 1H, J = 5.7 Hz), 8.15 (s, 1H), 8.11 (s, 1H), 7.68 (d, 1H, J = 5.7 Hz), 7.66 (s, 1H), 7.35 (s, 1H), 7.20 (d, 1H, J = 5.7 Hz), 7.09 (d, 1H, J = 5.7 Hz), 6.53–6.40 (m, 2H), 5.73 (dd, 2H, J = 8.7 Hz, 1.8 Hz), 5.61 (dd, 2H, J = 8.7 Hz, 1.8 Hz), 2.59 (s, 3H), 2.58 (s, 3H). 13 C-NMR (100 MHz, CD₃OD): δ (ppm) 174.03 (OC=O), 165.92 (d, $^{1}J_{\rm CF}$ = 112 Hz), 163.58, 156.81, 152.54 (d, $^{2}J_{\rm CF}$ = 15 Hz), 149.91, 149.12, 136.82 (d, $^{1}J_{\rm CF}$ = 112 Hz), 125.23, 125.03, 124.84, 124.69, 123.17, 115.68 (dd, $^{2}J_{\rm CF}$ = 17 Hz, 17 Hz), 98.29 (dd, $^{2}J_{\rm CF}$ = 28 Hz, 28 Hz), 21.71. 19 F-NMR (564 MHz, CD₃OD): δ (ppm) –110.65 (dd, J = 17 Hz, 11 Hz, 1F), –111.04 (dd, J = 17 Hz, 11 Hz, 1F), –112.41 (dd, J = 11 Hz, 11 Hz, 1F), –112.51 (dd, J = 11 Hz, 11 Hz, 152, found 713.1075.

 $[(2-(2',4'-Diffuorophenyl)-4-methylpyridine)]_2$ Ir(N-methylimidazole-2-carboxylate) (Ir3) (60%). ¹H-NMR (CDCl₃, 300 MHz): δ (ppm) 8.54 (d, J = 5.7 Hz, 1H), 8.07 (s, 1H), 8.01 (s, 1H), 7.49 (d, 1H, J = 5.7 Hz), 7.01 (d, 1H, J = 5.7 Hz), 6.87 (s, 1H), 6.83 (d, 1H, J = 5.7 Hz), 6.44 (s, 1H), 6.42–6.30 (m, 2H), 5.80 (dd, 1H, J = 9.0 Hz, 1.8 Hz), 5.62 (dd, 2H, J = 9.0 Hz, 1.8 Hz), 4.09 (s, 3H), 2.54 (s, 3H), 2.53 (s, 3H). ¹³C-NMR (100 MHz, CDCl₃): δ (ppm) 164.89 (OC=O), 164.52 (d, ${}^{1}J_{CF}$ = 165 Hz), 164.45 (d, ${}^{1}J_{CF}$ = 165 Hz), 164.15 (d, ${}^{2}J_{CF}$ = 30 Hz), 164.03 (d, ${}^{2}J_{CF}$ = 30 Hz), 162.21, 161.62 (d, ${}^{2}J_{CF}$ = 30 Hz), 161.49 (d, ${}^{2}J_{CF}$ = 30 Hz), 159.64, 159.41, 154.47 (d, ${}^{3}J_{CF}$ = 7 Hz), 148.94 (d, ${}^{1}J_{CF}$ = 149 Hz), 148.68 (d, ${}^{3}J_{CF}$ = 7 Hz), 148.64 (d, ${}^{1}J_{CF}$ = 149 Hz), 141.84, 128.56, 128.13, 125.45, 124.81, 123.84, 123.32, 123.04, 114.64 (dd, ${}^{3}J_{CF}$ = 3 Hz, 3 Hz), 114.44 (dd, ${}^{3}J_{CF}$ = 3 Hz, 3 Hz), 97.70 (dd, ${}^{2}J_{CF}$ = 27 Hz, 27 Hz), 97.01 (dd, ${}^{2}J_{CF}$ = 27 Hz, 27 Hz), 34.35, 21.48, 21.45. ¹⁹F-NMR (564 MHz, CDCl₃): δ (ppm) -108.95 (dd, J = 17 Hz, 11 Hz, 1F), -109.19 (dd, J = 17 Hz, 11 Hz, 1F), -110.91 (dd, *J* = 11 Hz, 11 Hz, 1F), -110.98 (dd, *J* = 11 Hz, 11 Hz, 1F). HRMS (FAB) M⁺, calcd for C₂₉H2₁F₄IrN₄O₂ 726.1230, found 726.1233.

