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ARTICLE TYPE

Syntheses, photoluminescence and electroluminescence of four heteroleptic iridium complexes with 2-(5-phenyl-1,3,4-oxadiazol-2-yl)-phenol derivatives as ancillary ligands

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Four new iridium(III) cyclometallated complexes (**Ir1** - **Ir4**) with 4-trifluoromethylphenylpyridine as main ligands and 2-(5-phenyl-1,3,4-oxadiazol-2-yl)-phenol and its fluoro/trifluoromethyl substituted derivatives as ancillary ligands have been developed. All complexes are green phosphors ($\lambda_{max} = 519 - 537$ nm) with photoluminescence quantum efficiency yields of 10 - 53% in CH₂Cl₂ solutions at room temperature, respectively. The organic light emitting diodes (OLEDs) with the structure of ITO / TAPC (1,1-bis[4-(di-*p*-tolylamino)phenyl]cyclohexane, 60 nm) / Ir complexes (8 wt%) : SimCP2 (bis[3,5-di(9*H*-carbazol-9-yl)phenyl] diphenylsilane, 30 nm) / TPBi (1,3,5-tri(1-phenyl-1*H*-benzo[d]imidazol-2-yl)phenyl, 90 nm) / LiF (1 nm) / Al (100 nm) show good performances. Particularly, device G4 based on complex **Ir4** (2-(5-pentafluorophenyl-1,3,4-oxadiazol-2-yl)-phenol as ancillary ligand) 15 with 8 wt% doped concentration showed superior performances with a peak current efficiency (η_{cl}) of 70.48 cd A⁻¹ and a peak external quantum efficiency (η_{ext} , EQE) of 19.7%. The study demonstrates that the ancillary ligand attached with 1,3,4-oxadiazole group could facilitate charge trapping across the bulk of the device for efficient OLEDs.

Introduction

- ²⁰ Organic light-emitting diodes (OLEDs) have been studied intensely during the last decade due to their encouraging applications in high-resolution, full-color, flat-panel displays and lighting sources.¹ As the emitters, phosphorescent Ir(III) complexes play an important part in efficient OLEDs fabrication
 ²⁵ due to their high quantum efficiency and short lifetime of triplet excited states. These Ir(III) complexes have very strong spin-orbit coupling which introduces intersystem crossing to mix the singlet and triplet exited states and change the spin-forbidden radiative relaxation from the triplet excited state to be allowed. As a result,
 ³⁰ both singlet and triplet excitons can be harvested for light emission and the internal quantum efficiency of the Ir(III)
- complexes can achieve 100% theoretically. Therefore, the design and preparation of highly efficient light-emitting Ir(III) complexes have attracted the growing interest of the scientific ³⁵ community.²

Many researchers have focused on the important class of Ir(III) phosphorescent complexes consisting of two cyclometallated (C^N) ligands and a bidentate ancillary ligands (LX), i.e. Ir(C^N)₂(LX). And, many efforts have devoted to the 40 modification of C^N ligands and the use of suitable ancillary ligands to tune the photophysical and electrochemical properties of Ir(III) complexes.³ For example, $Ir(ppy)_2(acac)$ (ppy = 2-phenylpyridine, acac = acetylacetonate) is well known to give emission.4 green light By the introduction of 45 electron-withdrawing fluoro atoms to the 4,6-positions of phenyl ring in ppy and the use of pic (picolinate) as the ancillary ligand, FIrpic is used as an excellent dopant for the construction of blue phosphorescence OLEDs.⁵ The famous sky-blue iridium complex, FIr6 was prepared based on the 2-(2,4-difluorophenyl)pyridine ⁵⁰ and different ancillary ligand tetrakis(1-pyrazolyl)-borate.⁶ Our group has also reported high efficient phosphorescent OLEDs by introducing tetraphenylimidodiphosphinate (tpip) derivatives as an ancillary ligands into Ir(III) complexes.⁷ Tpip derivatives have

stronger polar P=O bonds, which may improve the electron mobility of the Ir(III) complexes and benefit its OLEDs performances.⁷ Therefore, Ir(III) complexes attached ancillary ligands with good electron mobility are possible to produce s efficient materials and devices.

1.3.4-Oxadiazole derivatives have received considerable attention in electro/opto-active materials due to their high electron affinity, high photoluminescence quantum yield and good thermal and chemical stability, which make them good ¹⁰ candidates for electron injection and transportation.⁸ In the last five years, Yang and Ma et. al.⁹, Tian et. al.¹⁰, Bryce et. al.¹¹ and our group¹² have reported efficient iridium complexes and devices using 1,3,4-oxadiazole derivatives as cyclometalated ligands to increase the complexes' electron transporting ability 15 and consequently facilitate charge trapping across the bulk for high performance OLEDs. However, few heteroleptic Ir(III) complexes using 1,3,4-oxadiazole derivatives as ancillary ligands have been reported.¹³ In addition, fluorination can enhance the electron mobility and result in a better balance of charge injection 20 and transfer, lower vibrational frequency of C-F bond can reduce the rate of radiationless deactivation and the bulky CF₃ substituents can affect the molecular packing and the steric protection around the metal can suppress the self-quenching behavior.¹⁴ On this basis, as shown in Scheme 1, we designed 25 and synthesized four new heteroleptic Ir(III) complexes containing the cyclometalated ligand of 4-trifluoromethylphenyl pyridine and the ancillary ligands of 2-(5-phenyl-1,3,4oxadiazol-2-vl)-phenol and its fluoro/trifluoromethyl substituted derivatives. Here, we describe the results of our investigation on 30 the synthesis, structural characterization, photophysical and redox properties, theoretical computations and OLEDs performance of these four Ir(III) complexes.

