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Photoluminescence and electroluminescence of iridium(III) complexes with 2',6'bis(trifluoromethyl)-2,4'-bipyridine and 1,3,4oxadiazole/1,3,4-thiadiazole derivatives ligands

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Using 2',6'-bis(trifluoromethyl)-2,4'-bipyridine as a monoanionic cyclometalated ligand, 2-(5-(4-(trifluoromethyl)phenyl)-1,3,4-oxadiazol-2-yl)phenol or 2-(5-(4-(trifluoromethyl) phenyl)-1,3,4-thiadiazol-2-yl)phenol as ancillary ligands, two new heteroleptic iridium(III) complexes (Ir1 and Ir2) were prepared and investigated. The ancillary ligand variations affected their emissions greatly, and the complexes Ir1 and Ir2 emit green (503 nm) and orange (579 nm) light, respectively. Moreover, the electron mobility of the two complexes as that of the electron transport material Alq₃ is high (tris-(8as hydroxyquinoline)aluminium), which is useful for their performances in the organic lightemitting diodes (OLEDs). The OLEDs with Ir1 as the emitter showed excellent performances with a maximum current efficiency of 74.8 cd A⁻¹, a maximum external quantum efficiency of 27.0%, a maximum power efficiency of 33.4 lm W⁻¹, and the efficiency roll-off is mild. These results suggest that the complexes with 1,3,4oxadiazole/1,3,4-thiadiazole derivatives has potential application as efficient emitters in OLEDs.

Introduction

Organic light-emitting diodes (OLEDs) have been studied intensely during the last decade due to their encouraging application in high-resolution, full-color, flat-panel displays and lighting sources.¹ Especially, phosphorescent iridium(III) complexes play an important part as the emitters in efficient OLEDs due to the high quantum efficiency and short lifetime of triplet excited states.² The strong spin-orbit coupling (SOC) introduced by the central heavy atom can promote the triplet to singlet radiative transition, such complexes may exhibit unusually high phosphorescence quantum yields at room temperature.³ On the other hand, since the phosphorescence of Ir(III) complexes primarily originates from the metal-to-ligand charge transfers (MLCT) and the ligand-centered (LC) transitions,⁴ the energy level of the excited state can be controlled by tuning the energy levels of the ligands through substituent effects, which leads to a wide flexible emission color range.⁵

According to the density functional theory calculation, the highest occupied molecular orbital (HOMO) is basically centered on the Ir(III) metal while the lowest unoccupied molecular orbital (LUMO) is generally localized on the cyclometalated ligands. Although most ancillary ligands do not make contribution to the lowest excited state directly, they indeed alter the energy levels of the excited states by modifying the electron density at the metal center. Thus, the photophysical property and carrier mobility of iridium complexes can be tuned trough functional substitutes on both cyclometalated and ancillary ligands. However, for many OLEDs with high efficiency based on Ir(III) complexes, the device efficiency roll-off ratios are serious, which can mainly be attributed to the deterioration of charge carrier balance and the increase of nonradioactive quenching processes, including triplet-triplet annihilation (TTA), triplepolaron annihilation (TPA), and electric field induced dissociation of excitons at high current density.⁶ Therefore, the balanced injection and transport of the electron-hole is a crucial factor for high efficient OLEDs. Furthermore, as we know, because the hole mobility of most hole transport materials is roughly 2-3 orders of magnitude higher than the electron mobility of the electron transport materials, the efficiency and efficiency roll-off of OLEDs rely on the capability of electron transport. Thus, it is necessary to use the ambipolar host materials and synthesize Ir(III) dopants with outstanding electron mobility to obtain phosphorescent OLEDs with low efficiency roll-off.

Our group has reported high efficient phosphorescent **OLEDs** using Ir(III) complexes with 2',6'bis(trifluoromethyl)-2,4'-bipyridine (BTBP) as the main ligand and tetraphenylimidodiphosphinate (tpip) derivatives as ancillary ligands.⁷ Trifluoromethyl unit can enhance the electron mobility and result in a better balance of charge injection and transfer. Furthermore, the lower vibrational frequency of the C-F bond also 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.⁸ In addition, nitrogen heterocycle will increase the electron affinity and a more negative framework of ligand C^N such as bipyridine may improve the electron mobility of the complexes. Moreover, OLEDs based on Ir(III) complexes with 1,3,4-oxadiazole derivatives as ancillary ligands also have good performances due to their high electron mobility, photoluminescence quantum yield and high good thermal/chemical stability.9,10 On this basis, as shown in Scheme 1, we synthesized two new heteroleptic Ir(III) complexes (Ir1 and Ir2) using 2',6'-bis(trifluoromethyl)-2,4'bipyridine (BTBP) as the cyclometalated ligand and 2-(5-(4-(trifluoromethyl)phenyl)-1,3,4-oxadiazol-2-yl)phenol

(HCF₃POP) and 2-(5-(4-(trifluoromethyl)phenyl)-1,3,4-thiadiazol-2-yl)phenol (HCF₃POPTDZ) as the ancillary ligands. When the 1,3,4-oxadiazole derivatives were replaced by the 1,3,4-thiadiazole derivatives, the emission color of the complex is tuned from green to red. Here, we described the results of our investigation on the synthesis, characterization, photoluminescence and electroluminescence properties of both Ir(III) complexes.

Results and discussion

Preparation and X-ray crystallography



Scheme 1. Synthetic routes of ligands and complexes.

Scheme 1 shows the chemical structures and synthetic protocols for ligands and Ir(III) complexes. The main ligand 2',6'bis(trifluoromethyl)-2,4'-bipyridine was synthesized using a Suzuki coupling reaction from (2,6-bis(trifluoromethyl)pyridin-4-2-bromopyridine. vl)boronic acid and The 2-(5-(4-(trifluoromethyl)phenyl)-1,3,4-oxadiazol-2-yl)phenol, 2-(5-(4-(trifluoromethyl)phenyl)-1,3,4-thiadiazol-2-yl)phenol ancillarv ligands and their potassium salt were prepared according to our previous publications.¹⁰ The Ir(III) complexes were obtained in two steps with popular methods via Ir(III) chloro-bridged dimer. Purification of the mixture by silica gel chromatography provided crude products, which were further purified by vacuum sublimation. All the new compounds were fully characterized by ¹H NMR and high resolution mass spectrometry (HR MS); the crystal structure obtained from vacuum sublimation further confirmed the identity of Ir1 complex.

