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The novel synthesis of tris-cyclometalated iridium(III) complexes for saturated red organic light-emitting diodes with low efficiency roll-off

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ABSTRACT

A series of homoleptic tris-cyclometalated iridium(III) complexes (**Ir2–Ir4**) have been synthesized by the direct functionalization of a template complex (**Ir1**) through a Suzuki cross-coupling reaction. We revealed the coordination arrangement of **Ir4** by single X-ray structural analysis and the molecule showed a facial configuration. All the complexes showed red emission with emission maxima at 591–624 nm, short lifetimes of 1.38–2.19 µs and photoluminescence quantum yields in the range of 28–42%. Most importantly, the full width at half maximum (FWHM) of the emission maxima of these complexes was less than 48 nm. These complexes exhibited good thermal stability with T_d of 368–400 °C. Density functional theory (DFT) calculations were used to study the electronic structure information of these iridium(III) complexes. Organic light emitting diodes (OLEDs) based on these complexes as dopant emissive materials were fabricated. Among them the device based on **Ir1** has a maximum current efficiency and EQE roll-off that 97–99% efficiency and EQE_{max} maintained at 1000 cd m⁻². Meanwhile, the CIE_(x,y) coordinates of these extended complexes were (0.65, 0.33), (0.66, 0.33) and (0.68, 0.31), respectively. These data were very close to the standard red emission required by National Television System Committee (NTSC) (0.67, 0.33). These results suggest that these materials have potential application in OLEDs.

1. Introduction

Oganic light-emitting diodes (OLEDs) have attracted widespread attention for new-generation full-color display technology because of their wide spectrum, high brightness, wide viewing angle, selfluminescence, low driving voltage, fast response speed, use of flexible substrates, low power consumption and wide operating temperature range [1–3]. Luminous materials are one of the key factors that restrict the performance of devices. Performance of devices in that the internal quantum efficiency of the fluorescent material is theoretically only 25% at the maximum. Using such a light-emitting material will greatly affect the light-emitting performance of the OLED. However, electrophosphorescent materials have attracted great attentions due to better luminous efficiency and the internal quantum efficiency is theoretically up to 100% [4,5]. Among them, cyclometalated iridium(III) complexes are considered to be one of the best phosphorescent material candidates due to their high-efficiency luminescence performance and convenient color adjustment [6–9]. Amongst the cyclometalated iridium(III) complexes, the tris-cyclometalated iridium(III) complexes have attracted much attention due to their high phosphorescence efficiency, high thermal stability and microsecond phosphorescence lifetime. The reason for these excellent properties is that the tris-cyclometalated iridium(III) complexes containing more Ir–C bonds, resulting in a stronger spin-orbit coupling (SOC) effect than the bis-cyclometalated iridium(III) complexes. On the other hand, more Ir–C bonds can increase the rigidity of molecules and inhibit the vibration and rotation of groups or bonds, which reduces the non-radiative transition and improve the luminous efficiency of materials [10,11]. Three primary colors blue, green and red phosphorescent materials have been used in the practical application of OLED. Among these materials, the main problems of the red

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phosphorescent have low luminous efficiency and poor brightness due to a small energy gap and high aggregation tendency [12,13]. Therefore the design and synthesis the appropriate red materials with excellent properties is an essential requirement. The most commonly used method to obtain red light materials is to increase conjugation. However, the increase of conjugation will cause a strong π - π interaction, which will cause the quenching of luminescence and reduce the luminous efficiency. In order to maintain high quantum efficiency in red light complexes with large conjugated structure, one way is to introduce a large steric group into the ligand, for example, Fang et al. [14], reported a maximum luminance (L_max) of 2941 cd m^{-2} and a maximum EQE of 13.6% with tris(1-(N,N-diphenyl-amino)-4-(4--(EQE_{max}) chlorophenyl)-phthalazine) iridium(III) complex as dopant material. The alternative strategy is to increase the number of Ir-C bonds to prepare red tris-cyclometalated iridium(III) complexes, for example, Niu et al. [15], achieved 6138 cd m^{-2} and 10.8% with bicyclic iridium(III) complex based on 2-(benzo[b]thiophen-2-yl)-4- (trifluoromethyl)pyridine and tetraphenylimidodiphosphinate as dopant material.

However, it is more difficult to prepare tris-cyclometalated iridium (III) complexes than their bis-cyclometalated analogues. Three methods have been extensively used to synthesize the tris-cyclometalated iridium (III) complexes: to use Ir(acac)₃ [16], a CF₃COOAg catalyst [17] or high temperature method between bis-cyclometalated iridium (III) complexes and the corresponding ligand [18] to synthesize tris-cyclometalated iridium(III) complexes. These methods are not only expensive but also complicated to operate. Therefore, the design and synthesis of red tris-cyclometalated iridium(III) complexes are still challenging.