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Scheme 1 The synthetic route of ancillary ligands LX1 - LX4 and iridium 35 complexes Ir1 - Ir4.

Results and discussion

Synthesis

All ancillary ligands LX1 - LX4 were synthesized via a general procedure using substituted benzoyl chloride and 40 2-methoxybenzohydrazine as the starting materials via the intermediate of substituted N²-benzoyl-2-methoxybenzohydrazine. The substituted N'-benzoyl-2-methoxybenzohydrazine POCl₃ were reacted give the substituted and to 2-(2-methoxyphenyl)-5-phenyl-1,3,4-oxadiazole with high yield. 45 At -78 °C, the substituted 2-(2-methoxyphenyl)-5-phenyl-1,3,4oxadiazole in CH₂Cl₂ was added of BBr₃ to yield colorless crystals of ancillary ligands after recrystallization from ethanol. The 4-trifluoromethylphenylpyridine (tfmppy), cyclometalated Ir(III) chloro-bridged dimmer and iridium complexes Ir1 - Ir4 ⁵⁰ were prepared according to our previous published procedures.⁷

X-ray crystallography



55 Fig. 1 ORTEP diagrams of Ir1 (left) and Ir3 (right) with the atom-numbering schemes. Hydrogen atoms are omitted for clarity. Ellipsoids are drawn at 30% probability level.

Single crystals of complexes **Ir1** and **Ir3** were grown from sublimation and characterized by X-ray crystallography. The ⁶⁰ ORTEP diagrams of these two complexes are shown in Fig. 1; the corresponding crystallographic data are summarized in Table 1; selected bond lengths and angles are listed in Tables S1. The iridium center adopts a distorted octahedral coordination geometry with two C^N cyclometalated ligands and one N^OO ⁶⁵ ancillary ligand. It is clear that the ancillary ligand was connected to iridium center by a N atom from 1,3,4-oxadiazole group and an O atom from phenol moiety. The dihedral angle between planes [Ir1-C51-N5] and [Ir1-N6-O3] is 74.6° in complex **Ir1** and that is 85.2° between planes [Ir1-C1-N3] and [Ir1-N1-O1] in 70 **Ir3**, which suggest that the introduction of fluorine atoms in Published on 15 November 2013. Downloaded by Heinrich Heine University of Duesseldorf on 19/11/2013 14:50:27.

likely due to the steric hindrance effect. The Ir-N bond lengths between iridium center and ancillary ligand observed ranging from 2.097(9) to 2.130(6) Å which are slightly longer than that between iridium center and C^N cyclometalated ligands, ranging 5 from 2.042(10) to 2.055(10) Å.

Table 1 Crystallographic data for Ir1 and Ir3.

	Ir1	Ir3
Formula	C38H23F6IrN4O2	$C_{38}H_{19}F_{10}IrN_4O_2$
FW	873.82	945.79
T (K)	296(2)	296(2)
Wavelength (Å)	0.71073	0.71073
Cryst syst	Triclinic	Monoclinic
Space group	P -1	P 21/c
a (Å)	12.9055(5)	21.344(9)
<i>b</i> (Å)	15.0122(5)	15.541(7)
c (Å)	20.3242(7)	11.071(5)
a (deg)	92.2090(10)	90
β (deg)	108.3910(10)	76.233(6)
γ (deg)	110.0690(10)	90
$V(\text{\AA}^3)$	3461.7(2)	3567(3)
Ζ	4	4
$\rho_{calcd} (g/cm^3)$	1.677	1.761
μ (Mo K α) (mm ⁻¹)	3.929	3.836
F (000)	1704	1832
Range of transm factors (deg)	1.46-26.00	1.64-25.00
Reflns collected	21314	25350
Unique	13551	6272
GOF on F^2	0.889	1.197
$R_{I}^{a}, w R_{2}^{b}$ (I>2s(I))	0.0484, 0.1128	0.0666, 0.1676
R_1^a , wR_2^b (all data)	0.0686, 0.1179	0.0972, 0.2040
CCDC NO.	946704	945705

 $\mathbf{R}_{1}^{a} = \Sigma ||F_{o}| - |F_{c}|| / \Sigma F_{o}|. \mathbf{w} \mathbf{R}_{2}^{b} = [\Sigma w (F_{o}^{2} - F_{c}^{2})^{2} / \Sigma w (F_{o}^{2})]^{1/2}$

Photophysical properties

- ¹⁰ The UV-vis absorption spectra of the complexes Ir1 Ir4 in CH_2Cl_2 at 5×10^{-6} M are shown in Fig. 2(a), and the electronic absorption data are listed in Table 2. The absorption spectra of these complexes show intense bands with extinction coefficients on the order of 10^4 M⁻¹ cm⁻¹ below 350 nm, which are assigned to ¹⁵ the spin-allowed intraligand ($\pi \rightarrow \pi^*$) transition of cyclometalated
- ppy derivatives and ancillary ligands. The lower-energy absorption bands in the range 350-500 nm can be assigned to the mixing of ¹MLCT and ³MLCT (metal-to-ligand charge-transfer) states, or LLCT (ligand-to-ligand charge-transfer) transition ²⁰ through strong spin-orbit coupling of iridium atom.¹⁴