[(2-(2',4'-Difluorophenyl)-4-methylpyridine)]₂Ir(*N*-methylimidazole-5-carboxylate) (Ir4) (92%). ¹H-NMR (CDCl₃, 300 MHz): δ (ppm) 8.60 (d, 1H, J = 5.7 Hz), 8.07 (s, 1H), 8.02 (s, 1H), 7.55 (d, 1H, J = 5.7 Hz), 7.50 (s, 1H), 7.01 (d, 1H, J = 5.7 Hz), 6.95 (s, 1H), 6.82 (d, 1H, J = 5.7 Hz), 6.42–6.30 (m, 2H), 5.81 (dd, 1H, J = 9.0 Hz, 1.8 Hz), 5.60 (dd, 1H, J = 9.0 Hz, 1.8 Hz), 3.68 (s, 3H), 2.55 (s, 3H), 2.54 (s, 3H). ¹³C-NMR (75 MHz, CDCl₃): δ (ppm) 170.22 (OC=O), 164.60 (d, ² $J_{CF} = 29$ Hz), 164.46 (d, ¹ $J_{CF} = 116$ Hz), 164.42 (d, ² $J_{CF} = 22$ Hz), 164.36 (d, ¹ $J_{CF} = 116$ Hz), 161.29 (d, ² $J_{CF} = 29$ Hz), 161.20 (d, ² $J_{CF} = 22$ Hz), 159.08, 154.22

(d, ${}^{3}J_{\rm CF}$ = 7.5 Hz), 149.01 (d, ${}^{1}J_{\rm CF}$ = 116 Hz), 149.00 (d, ${}^{3}J_{\rm CF}$ = 7.5 Hz), 148.64 (d, ${}^{1}J_{\rm CF}$ = 116 Hz), 137.75, 135.16, 128.45, 124.32, 123.94, 123.69, 123.38, 123.11, 114.84, 114.62, 114.46, 114.22, 197.63 (dd, ${}^{2}J_{\rm CF}$ = 27 Hz, 27 Hz), 97.03 (dd, ${}^{2}J_{\rm CF}$ = 27 Hz, 27 Hz), 34.94, 21.51. 19 F-NMR (564 MHz, CDCl₃): δ (ppm) –108.92 (dd, J = 17 Hz, 11 Hz, 1F), -109.21 (dd, J = 17 Hz, 11 Hz, 1F), -110.93 (dd, J = 11 Hz, 11 Hz, 1F), -111.02 (dd, J = 11 Hz, 11 Hz, 1F), HRMS (FAB) M⁺, calcd for C₂₉H2₁F₄IrN₄O₂ 726.1230, found 726.1234.

OLED fabrication and measurements

Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT: PSS) and 4,4'-cyslohexylidenebis[N,N-bis-(4-methylphenyl)benzenamine] (TAPC) were used as the hole injection layer and hole transport layer, respectively. 1,3-Bis(N-carbazolyl)benzene (mCP) was used as an exciton blocking layer. 3',5-Di(9H-carbazol-9-yl)-[1,1'-biphenyl]-3-carbonitrile (mCBP-CN)²⁶ was a host material for blue OLEDs, and the dopants were doped at doping ratios of 3-15%. Diphenyl(4-(triphenylsilyl)phenyl)phosphineoxide (TSPO1) was used as an exciton blocking layer, and 1,3,5tris(1-phenyl-1H-benzo[d]imidazole-2-yl)benzene (TPBi) was used as the electron injection layer. LiF and Al were deposited as the electron injection layer and cathode, respectively. The encapsulation of the devices was carried out using an adhesive and a glass cover. The device characterization method was voltage sweep-based current density and luminance measurement using CS2000 spectroradiometer and Keithley 2400 measurement system.

3. Results and discussion

Synthesis and characterization of heteroleptic Ir(m) complexes, Ir1–Ir4

New Ir(m) complexes, **Ir1–Ir4**, were synthesized, containing 2-(2',4'-difluorophenyl)-4-methylpyridine (dfpmpy) as the main ligand and imidazole- or *N*-methylimidazole carboxylate as an ancillary ligand. The derivative in which 2-phenylpyridine serves as the main ligand was prepared by a previously described method.^{7,21} 2-Imidazolecarboxylic acid, one of the ancillary ligands, was prepared according to the literature²³ (Scheme 1), and the



Scheme 1 Synthesis of new blue phosphorescent Ir(III) complexes, Ir1-Ir4.