Phthalazine compounds have a distorted heterocyclic structure with two adjacent N-atoms in one aromatic heterocycles and had been widely used in red phosphorescent iridium(III) complexes with excellent luminescent properties. Compared with the commonly used iridium(III) complexes containing C^N=CH ligands, the phthalazine derivatives with $C^{\wedge}N\!\!=\!\!N$ structure have stronger coordination ability and could easily form tris-cyclometalated iridium(III) complexes under mild conditions because the adjacent sp² N atoms in the C^{N} N ligand has no steric hindrance H atom [19]. So the smaller steric hindrance is beneficial to the coordination between ligand and metal center [20–23]. We first synthesized the tris-cyclometalated iridium(III) complexes containing aryl ether substituents in high yield, but their luminescence is orange [24]. In order to obtain pure red light, new ligands were designed by adding conjugation. However, it is difficult to form tris-cyclometalated iridium(III) complexes, and the color is in the deep red light, which is not suitable for display or illumination [25].

In this article, we synthesized 1-(2,6-dimethylphenoxy)-4-(4-bromophenyl)phthalazine ligand. Then this ligand and iridium trichloride trihydrate were readily reacted to obtain the template triscyclometalated iridium(III) complex Ir1. Then, the bromine atom on Ir1 was replaced with phenyl, 2,4-difluorophenyl and triphenylamine groups by Suzuki cross-coupling reaction to realize the direct functionalization of the template complex and obtain the corresponding complexes Ir2, Ir3 and Ir4, respectively. This new synthetic method can be used for the preparation of some novel tris-cyclometalated iridium(III) complexes that cannot be directly synthesized by the union of cyclometalated ligands and iridium(III) salts due to the steric hindrance or activity of these ligands. The devices produced by using these complexes as the dopant exhibit efficient red emission and have good performance with low driving voltage (about 3.0 V), high brightness (maximum of about 15000 cd m^{-2}) and EQE (value of more than 10%). At the same time, the influence of substituents on luminescence performance was also explored.

2. Experimental

2.1. Materials and characterization

An Aglilent 6460 mass spectrometer was used to record NMR spectra. A Bruker AV400 spectrometer was employed to measure NMR spectra. X-ray crystallography diffraction was measured on a Bruker SMART Apex CCD diffractometer. Positive-ion ESI mass spectra were recorded with an AB Triple TOF 5600^{plus} mass spectrometer. Thermogravimetric analysis (TGA) was carried out on a Shimadzu DTG-60H thermogravimetric analyses under nitrogen flux at a heating rate of 10 °C min⁻¹. A Purkinje General TU-1901 spectrophotometer recorded UV/Vis absorption spectra, and a PerkinElmer LS-55 fluorescence spectrophotometer was used to measure photoluminescence (PL) spectra. An Edinburgh FL920 time-correlated pulsed single-photoncounting instrument was employed to determine quantum efficiency and luminescence lifetime. Cyclic voltammetry (CV) were investigated on a CHI1140B Electrochemical Analyzer in a three-electrode configuration with a glassy carbon disk as the working electrode, platinum wire as the counter electrode, and Ag/AgCl reference electrode with 0.1 M tetrabutylammonium hexafluorophosphate as the electrolyte.

2.2. Syntheses

Scheme 1 shows the synthetic routes to the ligand and complexes Ir1, Ir2, Ir3 and Ir4. Unless otherwise indicated, all reagents with commercial availability were used without purification and all the reactions were conducted under a nitrogen atmosphere. The target products were characterized by ¹H NMR and high-resolution mass spectrometry.

2.2.1. General syntheses of the ligands

1-Chloro-4-(4-bromophenyl)phthalazine (3.2 g, 10 mmol), 2,6-dimethylphenol (1.2 g, 10 mmol) and K₂CO₃ (1.5 g, 10 mmol) were refluxed in *N*,*N*-dimethylformamide (10 mL) and toluene (10 mL) under a nitrogen atmosphere at 130 °C for 5 h. After cooling, the mixture was poured into water and filtered to obtain a white solid. Then washed with water (20 mL \times 3) and dried at 80 °C for 12 h. After removing the organic solvent, the crude products were purified through a flash silica gel column using petroleum ether (PE): dichloromethane (DCM) (V: V = 5 : 1) as the eluent to obtain **1-(4-Bromophenyl)-4-(2,6-dimethyl-phenoxy)phthalazine (L1)**.

L1 86% yield. ¹H NMR: (400 MHz, CDCl₃) δ 8.58 (d, J = 7.9 Hz, 1H), 8.07–7.97 (m, 2H), -7.93 (t, J = 7.2 Hz, 1H), 7.68 (d, J = 8.2 Hz, 2H), 7.62 (d, J = 8.5 Hz, 2H), 7.16–7.09 (m, 3H), 2.20 (s, 6H). HRMS ((+)-ESI): m/z calcd for C₂₂H₁₇BrN₂O: 405.2950, found 405.0592 [M]⁺.

2.2.2. General syntheses of the iridium (III)complexes

The mixture of IrCl₃·3H₂O (0.2 g, 0.7 mmol) and L1 (1.1 g, 2.8 mmol) were refluxed in ethylene glycol monomethylether (15 mL) and distilled water (5 mL) under a nitrogen atmosphere at 80 °C for 24 h. After cooling to room temperature, the precipitate obtained by filtration was washed with ethanol (10 mL \times 3) and then dried. The complex Ir1 was obtained by column chromatography on neutral alumina with PE: DCM (V: V = 3 : 1) as the eluent.