Photoluminescence measurements were conducted in deaerated CH₂Cl₂ solutions at room temperature (Fig. 2(b), Table

nm, the complexes Ir1 - Ir4 emit intense green phosphorescence 25 in CH₂Cl₂ at room temperature with peaks maxima in the range of 519 - 537 nm, which are belong to the mixed MLCT and CT transitions. Moreover, the quantum yields of the four complexes in solutions range from 10% to 53%, and Ir1 shows the strongest phosphorescence emission with quantum yield of 53%, indicating 30 the 2-(5-phenyl-1,3,4-oxadiazol-2-yl)-phenol derivatives as ancillary ligands can affect the luminescence properties of the Ir(III) complexes. Different to other three complexes, Ir1 exhibits two peaks maxima at 524 nm with a shoulder at 566 nm which indicate the different excited state. In our complexes the 35 introduction of F/CF₃ groups decreased the phosphorescence emission, while the two CF₃ groups in meta positions cause the serious effect. Furthermore, compared to the complex Ir1, a bathochromic shift of Ir2 and a small hypsochromic shift of Ir3 and Ir4 are observed in Fig. 2(b). The two CF₃ groups in meta 40 positions of the phenyl ring in the ancillary ligand are effective in tuning the emission towards the red region which is consistent with the inductive-only nature of the CF₃ group, which renders the *meta* positions the less electron deficient on the aromatic ring.¹⁵ Therefore, we conclude that the nature and positions of 45 substituents on the phenyl ring of ancillary ligand can affect the emitting properties of Ir(III) complexes.

2) and 77 K (Fig. S2(b), Table 2). Under the irradiation of 370



50 Fig. 2 UV-vis absorption (a) and relative emission (b) spectra of complexes Ir1 - Ir4 in degassed dichloromethane at room temperature.

Emission spectra at 77 K (Fig. S2(a)) are divided into two main emission peaks demonstrating that the emissive states of ⁵⁵ each complex have contributions from both MLCT and LLCT. The phosphorescence spectra of the Ir(III) complexes suffer the rigidochromic effect: the phosphorescence bands shift to blue on going from RT to 77 K. The rigidochromic effect on some kinds of transition metal complexes has been previously ⁶⁰ reported.¹⁶Because of the low viscosity of the medium at RT, solvent molecules in the vicinity of the excited-state molecule readily undergo reorientation by the dipole-dipole interaction within the lifetime of the excited state, resulting in the formation of the fully relaxed excited state. Thus, the emission at RT occurs from the fully relaxed excited state. On the other hand, the s excited state at 77 K emits before the solvent relaxation occurs, resulting in the rigidochromic effects on the emission spectra.

Table 2 Physical properties of compounds Ir1 - Ir4.

Complex	$T_{\rm m}/T_{\rm d}^{\rm a}$	Absorption [λ , nm	Emission (λ_{max} , nm)		${\Phi_{ m em}}^{ m d)}$	Lifetime
	(°C)	$(\varepsilon, 10^3 \mathrm{M}^{-1} \mathrm{cm}^{-1})]^{\mathrm{b})}$	298 K (L/S) ^{b)}	77 K ^{c)}	(%)	$ au_{(L)}(\mu s)^{b)}$
Ir1	290/385	261(44.8), 406(5.1)	524/566	521	53	2.31
Ir2	280/329	255(45.9), 420(8.7)	537/566	518	10	2.17
Ir3	300/334	255(62.6), 413(12.2)	520/556	516	43	2.03
Ir4	295/324	255(46.0), 410(8.5)	519/564	519	34	1.99

[a] $T_{\rm m}$: melting temperature, $T_{\rm d}$: decomposed temperature. [b] Absorption, emission spectra and lifetime of complexes were taken in degassed CH₂Cl₂ at 10 RT; L: liquid; S: solid. [c] Measured in degassed CH₂Cl₂ at 77 K. [d] Measured relative to Ir(ppy)₃ ($\Phi = 0.4$) in degassed CH₂Cl₂ solution. [e] HOMO/LUMO calculated based on the cyclovoltammety (CV) diagram using ferrocene as the internal standard and UV-vis spectra in dichloromethane. HOMO (eV) = -($E_{\rm ox}$ - $E_{1/2,Fe}$)-4.8, LUMO (eV) = HOMO + $E_{\rm bandgap}$.

Electrochemical properties and theoretical calculations

¹⁵ The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of the dopants are important for the design of the OLEDs. In order to determine the HOMO/LUMO values of the Ir1 – Ir4, the electrochemical properties were investigated by cyclic
²⁰ voltammetry in deaerated acetonitrile (Fig. 3, Fig. S3). The HOMO levels of the compounds were calculated from the oxidation potentials and the LUMO levels were calculated from the reduction potentials (Table 3).¹⁷



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Fig. 3 Cyclic voltammograms of complexes Ir1-Ir4 in the positive range.

The cyclic voltammograms of the complexes **Ir1 - Ir4** in the positive range show strong oxidation peaks, while the reduction peaks are not obvious, demonstrating that the redox process of ³⁰ the complexes **Ir1 - Ir4** is not reversible completely, which is

also observed in related Ir(III) complexes containing oxadiazole units.⁹⁻¹² In the negative potential scan rang (Fig. S3) all complexes exhibit quasi-reversible oxidation and reduction process due to the 1,3,4-oxadiazol substituents suggesting the 35 electron-transporting and electron trapping characteristics. From the Table 3 it is observed that the differences of the HOMO/LUMO values of the four complexes are neglectable. However, compared with Ir1, the oxidation peaks of Ir2 - Ir4 moved to the positive range. The results suggested that though 40 the introduction of the F/CF₃ groups has little effects on the the HOMO/LUMO levels, they make the Ir(III) complexes more electrochemical stable. Concerning the LUMOs, Ir2 - Ir4 present similar energy levels, while Ir1 shows a higher energy level about 0.11 - 0.15 eV above. This means that the introduction of electron-withdrawing 1,3,4-oxadiazole F/CF₃ 45 the and substitutions have more significant effects on LUMOs. The trend corresponds the DFT calculation results below very well.