The Oak Ridge Thermal Ellipsoidal plot (ORTEP) diagram of the Ir1 complex is shown in Fig. 1, the corresponding crystallographic data are summarized in Table S1, and selected bond lengths and angles are listed in Table S2. The central iridium atom is chelated by two anionic C^N main ligands and one monoanionic bidentate N^O ancillary ligand. The coordination sphere presents a distorted octahedral geometry, with the cis-C,C and trans-N,N in chelating disposition. Concerning the designed ancillary ligand with three rings, the phenol ring and the oxadiazole ring chelate with the iridium center via the O atom and a N atom, respectively, forming a relatively rigid hexatomic coordination ring. The Ir-C and Ir-N bonds between iridium center and C^N main ligands are 2.0 Å and the Ir-O(1) bond (2.1 Å) is the longest among all the coordination bonds. Furthermore, the C-C and C-N bond lengths and angles are in agreement with the corresponding parameters described in other similarly constituted complexes. The left 4-(trifluoromethyl)phenyl ring presents a rather obvious dihedral angle towards the other two rings, in order to minimize the steric effect.



Fig. 1. Oak Ridge Thermal Ellipsoidal plot (ORTEP) diagrams of the complex Ir1 with the atom-numbering schemes. Hydrogen atoms are omitted for clarity. Ellipsoids are drawn at 30% probability level. Crystal data: CCDC No. 1455234, $C_{39}H_{18}F_{15}IrN_6O_2$, Mw = 1079.79, Monoclinic,

 $P2_1/c$, a = 11.6755(5) Å, b = 13.7860(5) Å, c = 24.0468(9) Å, $a = \gamma = 90^\circ$, $\beta = 93.2230(10)^\circ$, V = 3864.4(3) Å³, Z = 4, F(000) = 2088, GOF = 1.093, $R_1 = 0.0306$, $wR_2 = 0.0604$.

Thermal stability



Fig. 2. TG and DSC thermograms of (a) Ir1 and (b) Ir2.

The thermal stability of the emitters is important for the stability of OLEDs. The thermal properties of **Ir1** and **Ir2** were characterized by thermogravimetric (TG) and different scanning calorimetry (DSC) measurements under a nitrogen steam. From the DSC curves in Fig. 2 it can be observed that the melting points of **Ir1** and **Ir2** are as high as 345 and 359 °C, respectively. The TG curves give the decomposition temperature (5% loss of weight) of 382 °C for **Ir1** and 378 °C for **Ir2**, respectively. Furthermore, all of the two complexes can be vacuum evaporated easily without decomposition and show good film-forming ability, which indicates that the complexes are potential emitting materials for the fabrication of stable OLEDs.

Photophysical property

Complex

Ir1

Ir2

Table 1. Physical properties of Ir1 and Ir2.

 $T_{\rm m}/T_{\rm d}^{\rm a}$

(°C)

345/382 359/378 The UV-vis absorption spectra of the Ir1 and Ir2 complexes in degassed CH₂Cl₂ at 5×10^{-5} mol·L⁻¹ are shown in Fig. 3(a) and the photophysical data are listed in Table 1. The intense bands at high energy (250-350 nm) are assigned to the spin-allowed ligand-centered ¹LC (π - π *) transition of the cyclometalated primary ligand (BTBP) and ancillary ligands. The relatively weak absorption bands at lower energies extending into the spectral region (350-500 nm) are attributed to the mixing of the spinallowed singlet metal-to-ligand charge-transfer (¹MLCT) and triplet metal-to-ligand charge-transfer (³MLCT) states, or LLCT (ligand-to-ligand charge-transfer) transition through strong spinorbit coupling of iridium atoms.^{8,11} From Fig. 3(a) and Table 1 it can be observed that the absorption bands of Ir2 with 2-(5-(4-(trifluoromethyl)phenyl)-1,3,4-thiadiazol-2-yl)phenol ancillary ligand has an obvious red shift compared with that of Ir1 which has the ancillary ligand of 2-(5-(4-(trifluoromethyl)phenyl)-1,3,4oxadiazol-2-yl)phenol suggesting that the ancillary ligand variation has effects on their excited state energy.



Fig. 3. Normalized (a) UV-vis absorption and (b) emission spectra of Ir1 and Ir2 in degassed CH_2Cl_2 solutions (5 × 10⁻⁵ mol·L⁻¹) at room temperature and 77 K.

$\lambda_{abs}^{b)}$		$\lambda_{\rm em}^{\rm c)}$		$\tau^{e)}$	HOMO/LUMO f)	
(nm)		(nm)	(%)	(µs)	(eV)	
	298 K	77 K	-			
247, 263, 409	503	495, 529	93.04	2.28	-5.59/-2.84	
249,267,456	579	530, 565	24.32	2.21	-5.57/-3.09	

^{a)} $T_{\rm m}$: melting temperature, T_d : decomposition temperature; ^{b)} Measured in degassed CH₂Cl₂ solution at a concentration of 5×10^{-5} mol·L⁻¹ at room temperature; ^{c)} Measured in degassed CH₂Cl₂ solution at a concentration of 5×10^{-5} mol·L⁻¹ at 298 and 77 K, respectively; ^{d)} Measured in degassed CH₂Cl₂ solution at room temperature using *fac*-Ir(ppy)₃ as the standard sample ($\Phi = 0.9$). ^{e)} Measured in degassed CH₂Cl₂ solution at a concentration of 5×10^{-5} mol·L⁻¹ at room temperature; ^{f)} From the onset of oxidation potentials of the cyclovoltammetry (CV) diagram using ferrocene as the internal standard and the optical band gap from the absorption spectra in degassed CH₂Cl₂.

Photoluminescence measurements were conducted in deaerated CH_2Cl_2 solutions at room temperature (Fig. 3(b) and Table 1) and 77 K (Fig. 3(b) and Table 1). Under the excitation of 380 nm, the **Ir1** complex emitted intense green phosphorescence in CH_2Cl_2 at room temperature with the peak maxima at 503 nm. It can be observed that when the 2-(5-(4-(trifluoromethyl)phenyl)-1,3,4-oxadiazol-2-yl)phenol derivative was replaced by 2-(5-(4-(trifluoromethyl)phenyl)-1,3,4-thiadiazol-2-yl)phenol derivative, the emission of **Ir2** is red shift compared with that of **Ir1**. Under the excitation of 470 nm, the **Ir2** complex emitted intense orange phosphorescence peaked at 579 nm, which agrees with the absorption spectra. The result

suggests the introduction of 1,3,4-thiadiazole into the ancillary ligand can affect the luminescence properties of the Ir(III) complexes. Moreover, the quantum yields of the two complexes in solution are 93.04% and 24.32%, respectively.