Ir1 (0.09 g, 0.065 mmol), phenylboronic acid (0.04 g, 0.32 mmol)/ 2,4-difluorophenylboronicacid (0.05 g, 0.32 mmol)/triphenylamine phenylboronic acid (0.08 g, 0.32 mmol) and tetrakis(triphenylphosphine)palladium (9.7 g, 8.4 mmol) were added into degassed 3 M NaOH solution (5 mL) and toluene (10 mL) under a nitrogen atmosphere at 36 °C for 36 h. Afterwards, cooling to room temperature and extracted with DCM (20 mL × 3). Finally, silica column purification (PE: DCM = 3:1) gave the **Ir2**, **Ir3** and **Ir4** complexes, respectively.

Ir1: red solid, 36% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.83 (d, J = 8.5 Hz, 3H), 8.28 (d, J = 8.2 Hz, 3H), 7.92 (m, 9H), 7.02 (dd, J = 8.7, 2.3 Hz, 3H), 7.13 (s, 3H), 7.02 (d, J = 7.8 Hz, 2H), 6.86 (s, 3H), 6.38 (d, J = 8.0 Hz, 3H), 6.11 (d, J = 5.6 Hz, 3H), 5.93 (d, J = 7.5 Hz, 2H), 1.57 (s,



Scheme 1. The synthetic routes of the ligands and complexes.

18H). ¹³C NMR (100 MHz, CDCl₃) δ 166.89, 159.02, 157.15, 149.75, 142.56, 138.81, 132.07, 130.89, 129.42, 128.99, 125.64, 124.56, 123.83, 123.60, 122.55, 119.53, 31.63. IR (KBr, cm⁻¹): 3054, ν (Ar–H); 2957, ν (C–H); 1569, 1519, 1463, 1421, ν (C=C); 1378, (C–H); 1182, ν (C–O). HRMS ((+)-ESI): *m/z* calcd for C₆₆H₄₈Br₃IrN₆O₃: 1405.0780, found 1405.0995 [M⁺].

Ir2: red solid, 56% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.95 (d, J = 8.7 Hz, 3H), 8.25 (d, J = 7.9 Hz, 3H), 8.13 (d, J = 8.4 Hz, 3H), 7.94 (d, J = 7.8 Hz, 3H), 7.83 (t, J = 7.6 Hz, 3H), 7.53 (m, 3H), 7.36 (dd, J = 13.6, 8.1 Hz, 12H), 7.22–7.08 (m, 15H), 1.56 (s, 18H). ¹³C NMR (100 MHz, CDCl₃) δ 159.62, 156.86, 149.91, 143.23, 141.76, 139.95, 135.22, 131.59, 130.32, 129.81, 129.14, 128.19, 127.07, 126.36, 125.98, 123.43, 119.50, 118.10, 29.73. IR (KBr, cm⁻¹): 3039, ν (Ar–H); 2961, ν (C–H); 1577, 1538, 1446, 1433, ν (C=C); 1386, (C–H); 1198, ν (C–O). HRMS ((+)-ESI): *m*/z calcd for C₈₄H₆₃IrN₆O₃: 1396.6840, found 1397.4634 [M⁺].

Ir3: red solid, 61% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.93 (d, J = 8.7 Hz, 3H), 8.27 (d, J = 8.1 Hz, 3H), 8.09 (d, J = 8.4 Hz, 3H), 7.95 (t, J = 7.8 Hz, 3H), 7.85 (t, J = 7.7 Hz, 3H), 7.05 (dd, J = 7.8, 4.6 Hz, 6H), 6.96 (s, 3H), 7.11 (d, J = 8.4, 3H), 6.67 (t, J = 7.8 Hz, 3H), 6.37 (t, J = 6.4 Hz, 3H), 6.18 (t, J = 6.8 Hz, 3H), 6.00 (t, J = 7.4 Hz, 3H), 2.16 (s, 18H). ¹³C NMR (100 MHz, CDCl₃) δ 165.06, 159.59, 157.03, 149.88, 143.40, 136.82, 134.44, 131.70, 131.60, 131.54, 131.45, 130.48, 129.77, 129.11, 127.85, 127.17, 125.88, 123.78, 123.50, 120.17, 119.52, 111.00, 110.77, 103.82, 29.34. ¹⁹F NMR (376 MHz, CDCl₃) δ -112.61 (d, J = 6.8 Hz, 3F), -113.37 (d, J = 7.2 Hz, 3F). IR (KBr, cm⁻¹): 3051, ν (Ar–H); 2945, ν (C–H); 1581, 1503, 1472, 1436, ν (C=C); 1389, (C–H); 1175, ν (C–O). HRMS ((+)-ESI): m/z calcd for C₈₄H₅₇F₆IrN₆O₃: 1504.4026, found 1505.4157 [M ⁺].