In order to provide insight into the electronic structures of the iridium complexes, we present the results of population ⁵⁰ calculation performed on the optimized S0 geometries in CH₂Cl₂ solution together with the plots of the HOMO/LUMO in Fig. 4. The molecular orbital energy levels and detailed compositions are reported in Table 3.

In Fig. 4, it is clear that the electronic structures of HOMOs ⁵⁵ and five nearest occupied molecular orbitals below are similar in all the complexes for both energy levels and compositions. Specifically, the HOMOs of **Ir1 - Ir4** are calculated in the small

energy range of -5.23 eV to -5.31 eV, meanwhile, they are assigned to be composed mainly by a combination of iridium dorbital (around 20%) and the π orbital of the coordinated ancillary ligands (around 73%) and the bulky ppy ligands almost 5 make no contributions (only about 6.5%). The results are also consistent with the consequence of the oxidation peaks of Ir1 -Ir4. This demonstrates that the introduction of electron-withdrawing substituents on the phenyl moiety in ancillary ligands does not have significant effect on the occupied 10 frontier molecular orbitals, which are in accordance with the calculated HOMO energy levels. However, concerning the composition, the LUMO of Ir1 is quite different from those of Ir2 - Ir4. For Ir1, the LUMO is almost located on the π orbitals of the ppy main ligands (92.24%). But for Ir2 - Ir4, since the 15 introduction of the electron-withdrawing 1,3,4-oxadiazole and fluoro/trifluoromethyl substituents on the ancillary ligands, the π orbitals of the ancillary ligand are drastically stabilized (-2.12, -1.99 and -2.02 eV for **Ir2 - Ir4** respectively, compared with -1.79 eV for **Ir1**), thus, their energy levels are lower than that of ²⁰ ppy π orbitals, turning them into lowest unoccupied molecular orbitals for **Ir2 - Ir4** (ancillary ligands make a contribution of 97.31%, 96.30% and 96.46% to the LUMOs respectively). Furthermore, the bandgap between LUMO and LUMO+1 of **Ir1** is smaller than that of **Ir2 - Ir4**. The differences of the MOs are ²⁵ responsible for the differences of the phosphorescence emission of **Ir1** to others. In addition, the LUMOs for **Ir2 - Ir4** are mainly contributed from the π orbital of fluorobenzene of the 1,3,4-oxadiazole. It seems the electron-trapping ability for these three complexes is mainly up to the fluorobenzene despite of the ³⁰ subordinate contribution from 1,3,4-oxadiazole.



Fig. 4 Calculated frontier molecular orbital energy levels for Ir1 - Ir4 in CH₂Cl₂ at B3LYP/6-31G**; LANL2DZ theory level. Also shown are isodensity surface plots of HOMO and LUMO for Ir1 - Ir4.

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Table 3 The frontier orbita	l energy and electron	density distribution	for Ir1 - Ir4
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Complex	Orbital	Ener	gy/eV	$E_{\text{bandgap}}/\text{eV}$	Composition %		
		Measured	Calculated	(Calculated)	Ir	LX	рру
Ir1	HOMO	-5.38	-5.23	3.44	19.85	73.65	6.50
	LUMO	-2.61	-1.79		3.64	4.12	92.24
Ir2	HOMO	-5.40	-5.31	3.19	20.54	72.87	6.59
	LUMO	-2.72	-2.12		0.53	97.31	2.16
Ir3	HOMO	-5.38	-5.30	3.31	20.53	72.90	6.57
	LUMO	-2.75	-1.99		0.49	96.30	3.21
Ir4	HOMO	-5.39	-5.30	3.28	20.45	72.92	6.63
	LUMO	-2.76	-2.02		0.44	96.46	3.10

Characterization of OLEDs

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Fig. 5 Energy level diagrams of HOMO and LUMO levels (relative to vacuum level) and molecular structures for materials investigated.

To evaluate the electroluminescence (EL) performances, the OLEDs using Ir(III) complexes Ir1 – Ir4 as the emitters were fabricated with the structure of ITO / TAPC (1,1-bis(4-(di-ptolyl-amino)phenyl)cyclohexane, 60 nm) / Ir1 - Ir4 (8 wt%) : 10 SimCP2 (bis[3,5-di(9H-carbazol-9-yl)phenyl]di-phenyl silane, 30 nm) / TPBi (1,3,5-tri(1-phenyl-1H-benzo[d]imidazol-2-yl) phenyl, 90 nm) / LiF (1 nm) / Al (100 nm) named G1 – G4, respectively. TAPC and SimCP2 were employed as the hole-transporting layer and bipolar host material, respectively. TPBi was used as an 15 electron-transporting and hole-blocking layer. The optimized Ir(III) complexes with 8 wt% doped concentration in SimCP2 was used as the emitting layer. The energy diagram of the devices, as well as the molecular structure of the materials used are shown in Fig. 5. Obviously, the HOMO/LUMO levels of the 20 Ir(III) complexes are all within the HOMO and LUMO levels of host material SimCP2. So, a good carrier trapping is expected in

- these devices, which is the dominated EL mechanism. Furthermore, holes and electrons will be well confined within the doped light-emitting layer.
- The EL spectra, power efficiency (η_p) versus current density (J), current efficiency (η_c) versus current density (J), and luminance (L) versus voltage (V) characteristics of each device are shown in Fig. 6. The key EL data are summarized in Table 4. All devices emit green light with the EL emission peaks at 526,
- ³⁰ 534, 520 and 519 nm for G1 G4, respectively, and the emission spectra are almost invariant of the current density and also do not show any concentration dependent. As shown in Fig. 6(a), the EL spectra are very close to the PL spectra of the complexes in

CH₂Cl₂ solution indicating that the EL emission of the device ³⁵ originates from the triplet excited states of the phosphors.^{9(a)} But it is noted that there is a little residual emission from the host SimCP2 for each device which means that the energy and/or charge transfer from the host exciton to the phosphor is not complete upon electrical excitation. The CIE color coordinates ⁴⁰ are x = 0.33, y = 0.63 for G1, x = 0.35, y = 0.59 for G2, x = 0.29, y = 0.62 for G3 and x = 0.31, y = 0.62 for G4 at 100 mA cm⁻², respectively.