As shown in Fig. 3(b), the structured emission at 77 K reveals that the mixing between the ³MLCT and the LLCT levels is so effective that an almost ligand-centered emission is observed upon freezing of the matrix. The rigidity of the solvent dramatically affects the stabilization of the charge-transfer states, which shift to higher energy at low temperature, and the electronic mixing of the two states decreases.

The phosphorescence lifetime (τ) is the crucial factor that determines the rate of triplet-triplet annihilation in OLEDs. Longer τ values usually cause greater triplet-triplet annihilation.¹² The lifetimes of **Ir1** and **Ir2** are in the range of microseconds (2.28 µs and 2.21 µs in CH₂Cl₂ solution respectively) at room temperature (Table 1) and are indicative of the phosphorescent origin for the excited states in each case.

Electrochemical properties and theoretical calculation



Fig. 4. Cyclic voltammogram curves (left) and contour plots of HOMOs/LUMOs with theoretical (black) and experimental (red) energy levels (right) of **Ir1** and **Ir2**.

The redox properties and HOMO/LUMO energy levels of the dopants are relative to the charge transport ability and the OLED structure. In order to calculate the HOMO and LUMO energy levels of the complexes, the electrochemical properties of Ir1 and Ir2 were measured by cyclic voltammetry in deaerated solution (CH₂Cl₂: CH₃CN = 1: 1) (Fig. 4 (left)). The HOMO levels were calculated from the oxidation peak potentials (E_{ox}) and the bandgaps (E_s) were calculated from the UV-vis absorption edges.¹³ Then the LUMO levels were determined according to the equation LUMO = HOMO + E_{o} . The electrochemical data are collected in Table S3.The cyclic voltammograms of the complexes in the positive range show strong oxidation peaks, while the reduction peaks are not obvious, demonstrating that the redox process of the complexes is not reversible completely, which is also observed in related Ir(III) complexes containing oxadiazole units.¹⁴ In the negative potential scan rang all complexes exhibit quasi-reversible oxidation and reduction process due to the 1,3,4oxadiazol/1,3,4- thiadiazole substituents suggesting the electron-transporting and electron trapping characteristics. From Fig. 4 and Table S3 it can be observed that the HOMO levels of Ir1 and Ir2 did not change significantly, which is -5.59 eV and -5.57 eV, respectively. But the 1,3,4-thiadiazole unit caused the lower LUMO level (-3.09 eV) and the HOMO-LUMO gap (2.48 eV). The trend corresponds to the DFT calculation results very well.

For providing further study of the electronic structures of the complexes, the theoretical calculation was performed on optimized geometries in CH₂Cl₂. The calculations on the ground electronic states of the complexes were carried out using density functional theory (DFT) and time-dependent DFT (TD-DFT) at the B3LYP level.¹⁵ The basis set used for C, H, N, O, F and S atoms was 6-31G(d, p) while the LanL2DZ basis set was used

for Ir atoms.¹⁶ The solvent effect of CH₂Cl₂ was taken into consideration using conductor-like polarizable continuum model (C-PCM).¹⁷ All these calculations were performed with Gaussian 09.¹⁸ OMForge program was used to give accurate percentage data of FMOs. Contour plots of the frontier molecular orbitals (FMOs) are shown in Fig. 4 (right). The energies and % composition of ligand and metal orbitals are shown in Table S4. The results are helpful for the assignment of the electron transition characteristics and the discussion on the photophysical variations. According to Fig. 4 (right) and Table S4, it is obviously that the HOMOs correspond to a mixture of the *d* orbitals of Ir (14.70-15.02%) and the π orbitals of the phenyl ring of the ancillary ligand (79.65-79.95%) with minor contribution from the BTBP ligand (5.23-5.36%). The oxidation processes occured with metal centered orbitals and a contribution from the phenyl ring of ancillary ligands.¹⁹ On the other hand, the locations of the LUMOs are various in different complexes. The LUMO level of Ir1 is mainly located on the primary ligand (BTBP) with the composition of 69.39% and a composition of 28.67% on the ancillary ligand. It is interesting that for Ir2, the composition of LUMO on the primary ligand is only as low as 9.23%, but the ratio on ancillary ligand reaches 89.81%, which is much higher than that of Ir1. The calculation results indicated that the frontier orbitals and the electronic properties of the complexes can be manipulated by introducing 1,3,4-thiadiazole derivatives.

Electron Mobility

As the hole mobility is roughly 2–3 orders of magnitude higher than the electron mobility in OLEDs,²⁰ their excitation lifetime relies on the electron transport capability. The good electron mobility of the phosphorescent emitters would facilitate the injection and transport of electrons, which will broaden the recombination zone, balance the distribution of hole–electron and reduce leakage current, leading to suppressed TTA and TPA effects, improved recombination probability, high device efficiency, and low efficiency roll-off.^{6,21} As discussed before, introducing nitrogen heterocycle with the strong electron withdrawing trifluoromethyl group and 1,3,4-oxadiazole derivatives or 1,3,4-thiadiazole derivatives may improve the electron mobility of the complexes, which would suppress the TTA and TPA effects effectively and obtain phosphorescent OLEDs with low efficiency roll-off.