Ir4: deep red solid, 41% yield. ¹H NMR (400 MHz, $CDCl_3$) δ 8.95 (d, J = 8.5 Hz, 3H), 8.26 (d, J = 8.1 Hz, 3H), 8.11 (d, J = 8.3 Hz, 3H), 7.94

(t, J = 7.7 Hz, 3H), 7.84 (t, J = 7.6 Hz, 3H), 7.39 (s, 3H), 7.18 (m, 21H),7.11 (d, J = 8.4, 3H), 6.96 (m, 27H), 6.00 (t, J = 7.4 Hz, 3H), 1.56 (s, 18H). ¹³C NMR (100 MHz, CDCl₃) δ 166.13, 159.47, 156.78, 149.92, 147.82, 146.32, 142.90, 139.12, 135.89, 134.54, 131.61, 130.31, 129.84, 129.19, 129.11, 128.33, 127.70, 127.11, 125.90, 124.07, 123.68, 123.44, 122.43, 119.48, 117.54, 31.63. IR (KBr, cm⁻¹): 3031, ν (Ar–H); 2961, ν (C–H); 1577, 1501, 1479, 1433, ν (C=C); 1378, (C–H); 1194, ν (C–O). HRMS ((+)-ESI): m/z calcd for C₁₂₀H₉₀IrN₉O₃: 1898.3170, found 1898.6764 [M⁺].

3. Results and discussion

3.1. Synthesis and characterization

Scheme 1 showed the chemical structures and synthetic routes of four iridium(III) complexes. Firstly, L1 1-(2,6-dimethylphenoxy)-4-(4-bromophenyl)phthalazine was synthesized by an document method [24]. The reaction conditions were mild and the yield of products was high. The bromine atom of the aromatic ring is very active and is easily replaced. This ligand was reacted with iridium(III) trichloride in ethylene glycol ether and deionized water solvent to obtain Ir1. Finally, the Suzuki cross-coupling reaction was used to synthesize the complexes Ir2, Ir3 and Ir4, and all the complexes had high yields. In this reaction, an excess of aromatic boronic acid must be added to ensure the complete reaction of the three bromine atoms in the template iridium(III) complexes. These compounds were characterized by ¹H NMR and MALDI-TOF-MASS spectrometer.

The molecular structure of **Ir4** was also proved via the single crystal and the crystal diagram was displayed in Fig. 1. The relevant bond lengths and bond angles were listed in Table S1. From the structure diagram of crystal it can be found that the molecule shows a facial



Fig. 1. ORTEP view of Ir4 (CCDC: 2018675) at the 30% probability level. Hydrogen atoms and solvent molecules are omitted for clarity.

configuration, which is more efficient than its meridional isomer [26]. Between the primary ligands and Ir atom, the Ir-C bond lengths are 2.01 (2) Å, and the Ir–N bond lengths are 2.08(2) Å, respectively, which are similar to the parameters of the tris-cyclometalated iridium(III) complexes that have been reported [10,11]. But more importantly, both the Ir-C average bond length and the Ir-N average bond length are smaller than that of tris-cyclometalated iridium(III) complex reported [19]. The results show that a stronger bond is formed between the metal and the ligand, which can lead to efficient mixing of the singlet and triplet excited states, and is beneficial for phosphorescence, and moreover, stronger bonding of Ir-N results in more thermally stable complexes. In complex Ir4, the dihedral angle between 2,6-dimethylphenol and the linked phthalazine ring is 68°, the dihedral angle between the phthalazine ring and cyclometalated phenyl group is 5.7°, the dihedral angle between triphenylamine and cyclometalated phenyl group is 33.1° and the dihedral angle inside the triphenylamine group is 38.0°. Meanwhile, the 2,6 dimethylphenol is almost perpendicular to the phthalazine ring.

The thermal stability of these iridium(III) complexes were determined by thermogravimetric analysis (TGA). All these complexes exhibit good thermal stabilities with decomposition temperatures (T_d) of 5% weight loss exceed 368 °C. This result further indicates that a stronger bond of Ir–C and Ir–N is formed between the metal and the ligand, which improves the thermal stability of the complexes. From the TGA curves of complexes of **Ir1**, **Ir2**, **Ir3** and **Ir4**, it can be seen that decomposition temperatures are 368, 390, 380 and 400 °C, respectively (Fig. 2 and **Table 1**). The relatively low T_d of **Ir3** may be due to intramolecular repulsion caused by fluorine groups. The excellent thermal stability of these complexes is conductive to sublimation and improvement of the service life of OLEDs based on them.

3.2. UV-vis absorption and PL properties

Fig. 3 showed the UV–vis absorption spectra of the iridium(III) complexes in DCM (10^{-5} M) solution at room temperature, and the key



Fig. 2. TGA curves of iridium(III) complexes.

dates are listed in Table 1. Structurally similar complexes have similar absorption peaks. The intense absorption bands under 360 nm are due to the spin-allowed ligand-centered (¹LC) π – π * transition, and the relatively week bands in the visible region 360–550 nm are attributed to the metal-to-ligand charge transfer (¹MLCT and ³MLCT), or the ligand-to-ligand charge transfer (LLCT) transition by strong spin-orbit coupling of the Ir(III) atoms [27]. Compared with the template complex Ir1, the absorption spectra of the functionalized iridium(III) complexes Ir2, Ir3 and Ir4 show a red shift. Among them, the conjugation degree of Ir2 increases due to the introduction of phenyl substituent to replace the bromine atom in the template complex, resulting in a red shift in the absorption band. The results show that the conjugation increases with

Physical properties for the Ir(III) complexes.