Fig. 3 Single-crystal packing structures of (a) Ir1 and (b) Ir3. (Pink: Ir, blue: N, green: F, dark gray: C, light grey: H.)

other ancillary ligands, 4-imidazolecarboxylic acid and 1-methyl-2(or -4)-imidazolecarboxylic acid were purchased from commercially available sources. The synthetic procedure used in preparing the new heteroleptic blue phosphorescent Ir(m) complexes involves two steps.²⁴ In the first step, $IrCl_3 \cdot 3H_2O$ is reacted with an excess of the desired C^N main ligand to give a μ -chloro-bridged dimer, **5**. The μ -chloro-bridged dimer can be readily converted to blue emissive, heteroleptic Ir(m) complexes by replacing the bridging chlorides with bidentate imidazole- or *N*-methylimidazole carboxylate as ancillary ligand. All the Ir(m) complexes were synthesized in the manner described above with high chemical yields of 60–92%.

Single crystals of **Ir1** and **Ir3** were obtained by slow diffusion of hexane into chloroform and dichloromethane solution of **Ir1** and **Ir3**, respectively, and characterized by X-ray crystallography. Crystallographic data are given in Tables S1 and S2 (ESI†) and Fig. 3. Both in **Ir1** and **Ir3**, the Ir(\mathfrak{m}) is octahedrally coordinated by three monoanionic bidentate ligands: two main ligands (the phenylpyridine derivatives) and one ancillary ligand (2-imidazolecarboxylate or *N*-methylimidazole-2-carboxylate). A heteroleptic Ir(\mathfrak{m}) complex of this type, with two bidentate main ligands and an ancillary ligand, has a chiral centre on the Ir atom, and because there was no chiral selectivity in the last synthetic step, the final heteroleptic Ir(\mathfrak{m}) complex necessarily exists as a racemic mixture.

The X-ray crystallographic analysis of Ir1 shows two enantiomers in the unit cell, each having the coordination geometry of the meridional configuration, with intermolecular hydrogen bonding between the imidazole carboxylate ancillary ligands of the two isomers (Fig. 3(a)). Ir3, which containing N-methylsubstituted imidazole carboxylate, shows the different crystal packing structure compared to that of Ir1 by the blocking of the intermolecular hydrogen bonding between two adjacent Ir(m) complexes which was achieved by N-methylation (Fig. 3(b)). There was no intermolecular hydrogen bonding between two adjacent Ir(m) complexes in Ir3 and it had a longer distance between the two adjacent ancillary ligands than that of Ir1. This fascinating intermolecular hydrogen bonding between adjacent Ir(III) complexes has an effect on the phosphorescence efficiencies of the synthesized Ir(III) complexes, compared with the corresponding Ir(m) complexes containing N-substituted imidazole carboxylate ancillary ligands. Further details are discussed in the next section.

Photophysical and electrochemical properties

Absorption and emission spectra of **Ir1–Ir4** in dichloromethane solution are shown in Fig. 4, and the photophysical data are listed in Table 1. **Ir1–Ir4** displayed weak absorption bands in



Fig. 4 (a) Absorption and (b) emission spectra of Ir1-Ir4 in dichloromethane solution.

Table 1 The photophysical and electrochemical properties of Ir1-Ir4

Comp. no.	Absorption ^a (nm)	Emission (nm)				EWIIM			F e	Electrochemical	
		$\lambda_{\rm em}{}^a$ (298 K)	$\lambda_{\mathrm{em}} \left(\mathrm{film}\right)^{b} (298 \mathrm{~K})$	$\lambda_{\rm em}^{\ \ c}$ (77 K)	T_1 (eV)	(nm)	${\Phi_{\mathrm{p}}}^d$	$\tau (\mu s) (eV)$	(eV)	HOMO (eV)	LUMO (eV)
Ir1	379, 454	465, 490	465, 490	_	_	55	0.03	_	2.77	-5.51	-2.74
Ir2	376, 454	467, 490	467, 490	—	_	56	0.10	_	2.77	-5.51	-2.74
Ir3	378, 452	467, 491	467, 492	459, 491	2.70	55	0.20	2.56	2.76	-5.45	-2.69
Ir4	372, 453	467, 490	468, 493	459, 491	2.70	56	0.18	2.58	2.76	-5.47	-2.71