To measure the electron mobility of both complexes, we conducted the transient electroluminescence (TEL) measurement based on the device of ITO (indium tin oxide) / TAPC (1,1-bis[4-[N,N-di(*p*-tolyl)amino]phenyl]cyclohexane, 50 nm) / Ir complexes (60 nm) / LiF (1 nm)/ Al (100 nm). ²² The TAPC is the hole-transport layer, whereas the Ir(III) complexes perform as both the emissive and electron-transport layers. To check the accuracy of our measurements, we also measured the electron mobility of Alq₃ (tris-(8-hydroxyquinoline)aluminum), which is the typically well-known electron transport material,

whose electron mobility has been reported in many references.²³ The experimental results (Fig. 5) show that the electron mobility in 60 nm **Ir1** and **Ir2** layers are between $3.69-4.39 \times 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $4.33-4.74 \times 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively, under an electric field from 1150 ($\text{V} \cdot \text{cm}^{-1}$)^{1/2} to 1300 ($\text{V} \cdot \text{cm}^{-1}$)^{1/2}, while that of Alq₃ is between $4.74-4.86 \times 10^{-6} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$. From Fig. 5(c) it can also be observed that **Ir1** and **Ir2** complexes have high electron mobility as that of Alq_3 . The good electron transport ability of **Ir1** and **Ir2** will facilitate the injection and transport of electrons, which broadens the recombination zone and balances the distribution of holes and electrons, particularly for high doping concentrations. Therefore, efficient OLEDs with suppressed efficiency roll-off are expected.



Fig. 5. The transient EL signals for the device structure of ITO/TAPC (50 nm)/Ir1 (a) and Ir2 (b) (60 nm) under different applied fields, and (c) the electric field dependence of charge electron mobility in the thin films of Ir1, Ir2 and Alq₃.

OLEDs performance



Fig. 6. Energy level diagram of HOMO and LUMO levels (relative to vacuum level) for materials investigated in this study and their molecular structures.

In order to evaluate the electroluminescence (EL) performances of two Ir(III) complexes, the devices **D1** and **D2** using **Ir1** and **Ir2** as the emitters, respectively, were fabricated with the

Table 2. EL performances of the devices D1 and D2.

structure of ITO/TAPC (30 nm)/ mCP (N,N'-dicarbazolyl-3,5benzene, 10 nm)/ Ir1 or Ir2 (8 wt%): PPO21 (3-(diphenylphosphoryl)-9-(4-(diphenylphosphoryl)phenyl)-9H-20 nm)/ TmPyPB (1,3,5-tri(m-pyrid-3-ylcarbazole, phenyl)benzene, 40 nm)/ LiF (1 nm)/ Al (100 nm). Fig. 6 shows the energy level diagram of HOMO and LUMO levels (relative to vacuum level) for materials investigated in this study and their molecular structures. TAPC, PPO21 and TmPyPB were employed as the hole transport, host and the electron transport material, respectively. PPO21 was introduced as the host material (HOMO = 6.21 eV), which has a similar transport capability of electrons and holes. Furthermore, holes and electrons will be well confined within the doped light-emitting layer. mCP was added as another hole transport material to lower the HOMO energy barrier between TAPC and PPO21.²⁴ Therefore, a good carrier trapping is expected in these devices, which is the dominated EL mechanism.

Table 2. EE performances of the devices of and b2.													
Device	Emitter	V _{turn-on} ^{a)} (V)	$L_{\max}^{b)}$ (cd m ⁻²)(V)	$\eta_{\mathrm{c,max}}^{\mathrm{c}^{\mathrm{c}}}$ (cd A ⁻¹) (EQE _{max} ^d)	$\eta_{c,L1000}^{e)}$ (cd A ⁻¹) (EQE _{L1000} f)	$\eta_{c,L10000}^{g)}$ (cd A ⁻¹) (EQE _{L10000} ^{h)})	$\eta_{\mathrm{p,max}}{}^{\mathrm{i})}$ (Im W ⁻¹) (V)	$\lambda_{\max}^{(j)}$ (nm)	$\operatorname{CIE}(x,y)^{k)}$				
D1	Ir1	3.9	37270 (13.9)	74.8 (27.0%)	71.6 (25.9%)	46.2 (16.7%)	33.4 (6.9)	497	0.18, 0.55				
D2	Ir2	4.0	18146 (12.4)	41.0 (13.9%)	37.1 (12.6%)	15.7 (5.30%)	18.7 (6.5)	579	0.52, 0.47				

^{a)} $V_{turn-on}$: turn-on voltage recorded at a luminance of 1 cd m⁻², ^{b)} L_{max} : maximum luminance, ^{e)} $\eta_{c,max}$: maximum current efficiency, ^{d)} EQE: maximum external quantum efficiency; ^{e)} $\eta_{c,L1000}$: current efficiency at 1000 cd m⁻², ^{f)} EQE_{L1000}: EQE at 1000 cd m⁻², ^{g)} $\eta_{c,L1000}$: current efficiency at 10000 cd m⁻², ^{h)} EQE_{L1000}: EQE at 10000 cd m⁻², ⁱ⁾ $\eta_{p,max}$: maximum power efficiency, ^{j)} values were collected at 8 V, ^{k)} CIE(x, y): Commission Internationale de l'Eclairage coordinates at 8V.

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Fig. 7. Characteristics of devices (D1 and D2) with configuration ITO/ TAPC (30 nm)/ mCP (10 nm)/Ir1 or Ir2 (8 wt%) : PPO21 (20 nm)/ TmPyPB (40 nm)/ LiF (1 nm)/ Al (100 nm): (a) Normalized EL spectra at 8 V, (b) current density-voltage-luminance (*J-V-L*), (c) current efficiency-luminance (η_c -L), and (d) power efficiency-luminance (η_p -L) curves.

The EL spectra, current density-voltage-luminance (*J-V-L*), current efficiency-luminance (η_c -*L*) and power efficiencyluminance (η_p -*L*) characteristics of each device are shown in Fig. 7. The key EL data are summarized in Table 2. As shown in Fig. 7(a), the device **D1** emits green light with the EL emission peak at 497 nm, while the device **D2** emits orange light with the EL emission peak at 579 nm, respectively. Both of them are close to the PL spectra of the **Ir1** and **Ir2** complexes in CH₂CL₂ solution, indicating that the EL emission of the devices originate from the triplet excited states of the phosphors. The EL emission spectra shapes are almost invariant of the current density and also do not show any concentration dependent. No emission from TAPC, mCP and TmPyPB suggests that the exciton was only formed in the emissive layers. The absence of the PPO21 emission demonstrates that the energy and charge transfer from the host excitons to the phosphors is complete upon electrical excitation. The CIE (Commission Internationale de l'Eclairage) color coordination are x = 0.18, y = 0.55 for D1, and x = 0.52, y = 0.47 for D2, corresponding to the green and orange region, respectively.