Complex	T_d^a (°C)	$\lambda_{abs,max}^{b}$ (nm)	$\lambda_{PL,max}^{b}$ (nm)	η ^c (%)	τ ^c (μs)	$E_{\rm HOMO}^{\rm d}$ (eV)	$E_{\rm LUMO}^{\rm e}$ (eV)	E_g^{opt} (eV)	$k_r^{\ f}$ (\times $10^{-6}\ s^{-1}$)	k_{nr}^{f} (\times $10^{-6}~s^{-1})$
Ir1	368	298,393,516	591	42	2.19	-5.64	-3.56	2.08	1.9	2.6
Ir2	390	332,417,540	619	29	1.38	-5.54	-3.55	1.99	2.1	5.2
Ir3	380	327,410,517	615	33	1.47	-5.58	-3.58	2.00	2.3	4.6
Ir4	400	301,373,528	624	28	1.40	-5.52	-3.54	1.98	2.0	5.2

^a Decomposition temperature of 5% weight loss.

^b Measured in DCM (10^{-5} M) at RT.

^c Quantum yield and lifetime are measured in DCM.

^d Calculated from empirical equation: $E_{HOMO} = -(E_{OX}+4.8)$ eV.

^e LUMO levels were calculated from HOMO and E_{σ}^{opt} . E_{σ}^{opt} was estimated from the absorption edge.

^f ($k_r + k_{nr}$) = $1/\tau(\mu s)$ where τ is the emission lifetime. The radiative decay rate constant k_r is calculated by $\eta(\%) = k_r/(k_r + k_{nr})$.



Fig. 3. UV–vis absorption and PL spectra of the iridium(III) complexes in DCM (10^{-5} M) solution at room temperature.

the introduction of phenyl substituent instead of bromine atom, and the absorption band gradually shifts to red. The absorption spectra of Ir4 is further red shifted by adding conjugation and introducing triphenylamine substituents. The UV absorption spectra of Ir2 and Ir3 are similar with a slight blue shift due to the introduction of fluorine atoms. The absorption edges of the complexes are at 630-700 nm Ir4 has the maximum absorption edge (700 nm) due to the largest ligand structure. In contrast, Ir1 has the smallest absorption edge (630 nm). The emission wavelength in DCM solution at room temperature of the complexes were red-shifted from 591 nm to 624 nm. The emission of the complexes peaks at 591 nm, 619 nm, 615 nm and 624 nm for Ir1, Ir2, Ir3 and Ir4, respectively. By introducing rigid conjugated groups, the emission peaks of Ir2, Ir3 and Ir4 are red-shifted, and the fluorine atom in Ir3 is an electron withdrawing group, which makes the emission peak slightly blue-shifted. The emission in PMMA films of 1 wt % at room temperature of the complexes peaks at 597 nm, 626 nm, 618 nm and 629 nm for Ir1, Ir2, Ir3 and Ir4, respectively (Fig. S1). Compared with the emission peaks in the DCM solution, the change is small and the change trend is consistent, indicating that these complexes have good stability and are relatively unaffected by the change in medium. The full width at half maximum (FWHM) of emission are 46 nm (Ir1), 48 nm (Ir2) and 47 nm (Ir3) and 48 nm (Ir4), respectively (Fig. S2). These values are very similar to Ir1, indicating that although different substituents are introduced, the intrinsic properties of these complexes are not changed, but the luminescent color is only slightly adjusted. These narrow FWHM values are essential to achieve high color purity OLEDs [28]. Moreover, the radiative decay rates (kr) values of Ir1-Ir4 in DCM solution are very high for complexes (Table 1). The triplet excitons excited by electrons can decay quickly through the radiation path, which is beneficial to the performance of the OLED and their kr values are in agreement with the above experimental results. As can be seen from Table 1, the complexes

showed different quantum efficiencies in DCM solution at room temperature as 42%, 29%, 33% and 28% for Ir1, Ir2, Ir3 and Ir4, respectively [29,30]. It is obvious that the luminescent efficiency of the three functionalized complexes Ir2, Ir3 and Ir4 is lower than that of the template complexe Ir1. This may be due to the fact that the distance between the aromatic rings introduced by coupling is far away from each other, and there is no strong interaction between the newly introduced substituents. They can rotate vibration freely, which effectively increases the non-radiative decay rates (k_{nr}) and reduces the luminous efficiency of the material. Furthermore, their corresponding lifetime values are measured in DCM solution (10^{-5} M) are 2.19 µs, 1.38 µs, 1.47 µs and 1.4 µs, showing that their emissions originate from triplet states [31,32]. These results proved that the all iridium(III) complexes are efficient candidates in OLEDs applications.