^{*a*} Solution state absorption and emission spectra were measured in CH_2Cl_2 solutions $(1 \times 10^{-5} \text{ M})$. ^{*b*} Films were prepared by spin coating with PMMA (5% wt). ^{*c*} Measured in 2-methyltetrahydrofuran (MTHF) solution $(1 \times 10^{-5} \text{ M})$ at 77 K. ^{*d*} Measured using FIrpic in CH_2Cl_2 solution as a reference. ^{*e*} Optical band gap energy was calculated from the absorption edge.

the region of 452-454 nm, corresponding to triplet metal-toligand charge transfer (MLCT³*) transitions, and strong structured absorption bands in the region of 372-379 nm, corresponding to singlet metal-to-ligand charge transfer (MLCT¹*) transitions (Fig. 4(a)). All the synthesized Ir(m) complexes showed blue phosphorescence with emission maxima in the range 465-467 nm (Fig. 4(b)). Ir1 (λ_{em} = 465 nm) showed the same emission maximum in dichloromethane solution as that of $(dfpmpy)_2 Ir(pic)^{22,27}$ ($\lambda_{em} = 465$ nm) which has picolinate (pic) as the ancillary ligand. The positions of the nitrogen atoms in the imidazole ring had little effect on the phosphorescence emission maxima, with shifts of only 1-2 nm. Ir1 showed a 2 nm hypsochromic shift of its peak emission (465 nm) from that of Ir2 (467 nm) in dichloromethane solution (Fig. 4(b)). However, the phosphorescence emission wavelength of Ir(III) complexes containing N-methylated imidazole as ancillary ligand was not affected by the positions of the nitrogen atoms in the imidazole ring. Ir3 and Ir4 exhibited identical emission maxima at 467 nm in solution. Substitution of an electrondonating methyl group on a nitrogen atom of the imidazole ring (N-methylation) had virtually no effect on the phosphorescence emission wavelengths but there were dramatic changes in the phosphorescence quantum efficiencies (Table 1). Ir(III) complexes containing N-methylated imidazolecarboxylates (Ir3 and Ir4) had phosphorescence quantum efficiencies

1.8-6.7 times higher than those of Ir(m) complexes containing imidazolecarboxylates (Ir1 and Ir2). This result indicates that blocking the intermolecular hydrogen bonding by N-methylation of the imidazole ring induced an increase in the efficiency of the phosphorescence process. Additionally, the emission bands of all of the synthesized Ir(III) complexes had a narrow full width at half maximum (FWHM), 55-56 nm, which could contribute to the high purity of the blue light in the OLED device. Ir1-Ir4 exhibited almost identical solid state emissions of 5 wt% doped in PMMA films compared to those of solution state emissions, indicating there were no significant aggregations in film states (Fig. S1-S4, ESI⁺). Low-temperature photoluminescence spectra and phosphorescence decay for Ir3 and Ir4 were measured in 2-methyltetrahydrofuran (MTHF) (Fig. 5). For these two Ir(III) complexes, the highest-energy emission wavelengths at 77 K exhibited 8 nm hypsochromic shifts relative to those at room temperature. Their triplet energies were determined to be 2.70 eV for both Ir3 and Ir4 from the emission λ_{max} at 77 K (Fig. 5(a)). The phosphorescence lifetimes of Ir3 and Ir4 were found to be 2.56 µs and 2.58 µs, respectively (Fig. 5(b)).

The oxidation potentials of **Ir1–Ir4** were obtained by cyclic voltammetry (CV), whereas their reduction potentials were not detectable (Fig. S5, ESI† and Table 1). The HOMO energy level was determined from the onset point of the oxidation potential,



Fig. 5 (a) Low temperature PL spectra and (b) phosphorescence decay profiles of **Ir3** and **Ir4** in 1×10^{-5} M MTHF at 77 K (Phosphorescence lifetimes were monitored at 480 nm with excitation at 355 nm.)

and the peak was referenced to the Fc/Fc^+ couple in dichloromethane solution as -4.8 eV (0.60 V vs. Ag/AgCl). The LUMO energy level was estimated from the HOMO energy level and the optical band gap (E_{α}) . Ir1-Ir4 had HOMO and LUMO energies in the ranges -5.45 to -5.51 eV and -2.76 to -2.77 eV, respectively. As expected, the replacement of a pyridine ring by an imidazole ring on the ancillary ligand raised the LUMO energy level. Both Ir1 and Ir2, which contain an imidazole ring as ancillary ligand, had the same LUMO of -2.74 eV, which is higher than that of $(dfpmpy)_2 Ir(pic)$ (-2.77 eV). However, the maximum emission wavelengths of Ir1 and Ir2 were virtually unchanged compared to that of (dfpmpy)₂Ir(pic) because the HOMO energy was also increased by the replacement of pyridine by imidazole. Substitution of an electron donating methyl group on a nitrogen (N-methylation) of the imidazole ring raised both the LUMO (0.03-0.1 eV) and HOMO (0.04-0.09 eV) energy levels of the Ir(m) complexes; Ir3 and Ir4 had higher LUMO and HOMO energies than those of non-N-methylated Ir1 and Ir2, respectively.