It can also be observed that the turn on voltages of the two devices are high (3.9 V for **D1** and 4.0 V for **D2**) though the dopants have good electron mobility, and the charge transport of TAPC/TmPyPb are also high. One reason is that the carrier

mobility of the host material PPO21 is very low ($\mu_h = 9 \times 10^{-6}$ cm² V⁻¹ s⁻¹ and $\mu_e = 3.0 \times 10^{-6}$ cm² V⁻¹ s⁻¹).⁶ Furthermore, the insertion of the mCP also would cause energy loss during the current flow. These two factors may lead to the high turn-on voltages of the devices.

Both devices show exciting performances at 8 wt% doped concentration. Respectively, the maximum current efficiency $(\eta_{c,max})$ and external quantum efficiency (EQE_{max}) of device **D1** are 74.8 cd A⁻¹ and 27.0 %, respectively, obtained at 7.2 V, the maximum power efficiency ($\eta_{p,max}$) is 33.4 lm W⁻¹ (6.9 V), and the maximum luminance (L_{max}) is 37270 cd m⁻² at 13.9 V. Device **D2** has a maximum luminance of 18146 cd m⁻² at 12.4 V and displays a maximum current efficiency of 41.0 cd A⁻¹ (6.9 V) with a maximum EQE of 13.9% and a maximum power efficiency of 18.7 lm W⁻¹ (6.5 V). Furthermore, the device D1 keeps high efficiency at relative high luminance and the roll-off of the efficiency is low. The current efficiencies and EQE for device **D1** at the brightness of 1000 cd m⁻² and 10000 cd m⁻² are 71.6 cd A⁻¹ (25.9%) and 46.2 cd A⁻¹ (16.7%), which indicates the complex Ir1 has encouraging application potential in OLEDs.

Compared with the complexes with the same cyclometalated ligand 2',6'-bis(trifluoromethyl)-2,4'-bipyridine (BTBP) main ligand and tetraphenylimidodiphosphinate (tpip) ancillary ligand in our former work (L_{max} : 52515 cd m⁻², $\eta_{c,max}$: 99.97 cd A⁻¹, $\eta_{p,max}$: 43.60 lm W⁻¹, *EQE*_{max}: 30.5%), ⁷ the device using Ir1 as the emitter performed lower performances because tpip resulted higher electron mobility $(5.11 - 5.29 \times 10^{-6} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1} \text{ under an}$ electric field from 1150 $(V \cdot cm^{-1})^{1/2}$ to 1300 $(V \cdot cm^{-1})^{1/2}$) than of 2-(5-(4-(trifluoromethyl)phenyl)-1,3,4-oxadiazol-2that yl)phenol (HCF₃POP).⁷ But the device performances are better that with Ir(III) complex containing 2-(4than (trifluoromethyl)phenyl)pyridine (4-tfmppy) or 2 - (2 trifluoromethyl)pyrimidine-pyridine (TPP) main ligands and HCF₃POP ancillary ligand (41.08 cd A⁻¹),¹⁰ suggesting BTBP ligand benefits better device performances than 4-tfmppy and TPP. However, the replacement of HCF₃POP by 2-(5-(4-(trifluoromethyl)phenyl)-1,3,4-thiadiazol-2-yl)phenol

(HCF₃POPTDZ) shifted the emission from green to orange area, which indicates that the variety of ancillary ligands would help to find more novel materials and adjust the device color.

The OLED using **Ir1** as the emitter exhibits better EL performance than that using **Ir2** as the emitter, the performances of OLEDs are attributed to not only the electron mobility of the iridium complexes but also the quantum efficiency. Although the electron mobility of the complex **Ir2** is better than that of **Ir1**, the quantum efficiency of **Ir2** is poorer than that of **Ir1**, which may cause the poor EL performance. The results show that the substituents of the ancillary ligand can influence the EL performances of the Ir(III) complexes. The introduction of S atom in the ancillary ligand can increase the electron mobility of the Ir(III) complexes, but it also decreases the PL yield and

shifts the peaks of PL and EL spectra to the orange area, all of these have an effect on the OLED performances.

The notable EL properties and EL efficiency roll-off effects of device D1 should be due to the application of 2-(5-(4-(trifluoromethyl)phenyl)-1,3,4-oxadiazol-2-yl)phenol as the ancillary ligand and 2',6'-bis(trifluoromethyl)-2,4'-bipyridine as the cyclometalated ligand. The dopant acts as the hole and elctron traps to retard the motion of both types of carriers. The lower LUMO level of the dopant is particularly important for the reason that the hole mobility of TAPC is higher than the electron mobility of TmPyPB in OLEDs,^{20(a)} the excition accumulation is expected in the hole blocking layer (TmPyPB) near the interface of the emitting layer (Ir1 : PPO21/ TmPyPB) due to the high energy barrier between TmPyPB and PPO21.25 The accumulation of exciton will cause the serious TTA, TPA of the Ir(III) complexes, and high efficiency roll-off consequently. In this case, the bipyridine and the 1,3,4oxadiazole units will benefit the electron transport properties. The good electron mobility of the phosphorescent emitter would facilitate the injection and transport of electrons, which broaden the recombination zone, balance the distribution of holes and electrons, particularly at the high doping concentration, leading to the suppressed the TTA, TPA effects and efficiency roll-off.²¹

Conclusions

In conclusion, two new heteroleptic iridium(III) complexes using 2',6'-bis(trifluoromethyl)-2,4'-bipyridine as the main ligand and 2-(5-(4-(trifluoromethyl)phenyl)-1,3,4-oxadiazol-2vl)phenol or 2-(5-(4-(trifluoromethyl)phenyl)-1,3,4-thiadiazol-2-yl)phenol as ancillary ligands were synthesized. Both complexes have a high electron mobility as that of a well-known electron transport material Alq₃. The OLEDs based on Ir1 and Ir2 with the structure ITO/TAPC (30 nm)/ mCP (10 nm)/ Ir complex (8 wt%): PPO21 (20 nm)/ TmPyPB (40 nm)/ LiF (1 nm)/ Al (100 nm) showed good performances. Especially, the device D1 with Ir1 as the emitter shows a maximum current efficiency of 74.8 cd A⁻¹, a maximum external quantum efficiency of 27.0%, a maximum power efficiency of 33.4 lm W⁻¹. Furthermore, the efficiency roll-off of **D1** from the peak value to that at the practical luminance is mild, which is helpful to obtain high efficiency at relatively high current density and high luminance. The study suggests that the 1,3,4-thiadiazol group would affect the PL spectra, the electron mobility, and the OLED performances of iridium(III) complexes.