3.3. Electrochemical properties and theoretical calculations

It is well know that in the frontier molecular orbitals, the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels (E_{HOMO}/E_{LUMO}) are significant for the structure design and manufacture of the OLEDs. The HOMO and LUMO energy levels of all iridium(III) complexes were calculated by cyclic voltammetry (CV) using ferrocene as the internal standard and the band gap observed from UV-vis absorption spectra [33]. Obvious oxide peaks were observed in the four Ir(III) complexes during the anodization process, among which the oxidation potentials of Ir1, Ir2, Ir3 and Ir4 are 0.84 V, 0.74 V, 0.78 V and 0.72 V, respectively, which can be attributed to the metal-centered Ir(III)/Ir(IV) oxide couple, consistent with the cyclometalated Ir(III) systems reported [34]. The HOMO energy levels of the Ir1, Ir2, Ir3 and Ir4 are -5.64 eV, -5.54 eV, -5.58 eV and -5.52 eV, respectively. Compared with the template complex Ir1, different electron donor substituents (phenyl, 2,4-difluorophenyl and triphenylamine groups) are introduced into the benzene ring of the cyclometalated ligand effectively increases the HOMO energy level of the complex. This is mainly because the HOMO orbitals of the cyclometalated ligand are mainly determined by the aromatic ring units that form Ir-C bonds. While LUMO is mainly distributed on aromatic heterocyclic units that form Ir-N bonds. The substituents on the aromatic heterocycles of the Ir1, Ir2, Ir3 and Ir4 are the same, so these complexes have almost the identical E_{LUMO} values. At the same time, it can be seen from Table 1 and Fig. 4 that the energy gap (Eg) values of Ir1, Ir2, Ir3 and Ir4 are 2.08, 1.99, 2.00 and 1.98 eV, respectively. These data indicate that the introduction of electron donating group into benzene ring can effectively improve its HOMO level and obtain the cyclometalated ligands with narrower band gap. This strategy can effectively adjust the template complex Ir1 of orange red emission to saturated red emission.

To further understand the electronic structure information, the HOMO/LUMO distributions of the iridium(III) complexes were studied by density functional theory (DFT). Based on the optimization structures, the HOMO and LUMO distribution of these iridium(III) complexes were obtained. According to the calculated results, these complexes



Fig. 4. (a) The cyclic voltammograms, (b) theoretical (blue) and experimental (red) HOMO/LUMO energy levels of the iridium complexes.

show pseudo-octahedral coordination around Ir(III) center, and the selected geometric parameters as well as the Mulliken charges on Ir(III) atom are summarized in Fig. 5. Through theoretical calculations, we get the Eg values of these complexes Ir1, Ir2, Ir3 and Ir4 are 3.13, 3.00, 3.03 and 2.88 eV, respectively and these values are consistent with the experimental values. For these complexes, the electron distribution of the HOMO is mainly located on both the whole Ir-C ligands and the Ir (III) atom, whereas that of LUMO primarily resides on the Ir-N ligands. The electron cloud has the largest distribution range on the iridium atom, indicating that the phosphorescent complex has high efficiency MLCT, which is of great significance for high PL quantum efficiency [35, 36]. Secondly, after adding electron donating aryl substituents, the charge distribution on the Ir(III) atom is reduced. For example, after the introduction of triphenylamine group in Ir4, the number of benzene rings in the molecule is the largest, and its Ir(III) atom distribution is the lowest whether on HOMO or LUMO, and the PL quantum efficiency is also the lowest. At the same time, the slight differences between the calculated $E_{\rm LUMO}$ (-2.05 to -1.73 eV) fit well with the changing trend of experimental values (-3.58 to -3.54 eV). The little differences between the calculated $E_{\rm HOMO}$ (-5.09 to -4.63 eV) also match well with the changing trend of the experimental ones (-5.64 to -5.52 eV) due to the small changes in substituted group, which correlate well with the electrochemical results.

3.4. Electroluminescent properties

To evaluate the electroluminescence (EL) properties of the iridium (III) complexes, the devices G1, G2, G3 and G4 using **Ir1**, **Ir2**, **Ir3** and **Ir4** emitters as dopants, respectively, with a structure of ITO/PEDOT:PSS (25 nm)/TAPC (35 nm)/TCTA (35 nm)/PVK: OXD-7: iridium(III) complexes x wt% (40 nm)/TPBi (35 nm)/Ca (10 nm)/Ag (100 nm). The weight ratio of TAPC:TCTA:PVK:OXD-7 is 18:18:5:9. PEDOT:PSS and Ca served as hole and electron-injecting interface modified materials, respectively. The (1,3,5- tris(*N*-phenylbenzimidazol-2-yl)-benzene



Fig. 5. Contour plots of the HOMOs and the LUMOs as well as their energy gaps.