The OLEDs based on complexes Ir1 – Ir4 exhibit encouraging EL performances. All devices G1 - G4 display low turn-on 45 voltages ($V_{turn-on}$) (3.3 V - 3.5 V) and high brightness. The maximum $\eta_{\rm p}$, $\eta_{\rm c}$ and external quantum efficiency ($\eta_{\rm ext}$) of G1 -G4 are in the range of 30.65 - 41.03 lm W⁻¹, 56.18 - 70.48 cd A⁻¹, and 15.8 - 19.7%, respectively. The good EL properties should be due to the application of 2-(5-phenyl-1,3,4-oxadiazol-2-yl)-50 phenol and its derivatives as the ancillary ligand. The dopants act as the hole and electron traps to retard the motion of both types of carriers. The lower LUMO levels of the dopants are particularly important for the reason that the hole mobility of the TAPC is high than the electron mobility of the TPBi in OLEDs.¹⁸ the 55 excitons accumulation is expected in hole blocking layer (TPBi) near the interface of emitting layer (Ir complexes (x wt%) : SimCP2) / TPBi due to the high energy barrier between TPBi and SimCP2.¹⁹ The accumulation of excitons is expected to cause the serious triplet-triplet annihilation (TTA) and triplet-polaron 60 annihilation (TPA) of the iridium complexes, and high efficiency roll-off consequently. Therefore, the excitation lifetime of OLEDs relies on the capability of electron transport. In our case, the F/CF₃ and 1,3,4-oxadiazole units, as part of the ligand framework, can decrease the LUMO levels, and the lower LUMO 65 levels of the dopants than that of the host (Fig. 5) will benefit the electron transport properties. The good electron mobility of the phosphorescent emitters would facilitate the injection and transport of electrons, which broadens the recombination zone, balances the distribution of holes and electrons and reduces 70 leakage current, particularly for the high doping concentration, leading to the suppressed the TTA, TPQ effects,²⁰ improved recombination probability and high device efficiency, low efficiency roll-off. Moreover, it can be observed that the maximum luminance (L_{max}) values can be retained during a 75 driving voltage range, suggesting that they exceed the

measurement limitation for our equipment (over 40000 cd m⁻²).

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Fig. 6 Characteristics of devices with configuration ITO / TAPC (60 nm) / **Ir1** 5 - **Ir4**: SimCP2 (30 nm, 8 wt%) / TPBi (90 nm) / LiF (1 nm) / Al (100 nm): (a) EL spectra at different current densities, (b) power efficiency (η_c) as a function of current density (*J*), (c) current efficiency (η_c) as a function of current density (*J*), and (d) luminance versus voltage (*L*-*V*) for G1 – G4.

Table 4 EL performances of the devices G1-G4.

According to the respective device, the $\eta_{c,max}$ of 69.90 cd A⁻¹ ¹⁰ and $\eta_{\text{ext,max}}$ of 18.4% were obtained in G1 at 5.4 V. The device G2 using Ir2, which has the lowest PL efficiency, as the emitter showed the relative poor performances, with a $\eta_{p, max}$ of 30.65 lm W⁻¹ at 5.2 V, a $\eta_{c, max}$ of 56.18 cd A⁻¹ and a peak η_{ext} of 15.8% at 6.4 V. For the device G3, it showed the comparative values to 15 that of G1 with a $\eta_{p, max}$ of 33.60 lm W⁻¹ at 5.9 V, a $\eta_{c, max}$ of 65.04 cd A⁻¹ and a peak η_{ext} of 18.3% at 6.7 V. The device G4 obtained a little higher maximum device efficiency with a $\eta_{c. max}$ of 70.48 cd A⁻¹ and a $\eta_{\text{ext.max}}$ of 19.7% at 6.2 V. The results show that the substituents of ancillary ligand can influence the EL 20 performances of the Ir(III) complexes. In the Ir(III) complexes studied in this work, the introduction of fluoro/trifluoromethyl units on the phenyl ring of ancillary ligands can enhance the external quantum efficiency of the OLEDs though the PL vields of Ir2 - Ir4 are lower than that of Ir1 due to the lower LUMOs 25 and possible higher electron transporting and trapping ability.

Device	V _{turn-on} ^{a)}	$L_{\rm max}^{\rm b)}$ [cd m ⁻²]	$\eta_{\mathrm{p,max}}^{\mathrm{c}}$ [lmW ⁻¹]	$\eta_{\mathrm{c,max}}^{\mathrm{d}}$ [cd A ⁻¹]	η_{ext}	$L_{100}^{e)}$	CIE ^{f)}
Device	[V]	voltage [V]	voltage [V]	voltage [V]	[%]	$[cd m^{-2}]$	(x,y)
G1	3.3	>40 000, 12.0	41.03, 4.5	69.90, 5.4	18.4	37677	(0.33, 0.63)
G2	3.3	>40 000, 12.4	30.65, 5.2	56.18, 6.4	15.8	26161	(0.35, 0.59)
G3	3.3	>40 000, 14.0	33.60, 5.9	65.04, 6.7	18.3	35016	(0.29, 0.62)
G4	3.5	>40 000, 13.5	39.11, 4.9	70.48, 6.2	19.7	29566	(0.31, 0.62)

a) $V_{\text{turn-on}}$: Turn-on voltage recorded at a brightness of 1 cd m⁻². b) L_{max} : Maximum luminance. c) $\eta_{\text{p, max}}$: Maximum power efficiency. d) $\eta_{\text{c, max}}$: Maximum current efficiency. e) L_{100} : Luminance measured at a current density of 100 mA cm⁻². f) Taken at 100 mA cm⁻².