Experimental section

Materials and measurements

All chemicals were commercial purchased without further purification. All the reactions were carried out under nitrogen atmosphere. ¹H NMR spectra were measured on a Bruker AM 500 spectrometer. Electrospray ionization mass spectra (ESI-MS) were obtained with ESI-MS (LCQ Fleet, Thermo Fisher Scientific). The high resolution mass spectra (HR EI-MS) were recorded on an Agilent 6540 UHD Accurate-Mass Q-TOF LC/MS. UV-vis absorption and photoluminescence (PL) spectra were measured on a Shimadzu UV-3100 and a Hitachi F-4600 spectrophotometer at room temperature, respectively. The luminescence quantum efficiencies were calculated by a comparison of the emission intensities (integrated areas) of a standard sample *fac*-Ir(ppy)₃ and the unknown samples in deaerated CH₂Cl₂ solutions of 5×10^{-5} mol/L.²⁶

X-ray crystallography

X-ray crystallographic measurements of the single crystals were carried out on a Bruker SMART CCD diffractometer (Bruker Daltonic Inc.) using monochromated Mo K α radiation ($\lambda = 0.71073$ Å) at room temperature. Cell parameters were retrieved using SMART software and refined using *SAINT*²⁷ program in order to reduce the highly redundant data sets. Data were collected using a narrow-frame method with scan width of 0.30° in ω and an exposure time of 5 s/frame. Absorption corrections were applied using *SADABS*²⁸ supplied by Bruker. The structures were solved by Patterson methods and refined by full-matrix least-squares on F^2 using the program *SHELXS-97.*²⁹ The positions of metal atoms and their first coordination spheres were located from direct-methods E-maps; other non-hydrogen atoms were found in alternating difference.

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 . All chemicals used for devices were sublimed in vacuum (2.0×10^{-4} Pa) prior to use. The deposition rate for organic compounds is 1-2 Å/s. The phosphor and host were co-evaporated from two separate sources. The cathode consisting of LiF/Al was deposited by evaporation of LiF with a deposition rate of 0.1 Å/s and then by evaporation of Al metal with a rate of 3 Å/s. The effective area of the emitting diode is 0.1 cm². The characteristics of the devices were measured with a computer controlled KEITHLEY 2400 source meter with a calibrated silicon diode in air without device encapsulation. On the basis of the uncorrected PL and EL spectra, the CIE coordinates were calculated using a test program of the Spectra scan PR650 spectrophotometer.

Syntheses.

The syntheses procedures of ligands were listed in Scheme 1. The cyclometallated ligand (2',6'-bis(trifluoromethyl)-2,4'bipyridine, BTBP), cyclometallated Ir(III) chloro-bridged dimer ([(BTBP)₂Ir(μ -Cl)]₂) and the ancillary ligands (HCF₃POP and HCF₃TDZ) were synthesized according to our previous report.^{9(a)(b),10} All reactions were performed under nitrogen. Solvents were carefully dried and distilled from appropriate drying agents prior to use.

General syntheses of complexes

The chloro-bridged dimer ([(BTBP)₂Ir(μ -Cl)]₂, 0.2 mmol) and the ancillary potassium salt (KCF₃POP or KCF₃TDZ, 0.5 mmol) in 2-ethoxyethanol (20 mL) was refluxed for 24 h. After the mixture was cooled, the solvent was evaporated at low pressure. The crude product was washed by water, and the column chromatography using CH₂Cl₂ as the eluent gave Ir(III) complexes which were further purified again by sublimation in vacuum.

Ir1. (yield: 48%): ¹H NMR (300 MHz, CDCl₃) δ 8.69 (d, J = 5.7 Hz, 1H), 8.15 (d, J = 7.8 Hz, 1H), 8.09 (d, J = 5.4 Hz, 2H), 8.04 (s, 1H), 7.93 – 7.79 (m, 5H), 7.75 (d, J = 8.4 Hz, 2H), 7.59 (dd, J = 8.2, 1.7 Hz, 1H), 7.20 (t, J = 6.8 Hz, 2H), 7.01 (t, J = 6.1 Hz, 1H), 6.64 (d, J = 8.4 Hz, 1H), 6.53 (t, J = 7.4 Hz, 1H). HR EI-MS *m*/*z* calcd for C₃₉H₁₈F₁₅IrN₆O₂: 1080.0959, found: 1081.0956 [M+H]⁺. Anal. Calcd for C₃₉H₁₈F₁₅N₆O₂Ir: C, 43.38; H, 1.68; N, 7.78. Found: C, 43.40; H, 1.71; N, 7.75.

Ir2. (yield: 53%): ¹H NMR (300 MHz, CDCl₃) δ 8.76 (d, J = 5.8 Hz, 1H), 8.13 (d, J = 8.2 Hz, 1H), 8.08 (d, J = 7.1 Hz, 2H), 8.05 (s, 1H), 7.91 – 7.78 (m, 3H), 7.66 (d, J = 8.4 Hz, 2H), 7.47 (d, J = 8.3 Hz, 2H), 7.23 – 7.11 (m, 3H), 6.96 (dd, J = 11.4, 5.4 Hz, 1H), 6.61 (d, J = 8.6 Hz, 1H), 6.52 – 6.40 (m, 1H). HR EI-MS: m/z calcd for C₃₉H₁₈F₁₅IrN₆OS: 1096.0731, found: 1097.0727 [M+H]⁺. Anal. Calcd for C₃₉H₁₈F₁₅N₆OSIr: C, 42.75; H, 1.66; N, 7.67. Found: C, 42.79; H, 1.62; N, 7.71.