The thermal stability of synthesized Ir(m) complexes is an important parameter for their purification by sublimation, and also for device stability. The thermal stabilities of **Ir3** and **Ir4** were measured by thermogravimetric analysis (TGA) (Fig. S6, ESI†). The TGA thermograms of **Ir3** and **Ir4** revealed that 5% weight loss occurs on heating at *ca.* 347 °C and 384 °C, respectively, indicating that they are resistant to thermal

decomposition above 300 °C and suitable for device applications. **Ir4** showed higher thermal stability than **Ir3**, which was expected that the **Ir4**-based device will be more stable than the **Ir3**-based device during the device operation.

PHOLED performances of Ir3 and Ir4

Among the four synthesized Ir(π) complexes, **Ir3** and **Ir4** were selected to evaluate their electroluminescence (EL) performance as blue phosphorescent dopant materials in OLEDs because of their higher phosphorescent quantum yields than those of **Ir1** and **Ir2**. The Ir(π) complexes were thermally evaporated as an emissive layer (EML) on indium tin oxide (ITO) in the following device configurations: ITO/PEDOT:PSS (60 nm)/TAPC (20 nm)/mCP (10 nm)/mCBP-CN: *x* wt% Ir dopant (3, 5, 10, or 15%) (25 nm)/TSPO1 (5 nm)/TPBi (20 nm)/ LiF(1.5 nm)/Al (200 nm) (Fig. 6). The reference device was fabricated using **FIrpic** as a blue dopant material to compare the device performances (Fig. S9 and S10, ESI[†]).

The PHOLED performances were evaluated at various dopant doping ratios from 3% to 15%, and showed the best results at 5% dopant concentration for both **Ir3** and **Ir4** (Table 2). The electroluminescence (EL) spectra of **Ir3** and **Ir4** at 5% dopant concentration show emission maxima at 469 and 471 nm, respectively, which are red-shifted about 2 nm compared to the solution photoluminescence (PL) (Fig. 7). The increase of dopant concentration from 3% to 15% resulted in 2 nm



Fig. 6 (a) Chemical structures and (b) energy diagram of the device structures.

Table 2	Blue PHOLED	performance	of Ir3 and	Ir4 based devices
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	$\lambda_{\rm max}$ /FWHM (nm)	$V_{\rm t}/V_{\rm d}{}^a$ (V)	$L_{\rm max} ({\rm cd} {\rm m}^{-2})$	$\operatorname{CIE}^{b}(x,y)$	EQE^{c} (%)	P.E. ^{<i>c</i>} ($lm W^{-1}$)	C.E. ^{c} (cd A ^{-1})
Ir3 (3%)	469/56	3.1/5.0	14624 @ 11.0 V	0.14, 0.31	19.6/18.3	32.3/22.3	38.1/35.7
Ir3 (5%)	469/56	3.1/5.0	17 951 @ 10.5 V	0.14, 0.31	20.0/19.1	32.9/23.4	39.2/37.5
Ir3 (10%)	470/57	3.1/5.0	19 190 @ 11.0 V	0.14, 0.33	18.7/17.5	30.9/22.1	37.7/35.3
Ir3 (15%)	471/56	3.1/5.0	19 273 (a) 11.0 V	0.14, 0.32	17.7/17.3	28.8/21.7	35.6/34.6
Ir4 (3%)	470/56	3.1/4.8	17 846 @ 10.5 V	0.14, 0.32	21.9/21.3	35.3/27.9	43.4/42.3
Ir4 (5%)	471/58	3.1/4.8	22 758 @ 10.5 V	0.14, 0.33	22.4/22.0	36.7/29.3	45.5/44.8
Ir4 (10%)	472/58	3.1/4.8	25 327 (a) 11.0 V	0.14, 0.34	20.8/20.6	32.8/27.8	43.0/42.5
Ir4 (15%)	473/58	3.1/4.9	24 617 (a) 11.0 V	0.15, 0.35	16.6/16.6	26.0/22.1	34.7/34.7
FIrpic (3%)	469/50	3.1/4.9	12 359 @ 11.0 V	0.14, 0.28	19.6/18.6	30.2/21.4	34.7/33.3
FIrpic (5%)	470/50	3.1/4.9	14 766 @ 10.5 V	0.14, 0.29	20.7/19.9	32.5/23.4	37.6/36.4

^a Turn-on voltage/driving voltage at 1000 cd m⁻². ^b Value measured at 1000 cd m⁻². ^c Value maximum/value measured at 1000 cd m⁻².