30 Conclusions

In conclusion, four bis-cyclometalated iridium complexes Ir1 -Ir4 with 2-(5-phenyl-1,3,4-oxadiazol-2-yl)-phenol and its derivatives as the ancillary ligands have been successfully prepared and applied in the OLEDs. EL devices in the ³⁵ configuration ITO / TAPC (60 nm) / Ir complexes (8 wt%) : SimCP2 (30 nm) / TPBi (90 nm) / LiF (1 nm) / Al (100 nm) showed good performances with a high $\eta_{c,max}$ of 70.48 cd A⁻¹, a peak η_{ext} of 19.7% and a maximum brightness over 40 000 cd m⁻². The study suggested the ancillary ligands ⁴⁰ phenyl-1,3,4-oxadiazole derivatives can be employed well in Ir(III) complexes and these Ir(III) complexes would have potential applications in OLEDs.

Experimental

Materials and measurements.

⁴⁵ All reagents and chemicals were purchased from commercial sources and used without further purification. ¹H NMR spectra were measured on a Bruker AM 400 spectrometer or a Bruker AM 500 spectrometer. Mass spectra (MS) were obtained with ESI-MS (LCQ Fleet, Thermo Fisher Scientific) or MALDI-TOF
⁵⁰ (Bruker Daltonic Inc.). Elemental analyses for C, H and N were performed on an Elementar Vario MICRO analyzer. Absorption and photoluminescence spectra were measured on a UV-3100 spectrophotometer and a Hitachi F-4600 photoluminescence spectrophotometer, respectively. The decay lifetimes were spectrometer in degassed CH₂Cl₂ solution at room temperature (RT). Cyclic voltammetry measurements were conducted on a MPI-A multifunctional electrochemical and chemiluminescent

system (Xi'an Remex Analytical Instrument Ltd. Co., China) at RT, with a polished Pt plate as the working electrode, platinum thread as the counter electrode and Ag-AgNO₃ (0.1 M) in CH₃CN as the reference electrode, *tetra*-n-butylammonium ⁵ perchlorate (0.1 M) was used as the supporting electrolyte, using Fc⁺/Fc as the internal standard, the scan rate was 0.1 V s⁻¹.

The luminescence quantum efficiencies were calculated by comparison of the emission intensities (integrated areas) of a standard sample (*fac*-Ir(ppy)₃) and the unknown sample ¹⁰ according to the equation (1).²¹

$$\Phi_{unk} = \Phi_{std} \left(\frac{I_{unk}}{I_{std}}\right) \left(\frac{A_{std}}{A_{unk}}\right) \left(\frac{\eta_{unk}}{\eta_{std}}\right)^2 \tag{1}$$

where Φ_{unk} and Φ_{std} are the luminescence quantum yield of the unknown sample and *fac*-Ir(ppy)₃ (0.4²²), respectively. The I_{unk} and I_{std} are the integrated emission intensities of the unknown sample and *fac*-Ir(ppy)₃ solution, respectively. The A_{unk} and A_{std} are the absorbance of the unknown sample and *fac*-Ir(ppy)₃ solution at their excitation wavelengths, respectively. The η_{unk} and η_{std} terms represent the refractive indices of the corresponding solvents (pure solvents were assumed).

²⁰ Density functional theory (DFT) calculations using B3LYP functional were performed. The basis set used for C, H, N, O, F and P atoms was 6-31G(d, p) while the LanL2DZ basis set were employed for Ir atoms. The solvent effect of CH₂Cl₂ was taken into consideration using conductor like polarizable continuum ²⁵ model (C-PCM). All these calculations were performed with Gaussian 09.²³

X-ray crystallography.

The single crystals of complexes were carried out on a Bruker SMART CCD diffractometer using monochromated Mo K α ³⁰ radiation ($\lambda = 0.71073$ Å) at RT. Cell parameters were retrieved using SMART software and refined using SAINT²⁴ on all observed reflections. Data were collected using a narrow-frame method with scan widths of 0.30° in ω and an exposure time of 10 s/frame. The highly redundant data sets were reduced using ³⁵ SAINT and corrected for Lorentz and polarization effects. Absorption corrections were applied using SADABS²⁵ supplied by Bruker. The structures were solved by direct methods and refined by full-matrix least-squares on *F*2 using the program SHELXS-97.²⁶ The positions of metal atoms and their first ⁴⁰ coordination spheres were located from direct-methods E-maps; other non-hydrogen atoms were found in alternating difference Fourier syntheses and least-squares refinement cycles and, during the final cycles, refined anisotropically. Hydrogen atoms were placed in calculated position and refined as riding atoms with a ⁴⁵ uniform value of Uiso.

OLEDs fabrication and measurement.