(TPBi) acted as an electron transport material as well as hole block layer due to its pretty electron mobility and low HOMO level (-6.20 eV). The di-[4-(N,N-ditolylamino)phenyl]cyclohexan (TAPC), 4,4',4"-tri(9-carbazolyl)triphenylamine (TCTA), poly(N-vinylcarbazole) (PVK) and 1,3bis(5-(4-(tert-butyl)phenyl)-1,3,4-oxadiazol-2-yl)benzene (OXD-7) were applied as mixed host material for its good hole-transporting ability [37–39]. The HOMO and LUMO are clearly compatible to the energy levels for the hosts TAPC (-5.5 eV to -2.0 eV), TCTA (-5.7 eV to -2.3 eV), TCTA (-5.7 eV), TCTA ($-5.7 \text{ e$ eV), PVK (-5.8 eV to -2.2 eV) and OXD-7 (-6.5 eV to -3.0 eV) so that the iridium(III) complex can trap both electrons and holes, and resulted in high device efficiency, the OLEDs can be satisfied [40]. As shown in Scheme 2, the E_{HOMO} (-5.47 to -5.09 eV) and E_{LUMO} (-3.48 to -3.11 eV) of four dopants were embedded between the E_{HOMO} (-5.80 eV) and E_{LUMO} (-3.00 eV) of the mixed host material, indicating that the carries can be injected to the host material or directly trapped by the Ir(III) emitters. Thence, a balanced distribution of carriers and a wide recombination zone is expected. The energy level diagram of the devices and chemical structures of the material mentioned above are depicted in Scheme 2. In order to understand the energy transfer of the iridium(III) complex in the host material, we doped the iridium(III) complex into the thin film (70% PVK + 30% PBD + iridium(III) complex x wt%, x = 2, 4, 8, 12, 16, 20, 24) and the photoluminescence spectrum of the iridium (III) complex film is shown in Fig. S3. Meanwhile, we can see the effective energy transfer from host guest material to host guest material when doping concentration is more than 8 wt%. In general, we use this result to determine the concentration range of the device (2.5–20 wt%). The device performance at different concentrations is shown in Figs. S4–S7. By observing the performance of each concentration device and facilitating comparison, we have selected the device when the doping concentration is 10%.

Fig. 6 displayed the EL spectra, luminance - voltage - current density (L - V - J), current efficiency - luminance ($\eta_c - L$) and the external quantum efficiency - luminance (EQE - L) curves of the devices and the corresponding key date are listed in Table 2. From Fig. 6 (a) it can be found that the peaks of EL emission are 596, 620, 620 and 632 nm for G1, G2, G3 and G4, respectively, which exhibit orange and red

emissions. In addition, there is no emission from the host material indicating the complete energy transfer from host to iridium(III) complexes. Furthermore, the EL spectra are almost similar to the PL spectra in DCM at room temperature, suggesting that the EL emissions are derived from the triplet excited states of the iridium(III) complexes. When the driving voltage was 7 V, the Commission International de L'Eclairage coordinates (CIE_{x,y}) were (0.65, 0.33), (0.66, 0.33) and (0.68, 0.31) of G2, G3 and G4, respectively (Fig. 7) and this is very close to the international standard red light color coordinates (0.67, 0.33).

Both devices displayed excellent performance. As we can see from Fig. 6 (b)–(d), the G1 device with Ir1 ($\eta_{PL} = 42\%$) as dopant exhibited a best performance. For the other three functionalized complexes Ir2, Ir3 and Ir4, the non-radiative decay rates (knr) of the complexes are increased due to the introduction of aryl substituents, and the efficiency is slightly reduced. However, they are all rigid tris-cyclometalated iridium(III) complexes, the devices prepared with them as phosphorescent guest have good performances. For G1, a L_{max} of 12851 cd m⁻², a maximum current efficiency ($\eta_{c,max}$) of 15.67 cd A⁻¹, a maximum power efficiency ($\eta_{p,max}$) of 11.1 lm w⁻¹ and a EQE_{max} of 10.06% are obtained. For G2, G3 and G4, their L_{max}, $\eta_{c,max}$, $\eta_{p,max}$ and EQE_{max} are (11443 cd m⁻², 6.97 cd A⁻¹, 3.93 lm w⁻¹ and 7.78%), (15044 cd m⁻², 6.39 cd A⁻¹, 3.09 lm w^{-1} and 7.25%) and (11955 cd m⁻², 5.36 cd A⁻¹, 4.16 lm w⁻¹ and 8.04%), respectively. It is worth noting that both devices exhibit very modest efficiency roll-off. At the luminance of 1000 cd m^{-2} , the EQE of G1, G2, G3 and G4 can be kept at 9.81%, 7.7%, 7.02% and 7.81% with a low efficiency roll-off ratio of 2.5%, 1%, 3.2% and 2.9% compared with their corresponding EQE_{max}. About 97–99% efficiency and EQE_{max} maitained at 1000 cd m^{-2} . At the luminance of 5000 cd $\rm m^{-2},$ the EQE of G1, G2, G3 and G4 can be kept at 6.91%, 6.11%, 6.1% and 6.03% with a low efficiency roll-off ratio of 31.3%, 21.5%, 15.9% and 25% compared with their corresponding $\ensuremath{\text{EQE}_{\text{max}}}\xspace$. The reasons for above phenomenon that the triphenylamine group is a non-coplanar sterically hindered group and the fluorine atom is equivalent to a relatively large sterically hindered group, which can reduce intermolecular aggregation and effectively reduce roll-off. At the same time, these characteristics become more outstanding for G1, G2, G3 and G4, the η_c



Scheme 2. The OLED device structure and the molecular structures used in this work.