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Notes and references

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- (a) K. Udagawa, H. Sasabe, C. Cai and J. Kido, *Adv Mater*, 2014, 26, 5062;
 (b) H. Shin, S. Lee, K. H. Kim, C. K. Moon, S. J. Yoo, J. H. Lee and J. J. Kim, *Adv Mater*, 2014, 26, 4730;
 (c) K. H. Kim, C. K. Moon, J. H. Lee, S. Y. Kim and J. J. Kim, *Adv Mater*, 2014, 26, 3844;
 (d) W. C. Choy, W. K. Chan and Y. Yuan, *Adv Mater*, 2014, 26, 5368.
- (a) L. Zhou, L. Li, Y. Jiang, R. Cui, Y. Li, X. Zhao and H. Zhang, ACS Appl Mater Interfaces, 2015, 7, 16046; (b) B. J. Powell, Coord. Chem. Rev., 2015, 295, 46; (c) X. Yang, G. Zhou and W. Y. Wong, Chem Soc Rev, 2015, 44, 8484; (d) Y. Yin, J. Yu, H. Cao, L. Zhang, H. Sun and W. Xie, Sci Rep, 2014, 4, 6754; (e) K. H. Kim, S. Lee, C. K. Moon, S. Y. Kim, Y. S. Park, J. H. Lee, J. Woo Lee, J. Huh, Y. You and J. J. Kim, Nat Commun, 2014, 5, 4769; (f) C. Fan and C. Yang, Chem Soc Rev, 2014, 43, 6439; (g) W. Y. Wong and C. L. Ho, J. Mater. Chem., 2009, 19, 4457; (h) W. Y. Wong and C. L. Ho, Coord.

Chem. Rev., 2009, **253**, 1709; (i) G. Zhou, W. Y. Wong and S. Suo, *J. Photochem. Photobio. C: Photochem. Rev.*, 2010, **11**, 133; (j) G. Zhou, W. Y. Wong and X. Yang, *Chem. Asian J.*, 2011, **6**, 1706.

- (a) J. Lee, H. F. Chen, T. Batagoda, C. Coburn, P. I. Djurovich, M. E. Thompson and S. R. Forrest, *Nat Mater*, 2016, **15**, 92; (b) J. B. Kim, S. H. Han, K. Yang, S. K. Kwon, J. J. Kim and Y. H. Kim, *Chem. Commun.*, 2015, **51**, 58; (c) J. Zhao, Y. Yu, X. Yang, X. Yan, H. Zhang, X. Xu, G. Zhou, Z. Wu, Y. Ren and W. Y. Wong, *ACS Appl Mater Interfaces*, 2015, **7**, 24703; (d) L. S. Cui, Y. Liu, X. Y. Liu, Z. Q. Jiang and L. S. Liao, *ACS Appl Mater Interfaces*, 2015, **7**, 11007; (e) L. Ying, C. L. Ho, H. Wu, Y. Cao and W. Y. Wong, *Adv. Mater.*, 2014, **26**, 2459; (f) X. Yang, G. Zhou and W. Y. Wong, *J. Mater: Chem. C*, 2014, **2**, 1760; (g) C. L. Ho, H. Li and W. Y Wong, *J. Organomet. Chem.*, 2014, **751**, 261; (h) X. Xu, X. Yang, J. Zhao, G. Zhou and W. Y Wong, *Asian J. Org. Chem.*, 2015, **4**, 394; (i) C. L. Ho and W. Y. Wong, *New J. Chem.*, 2013, **37**, 1665.
- (a) S. Lamansky, P. Djurovich, D. Murphy, F. Abdel-Razzaq, H. E. Lee, C. Adachi, P. E. Burrows, S. R. Forrest and M. E. Thompson, J. Amer. Chem. Soc., 2001, 123, 4304; (b) X. Yang, X. Xu, J. S. Dang, G. Zhou, C. L. Ho and W. Y. Wong, Inorg. Chem., 2016, 55, 1720; (c) G. Zhou, C. L. Ho, W. Y. Wong, Q. Wang, D. Ma, L. Wang, Z. Lin, T. B. Marder and A. Beeby, Adv. Funct. Mater., 2008, 18, 499; (d) S. Chen, G. Tan, W. Y. Wong and H. S. Kwok, Adv. Funct. Mater., 2011, 21, 3785; (e) C. L. Ho, Q. Wang, C. S. Lam, W. Y. Wong, D. Ma, L. Wang, Z. Q. Gao, C. H. Chen, K. W. Cheah and Z. Lin, Chem. Asian J., 2009, 4, 89; (f) C. L. Ho, B. Yao, B. Zhang, K. L. Wong, W. Y. Wong, Z. Xie, L. Wang and Z. Lin, J. Organomet. Chem., 2013, 730, 144; (g) C. L. Ho, L. C. Chi, W. Y. Hung, W. J. Chen, Y. C. Lin, H. Wu, E. Mondai, G. J. Zhou, K. T. Wong and W. Y. Wong, J. Mater. Chem. C, 2012, 22, 215; (h) G. J. Zhou, Q. Wang, W. Y. Wong, D. Ma, L. Wang and Z. Lin, J. Mater. Chem., 2009, 19, 1872.
- (a) Y. Zheng, A. S. Batsanov, M. A. Fox, H. A. Al-Attar, K. Abdullah, V. Jankus, M. R. Bryce and A. P. Monkman, *Angew. Chem. Int. Ed.*, 2014, **53**, 11616; (b) X. Xu, X. Yang, J. Dang, G. Zhou, Y. Wu, H. Li and W. Y. Wong, *Chem. Commun.*, 2014, **50**, 2473; (c) T. Yu, Y. Cao, W. Su, C. Zhang, Y. Zhao, D. Fan, M. Huang, K. Yue and S. Z. D. Cheng, *RSC Advances*, 2014, **4**, 554; (d) G. Li, D. Zhu, T. Peng, Y. Liu, Y. Wang and M. R. Bryce, *Adv. Funct. Mater.*, 2014, **24**, 7420.
- (a) W. S. Jeon, T. J. Park, S. Y. Kim, R. Pode, J. Jang and J. H. Kwon, *Appl. Phys. Lett.*, 2008, 93, 063303; (b) G. J. Zhou, W. Y. Wong, B. Yao, Z. Xie and L. Wang, *J. Mater. Chem.*, 2008, 18, 1799.
- Q.-L. Xu, X. Liang, S. Zhang, Y.-M. Jing, X. Liu, G.-Z. Lu, Y.-X. Zheng and J.-L. Zuo, *J. Mater. Chem. C*, 2015, 3, 3694.
- 8. Y. Tao, C. Yang and J. Qin, Chem. Soc. Rev., 2011, 40, 2943.
- 9. (a) Y.-M. Jing, C.-C. Wang, L.-S. Xue, T.-Y. Li, S. Zhang, X. Liu, X. Liang, Y.-X. Zheng and J.-L. Zuo, *J. Organomet.Chem.*, 2014, **765**, 39;
 (b) Z. He, W. Y. Wong, X. Yu, H. S. Kwok and Z. Lin, *Inorg. Chem.*, 2006, **45**, 10922;
 (c) W. Y. Wong, Z. He, S. K. So, K. L. Tong and Z. Lin, *Organometallics*, 2005, **24**, 4079.
- (a) H.-Y. Li, T.-Y. Li, M.-Y. Teng, Q.-L. Xu, S. Zhang, Y.-M. Jin, X. Liu, Y.-X. Zheng and J.-L. Zuo, *J. Mater. Chem. C*, 2014, **2**, 1116; (b) X. Liu, S. Zhang, Y.-M. Jin, G.-Z. Lu, L. Jiang, X. Liang, Q.-L. Xu