All OLEDs with the emission area of 0.1 cm^2 were fabricated on the pre-patterned ITO-coated glass substrate with a sheet resistance of 15 Ω sq⁻¹. Substrate was cleaned by ultrasonic baths 50 in organic solvents followed by ozone treatment for 20 min. All chemicals used for EL devices were sublimed in vacuum (2.2 \times 10^{-4} Pa) prior to use. The 60 nm hole-transporting material of TAPC film was first deposited on the ITO glass substrate. The phosphor (8 wt%) and SimCP2 host were co-evaporated to form 55 30 nm emitting layer from two separate sources. Successively, TPBi (90 nm), LiF (1 nm), and Al (100 nm) were evaporated. The vacuum was less than 1×10^{-4} Pa during all materials deposition. The L - V characteristics and η - J curves of the devices were measured with a computer controlled KEITHLEY 60 2400 source meter with a calibrated silicon diode in air without device encapsulation. The electroluminescence spectra were measured with a Hitachi F-4600 photoluminescence spectrophotometer. On the basis of the uncorrected PL and EL spectra, the Commission Internationale de l'Eclairage (CIE) 65 coordinates were calculated using a test program of the Spectra scan PR650 spectrophotometer.

Syntheses.

The syntheses procedures of ligands were listed in Scheme 1. All reactions were performed under nitrogen. Solvents were carefully 70 dried and distilled from appropriate drying agents prior to use.

General syntheses of ancillary ligands LX.

All ancillary ligands LX1 - LX4 were synthesized via a general procedure where used the syntheses of we 2-(5-phenyl-1,3,4-oxadiazol-2-yl)-phenol as an example. Benzoyl 75 chloride (1.40 g, 10 mmol) was added dropwise to a solution of 2-methoxybenzohydrazine (1.66 g, 10 mmol) and triethylamine (1.01 g, 10 mmol) in chloroform (20 mL) at room temperature (RT). The resulting mixture was stirred for 2 h and then filtered. The collected solid was washed with water and ethanol to give ⁸⁰ N'-benzoyl-2-methoxybenzohydrazine (2.57 g, 95 % yield). A mixture of N²-benzoyl-2-methoxybenzohydrazine and POCl₃ (20 mL) in a 50 mL flask was refluxed under nitrogen for 5 h. The

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excessive POCl₃ was then distilled out, and the residue was poured into water. The crude solid product was collected by filtration and purified by recrystallization from chloroform/hexane to give 2-(2-methoxyphenyl)-5-phenyl-⁵ 1,3,4-oxadiazole (1.91 g, 80 % yield). Then, to a mixture of 2-(2-methoxyphenyl)-5-phenyl-1,3,4-oxadiazole (1.91 g) in 50 mL CH₂Cl₂ cooled to -78 °C was added BBr₃ (12.5 g, 50 mmol in 20 mL CH₂Cl₂) dropwise. The mixture was stirred for 24 h at -78 °C and the resulting solution was poured into water, extracted

 $_{10}$ with CH₂Cl₂ (50 mL \times 3 times) and then dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and recrystallization of the residue from ethanol gave colorless crystals.

2-(5-Phenyl-1,3,4-oxadiazol-2-yl)-phenol (LX1). 80% yield. ¹H

¹⁵ NMR (500 MHz, CDCl₃) δ 10.22 (s, 1H), 8.18 (d, J = 7.5 Hz, 2H), 7.90 (d, J = 7.8 Hz, 1H), 7.66 – 7.54 (m, 3H), 7.49 (t, J = 7.8 Hz, 1H), 7.18 (d, J = 8.4 Hz, 1H), 7.07 (t, J = 7.5 Hz, 1H). MS(ESI): m/z 237 [M-H]⁺.

2-[5-(3,5-Bis-trifluoromethyl-phenyl)-1,3,4-oxadiazol-2-yl]-ph ²⁰ **enol (LX2)**. 78% yield. ¹H NMR (500 MHz, CDCl₃) δ 10.03 (s, 1H), 8.62 (s, 2H), 8.12 (s, 1H), 7.95 (d, *J* = 7.4 Hz, 1H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.20 (d, *J* = 8.4 Hz, 1H), 7.11 (t, *J* = 7.6 Hz, 1H). MS(ESI): m/z 373 [M-H]⁺.

2-[5-(2,3,4,5-Tetrafluoro-phenyl)-1,3,4-oxadiazol-2-yl]-phenol ²⁵ **(LX3)**. 61% yield. ¹H NMR (500 MHz, CDCl₃) δ 9.99 (s, 1H), 7.90-7.82 (m, 2H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.18 (d, *J* = 8.4 Hz, 1H), 7.08 (t, *J* = 7.6 Hz, 1H). MS(ESI): m/z 309 [M-H]⁺.

2-(5-Pentafluorophenyl-1,3,4-oxadiazol-2-yl)-phenol (LX4). 65% yield. ¹H NMR (500 MHz, CDCl₃) δ 9.98 (s, 1H), 7.85 (dd, ³⁰ J = 7.9, 1.2 Hz, 1H), 7.53 (t, J = 7.5 Hz, 1H), 7.19 (d, J = 8.4 Hz, 1H), 7.08 (t, J = 7.5 Hz, 1H). MS(ESI): m/z 327 [M-H]⁺.

Synthesis of KLX. LX (0.50 mmol) was dissolved in 5 mL methanol solution and a solution of KOH (0.028 g, 0.50 mmol) in 3 mL methanol was added dropwise. After reacting for two hours

- ³⁵ at room temperature, the solvent volume was concentrated to 2 mL and kept for next step.
- General syntheses of complexes. The complexes Ir1-Ir4 were synthesized according to the similar procedures. A mixture of $IrCl_3 \cdot 3H_2O$ (1 mmol) and tfmppy (2.5 mmol) in 2-ethoxyethanol
- ⁴⁰ and water (20 mL, 3 : 1, v/v) was refluxed for 24 h. After cooling, the yellow solid precipitate was filtered to give the crude cyclometalated Ir(III) chloro-bridged dimer. Then the slurry of crude chloro-bridged dimer (0.2 mmol) and KLX (0.5 mmol) in

2-ethoxyethanol (20 mL) was refluxed for 24 h. After the mixture ⁴⁵ was cooled to RT, the solvent was evaporated at low pressure. The crude product was washed by water, and then chromatographed using CH₂Cl₂ to give complexes **Ir1 - Ir4** which were further purified again by sublimation in vacuum.