Fig. 6. Characteristics of the devices G1, G2, G3 and G4. (a) The electroluminescence spectra at 7 V, (b) the luminance - voltage - current density (L - V - J) curves, (c) the current efficiency - luminance ($\eta_c - L$) curves and (d) the external quantum efficiency - luminance ($\eta_E - L$).

Table 2

The EL performances of the devices G1, G2, G3 and G4.

Device (concentration)	$\lambda_{EL,max}^{a}$ (nm)	V _{on} ^b (V)	L_{max}^{c} (cd m ⁻²)	$\eta_{c,max}^{d}(cd A^{-1})$ $(\eta_{c,L1000}^{f}(cdA^{-1}))$	EQE _{max} ^e (EQE _{L1000} ^g)	$\eta_{\rm p,max}^{\rm h}$ (lm W ⁻¹)	CIE ⁱ (x,y)
G1 (10%)	596	2.9	12851	15.67(15.29)	10.06%(9.81%)	11.1	(0.60, 0.37)
G2 (10%)	620	3.1	11443	6.97(6.89)	7.78%(7.7%)	3.93	(0.65, 0.33)
G3 (10%)	620	3.4	15044	6.39(6.19)	7.25%(7.02%)	3.09	(0.66, 0.33)
G4 (10%)	632	2.8	11955	5.36(5.21)	8.04%(7.81%)	4.16	(0.68, 0.31)

^a EL at 7 V

^b Turn-on voltage recorded at a luminance of 1 cd m^{-2}

^c Maximum luminance.

- ^e Maximum external quantum efficiency (EQE).
- ^f Current efficiency at 1000 cd m⁻²

g EQE at 1000 cd m⁻²

^h Maximum power efficiency.

ⁱ Commission International de L'Eclairage coordinates (CIE).

values at the practical brightness of 1000 cd m⁻² are 15.29, 6.89, 6.19 and 5.21 cd A⁻¹, respectively, which only decrease by 2.4, 1.1, 3.1 and 2.8% compared with their corresponding $\eta_{c,max}$. Not only that, when the doping concentration is increased from 10% to 20%, the EQE_{max} and L_{max} of **Ir1**, **Ir2**, **Ir3** and **Ir4**-based OLEDs are (9.31%, 9313 cd m⁻²), (7.45%, 9907 cd m⁻²), (6.68%, 15044 cd m⁻²) and (7.88%, 11955 cd m⁻²), respectively, where the roll-off ratio of EQE are 7.5%, 4.2%, 7.9% and 2%, respectively, which indicating that each device maintains good stability at high doping concentrations. These results indicate that the saturated red OLEDs made using these materials as dopants have lower efficiency roll-off.

4. Conclusion

Using 1-(2,6-dimethylphenoxy)-4-(4-bromophenyl)phthalazine as ligand, three saturated red homoleptic tris-cyclometalated iridium(III) complexes (**Ir2–Ir4**) have been synthesized by the direct

functionalization of template complex (Ir1) through Suzuki crosscoupling reaction. Organic light emitting devices (OLEDs) based on these complexes as dopant emissive materials were fabricated. The Ir1, Ir2, Ir3 and Ir4-based OLEDs exhibited L_{max} of 12851, 11443, 15044 and 11955 cd m^{-2} and EQE_{max} of 10.06, 7.78, 7.25 and 8.04%, respectively. Even at a practical brightness of 1000 cd m⁻², these EQE values are still maintained at 9.81, 7.7, 7.02 and 7.81%. The reason for these excellent properties is that the four complexes are triscyclometalated iridium(III) complexes containing three Ir-C bonds in each molecule. Compared with the bis-cyclometalated iridium(III) complexes, they have stronger spin coupling. On the other hand, more Ir-C bonds can increase the rigidity of molecules and inhibit the vibration and rotation of groups or bonds, which reduces the non-radiative transition and improve the luminous efficiency of materials. These results suggest that our research provides an efficient strategy to obtain high efficiency red phosphorescence tris-cyclometalated iridium(III) complexes for OLEDs with low efficiency roll-off.

^d Maximum current efficiency.



Fig. 7. CIE coordinates dependence on the luminance.

Author contribution statement

Qun-bo Mei have made substantial contributions to the conception or design of the work, the formulation of overarching research goals and the concrete implementation plan, including acquisition, analysis, or interpretation of data for the work. She have drafted the overall framework of the article and revised it critically for the whole content of the article. Lei Liu performed the experiment, contributed data collection and collation or drafted manuscript preparation. Jiu-chang Yang assisted in preparing basic raw materials and drawing the table of contents. Shang-hui Ye provided the help of OLED tests. Bi-hai Tong provided help in NMR and high resolution mass spectrometry. He helped to cultivate the single crystal and analyze the single crystal. He performed the data analyses with constructive discussions. He prodided the financial support for the project leading to this publication.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.dyepig.2021.109360.

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