and Y.-X. Zheng, J. Organomet. Chem., 2015, 785, 11-18.

- (a) T. Hofbeck and H. Yersin, *Inorg. Chem.*, 2010, **49**, 9290; (b) E.
 E. Langdon-Jones, A. J. Hallett, J. D. Routledge, D. A. Crole, B. D.
 Ward, J. A. Platts and S. J. Pope, *Inorg. Chem.*, 2012, **52**, 448; (c) S. K. Leung, K. Y. Kwok, K. Y. Zhang and K. K.-W. Lo, *Inorg. Chem.*, 2010, **49**, 4984; (d) M. Tavasli, T. N. Moore, Y. Zheng, M. R. Bryce,
 M. A. Fox, G. C. Griffiths, V. Jankus, H. A. Al-Attar and A. P.
 Monkman, *J. Mater. Chem.*, 2012, **22**, 6419.
- (a) M. A. Baldo, C. Adachi and S. R. Forrest, *Phys. Rev. B*, 2000, 62, 10967;
 (b) E. B. Namdas, A. Ruseckas, I. D. Samuel, S.-C. Lo and P. L. Burn, *Appl. Phys. Lett.*, 2005, 86, 91104.
- P. Brulatti, R. J. Gildea, J. A. Howard, V. Fattori, M. Cocchi and J. G. Williams, *Inorg. Chem.*, 2012, **51**, 3813.
- 14. (a) L.Q. Chen, C. L. Yang, M. Li, J. G. Qin, J. Gao, H. You and D.G. Ma, *Crystal Growth & Design*, 2007, 7, 39; (b) L. Q. Chen, H. You, C. L. Yang, D. G. Ma and J. G. Qin, *Chem. Comm.*, 2007, 13, 1352; (c) Z. W. Xu, Y. Li, X. M. Ma, X. D. Gao and H. Tian, *Tetranhedron*, 2008, 64, 1860; (d) Y. H. Zheng, A. S. Batsanov and M. R. Bryce, *Inorg. Chem.*, 2011, 50, 3354.
- (a) B. W. D'Andrade, S. Datta, S. R. Forrest, P. Djurovich, E. Polikarpov and M. E. Thompson, *Org. Electron.*, 2005, 6, 11; (b) E. Runge and E. K. U. Gross, *Phys. Rev. Lett.*, 1984, 52, 997; (c) A. D. Becke, *J. Chem. Phys.*, 1993, 98, 5648; (d) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, 37, 785.
- (a) M. M. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. DeFrees and J. A. Pople, *J. Chem. Phys.*, 1982, 77, 3654; (b) P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, 82, 299.
- 17. V. Barone and M. Cossi, J. Phys. Chem. A, 1988, 102, 1995.
- 18. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian 09, Revision A.01, Gaussian, Inc., Wallingford, CT, 2009.
- (a) C. Dragonetti, L. Falciola, P. Mussini, S. Righetto, D. Roberto, R. Ugo and A. Valore, *Inorg. Chem.*, 2007, 46, 8533; (b) J. Zhang, L. Zhou, H. A. Al-Attar, K. Shao and L. Wang, *Adv. Funct. Mater.*, 2013, 23, 4667.
- 20. (a) H. Fong, K. Lun and S. So, *Chem. Phys. Lett.*, 2002, 353, 407;
 (b) S. Heun and P. Borsenberger, *Chem. Phys.*, 1995, 200, 245.
- 21. J. Kalinowski, W. Stampor, J. Mężyk, M. Cocchi, D. Virgili, V. Fattori and P. Di Marco, *Phys. Rev. B*, 2002, **66**, 235321.

- 22. (a) M.-Y. Teng, S. Zhang, S.-W. Jiang, X. Yang, C. Lin, Y.-X. Zheng, L. Wang, D. Wu, J.-L. Zuo and X.-Z. You, *Appl. Phys. Lett.*, 2012, 100, 073303; (b) S. Tse, H. Fong and S. So, *J. Appl. Phys.*, 2003, 94, 2033.
- 23. (a) A. Pal, R. Österbacka, K.-M. Källman and H. Stubb, *Appl. Phys. Lett.*, 1997, **71**, 228; (b) H. Scher and E. W. Montroll, *Phys. Rev. B*, 1975, **12**, 2455.
- 24. P. Borsenberger, L. Pautmeier, R. Richert and H. Bässler, *J. Chem. Phys.*, 1991, **94**, 8276.
- 25. I. D. Parker, J. Appl. Phys., 1994, 75, 1656.
- 26. T. Hofbeck and H Yersin, Inorg. Chem., 2010, 49, 9290.
- 27. *SAINT-Plus*, version 6.02, Bruker Analytical X-ray System, Madison, WI, 1999.
- 28. G. M. Sheldrick, *SADABS An empirical absorption correction program*, Bruker Analytical X-ray Systems, Madison, WI, 1996.
- 29. G. M. Sheldrick, *SHELXTL-97*, Universität of Göttingen, Göttingen, Germany, 1997.

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Graphical abstract



Highly efficient OLEDs based on green and orange iridium(III) complex based on 2',6'-bis(trifluoromethyl)-2,4'-bipyridine and 2-(5-(4-(trifluoromethyl)phenyl)-1,3,4-oxadiazol-2-yl)phenol show peak current efficiencies of 74.8 and 41.0 cd· A^{-1} , respectively, with low efficiency roll-off.