Ir1 (yield: 44%): ¹H NMR (500 MHz, DMSO-d₆) δ 8.72 (d, J =

- ⁵⁰ 5.6 Hz, 1H), 8.55 (d, J = 5.6 Hz, 1H), 8.34 (t, J = 7.9 Hz, 2H), 8.08 – 7.94 (m, 4H), 7.82 (d, J = 8.0 Hz, 1H), 7.77 (d, J = 7.8 Hz, 2H), 7.62 – 7.46 (m, 4H), 7.32 (t, J = 6.6 Hz, 1H), 7.18 – 7.14 (m, 3H), 6.59 (d, J = 8.6 Hz, 1H), 6.49 (t, J = 7.4 Hz, 1H), 6.42 (s, 1H), 6.28 (s, 1H). ¹³C NMR (300 MHz, Acetone- d_6) δ 167.9, 167 L 166 0, 150 2, 148 6, 148 0, 128 4, 128 2, 122 5, 122 0
- ⁶⁰ **Ir2** (yield: 48%): ¹H NMR (500 MHz, DMSO-d₆) δ 8.71 (d, J = 5.1 Hz, 1H), 8.50 (d, J = 5.3 Hz, 1H), 8.43 8.29 (m, 5H), 8.03 (t, J = 7.4 Hz, 4H), 7.98 (d, J = 7.8 Hz, 1H), 7.52 (t, J = 6.4 Hz, 1H), 7.32 (t, J = 6.3 Hz, 1H), 7.25-7.15 (m, 3H), 6.62 (d, J = 8.6 Hz, 1H), 6.50 (t, J = 7.4 Hz, 1H), 6.47 (s, 1H), 6.25 (s, 1H). ¹³C NMR
- ⁶⁵ (300 MHz, Acetone-*d*₆) δ 168.2, 167.1, 167.0, 152.6, 150.0, 148.6, 147.6, 138.5, 138.3, 133.9, 132.4, 131.9, 128.6, 128.1, 127.7, 126.7, 125.0, 123.9, 123.5, 120.3, 120.0, 118.3, 117.4, 113.8, 106.9 ppm. MALDI-TOF: m/z 1008 [M-H]⁺. Anal. calcd for C₄₀H₂₁F₁₂IrN₄O₂: C 47.58, H 2.10, N 5.55. Found: C 47.74, H ⁷⁰ 2.21, N 5.68.

Ir3 (yield: 37%): ¹H NMR (500 MHz, DMSO-d₆) δ 8.69 (d, J = 5.1 Hz, 1H), 8.52 (d, J = 5.4 Hz, 1H), 8.35 (dd, J = 14.7, 8.0 Hz, 2H), 8.08 – 7.99 (m, 4H), 7.96 (d, J = 8.1 Hz, 1H), 7.89 (d, J = 8.1 Hz, 1H), 7.51 (t, J = 7.5 Hz, 1H), 7.34 (t, J = 7.5 Hz, 1H),

- ⁷⁵ 7.20 (t, J = 10.0 Hz, 2H), 7.15 (d, J = 7.7 Hz, 1H), 6.60 (d, J = 8.6 Hz, 1H), 6.49 (t, J = 7.3 Hz, 1H), 6.39 (s, 1H), 6.26 (s, 1H). ¹³C NMR (300 MHz, Acetone- d_6) δ 168.2, 167.1, 167.0, 152.6, 150.1, 149.4, 149.0, 148.6, 147.5, 138.5, 138.3, 133.9, 128.5, 128.0, 127.7, 125.0, 123.9, 123.5, 120.2, 120.0, 118.2, 117.5,
- ⁸⁰ 113.8, 110.6, 110.4, 106.8 ppm. MALDI-TOF: m/z 944 [M-H]⁺. Anal. calcd for C₃₈H₁₉F₁₀IrN₄O₂: C 48.26, H 2.02, N 5.92. Found: C 48.47, H 2.10, N 5.89.

Ir4 (yield: 39%): ¹H NMR (500 MHz, DMSO-d₆) δ 8.70 (d, J = 5.8 Hz, 1H), 8.53 (d, J = 5.6 Hz, 1H), 8.36 (dd, J = 15.5, 8.2 Hz, 85 2H), 8.03 (t, J = 7.4 Hz, 3H), 7.96 (d, J = 8.1 Hz, 1H), 7.62 (d, J = 6.7 Hz, 1H), 7.51 (t, J = 6.4 Hz, 1H), 7.35 (t, J = 6.8 Hz, 1H),

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7.25-7.18 (m, 2H), 7.14 (d, J = 7.7 Hz, 1H), 6.61 (d, J = 8.7 Hz, 1H), 6.51 (t, J = 7.4 Hz, 1H), 6.39 (s, 1H), 6.27 (s, 1H). ¹³C NMR (300 MHz, Acetone- d_6) δ 168.3, 167.1, 166.9, 152.4, 150.3, 150.0, 149.4, 149.1, 148.6, 147.3, 138.5, 138.4, 134.0, 128.5, 5 127.7, 125.1, 123.9, 123.5, 120.3, 119.9, 118.3, 117.5, 113.9, 106.6 ppm. MALDI-TOF: m/z 962 [M-H]⁺. Anal. calcd for C₃₈H₁₈F₁₁IrN₄O₂: C 47.36, H 1.88, N 5.81. Found: C 47.32, H 1.98, N 5.87.

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