Fig. 8 *I-V-L* curves of (a) Ir3 and (b) Ir4 at different doping ratio.



Fig. 9 External quantum efficiency *versus* luminance (solid) and power efficiency *versus* luminance (open) curves of **Ir3**, **Ir4**, and **FIrpic** at 5% doping ratio.

red-shifted EL maxima for both **Ir3** and **Ir4** devices, as a result of molecular aggregation at high dopant concentration. The CIE color coordinates of the **Ir3** and **Ir4** devices at the optimized doping concentration for a brightness of 1000 cd m⁻² were (0.14, 0.31) and (0.14, 0.33), respectively. **FIrpic** showed slightly deeper blue emission of (0.14, 0.29) at 5% doping concentration compared to **Ir3** and **Ir4**. However, **Ir3** and **Ir4** still showed high color



purity compared with other phosphorescent Ir(III) dopants which have similar emission wavelengths.²⁸⁻³³ Fig. 8 shows the current-density-voltage-luminance (J-V-L) characteristics of the Ir3 and Ir4 devices at different doping ratios. All devices exhibited a low turn-on voltage of 3.1 V and a driving voltage of 4.8-5.0 V. The device doped with Ir4 showed a lower driving voltage of 4.8 V at 1000 cd m^{-2} than the Ir3 device (5.0 V), suggesting better charge balance and carrier hopping, with consequent higher device efficiency. Fig. 9 shows the external quantum efficiencies (EQEs) and power efficiencies (PEs) of the devices as a function of the luminance at 5% doping ratio. The maximum EQEs of the optimized devices doped with Ir3 and Ir4 were 20.0% and 22.4%, respectively. Furthermore, the EQEs of Ir3 and Ir4 devices remained at 19.1% and 22.0% at 1000 cd m⁻², indicating a small efficiency roll-off of both Ir3- and Ir4-based devices (Fig. 9 and 10). Ir4 exhibited higher device performances than FIrpic in the same device conditions, which indicated that Ir4 can be a good candidate for the blue phosphorescent emitter of OLEDs. While high EQEs were obtained in Ir3 and Ir4 devices, the EQEs were considered to be higher given the PLQY of the Ir3 (58.8%) and Ir4 (67.5%) emitters in the solid films. These high EQEs of Ir3 and Ir4 devices are assumed to be due to the anisotropic dipole orientation obtained by the heteroleptic molecular structure design, based on previously reported studies.^{11,13}



Fig. 10 Current efficiency versus luminance curves of (a) Ir3, (b) Ir4, and (c) FIrpic at different doping ratio.

4. Conclusions

We successfully developed novel blue phosphorescent heteroleptic Ir(III) complexes, Ir1-Ir4, with imidazole-2(or -5)-carboxylate or N-methylimidazole-2(or 5)-carboxylate as an ancillary ligand, which can be easily synthesized in good chemical yields. At room temperature, Ir1-Ir4 exhibited phosphorescence emission in the blue region at 465-467 nm. Using an imidazole- or N-methylimidazole ring in the ancillary ligand in place of a pyridine ring led to an increase in LUMO levels, but because of an accompanying increase in HOMO levels, there were no significant changes in the emission wavelengths. N-Methylation on the imidazole ring of the ancillary ligand resulted in a 1.8-6.7-fold improvement in phosphorescence quantum efficiency by blocking the intermolecular hydrogen bonding between the imidazole carboxylates of neighboring Ir(III) complexes. The OLED devices doped with Ir3 and Ir4 as blue dopants showed high EQE and low efficiency roll-off. Ir4 showed better device performances than Ir3, with a maximum EQE of 22.4%, maximum PE of 36.7 lm W^{-1} , and maximum CE of 45.5 cd A⁻¹. The different positions of the nitrogen atoms in the imidazole ring of the ancillary ligand had little effect on the optical bandgap but affected the device performances.

Conflicts of interest

There are no conflicts to declare.

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