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Homoleptic thiazole-based Ir^{III} phosphorescent complexes for achieving both high EL efficiencies and optimized trade-off among key parameters of solution-processed WOLEDs[†]

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[†] Electronic supplementary information (ESI) available: EL data including EL spectra, *J-V-L* and EL efficiency curves.

Abstract

Two homoleptic thiazole-based Ir^{III} phosphorescent emitters **Ir-3Tz1F** and **Ir-3Tz2F** with fluorinated 2-phenylthiazole-type ligands have been designed and prepared. Their thermal stability, photophysical and electrochemical properties as well as electroluminescent (EL) performances in both monochromic OLEDs and solution-processed WOLEDs have been investigated. Doped in monochromic OLEDs made by vacuum deposition, **Ir-3Tz1F** gave the maximum EL efficiencies with η_L of 56.2 cd A⁻¹, η_{ext} of 15.8% and η_p of 50.2 lm W⁻¹. Critically, solution-processed WOLEDs based on **Ir-3Tz1F** with three primary colors can achieve excellent trade-off among stable balanced white EL spectra, high EL efficiency and high color rendering index (CRI). The optimized solution-processed WOLED can exhibit very attractive EL efficiencies of 33.4 cd A⁻¹, 16.5% and 30.6 lm W⁻¹ while maintaining both high CRI of *ca*. 80 and very stable Commission Internationale de L'Eclairage (CIE) coordinates in a wide driving voltage range from 4 V to 11 V.

Introduction

Regarded as a hybrid of electron-deficient pyridyl moiety and electron-rich thiophenyl ring.¹ thiazolyl group can afford distinct electronic features to tune the photophysical properties of the phosphorescent Ir^{III}/Pt^{II} 2-phenylpyridine (ppy) type complexes bearing thiazole-based ligands, since the emission color, phosphorescent quantum yield (Φ_P), phosphorescent lifetime (τ_P) and charge carrier injection/transporting properties of these phosphorescent (triplet) complexes can be greatly affected by the electronic structures of the chelated organic ligands.²⁻¹⁰ All of these photophysical properties can play critical role in optimizing electroluminescent (EL) performances of the concerned phosphorescent (triplet) complexes in organic light-emitting diodes (OLEDs), which can show great potential in developing both new-generation flat panel displays and future energy-saving lighting sources.¹¹⁻¹⁵ More commonly, it is the benzothiazole rather than thiazole group that has been employed to construct the ligands of phosphorescent Ir^{III}/Pt^{II} ppy-type complexes.^{3,16} Quite a number of benzothiazole-based Ir^{III} ppy-type triplet emitters have been developed to show high EL efficiencies.¹⁷⁻²² Furthermore, some functional groups, such as carbazole,²¹ dibenzothiophene-S,S-dioxide¹⁸ and triphenylphosphoryl unit,¹⁸ have also been introduced to furnish carrier injection/transporting capabilities to the concerned benzothiazole-based Ir^{III} ppy-type triplet emitters to optimize their EL performances.

Recently, thiazole group has been introduced to ppy-type ligands to develop thiazole-based phosphorescent Ir^{III}/Pt^{II} emitters.²³⁻²⁶ We have prepared ppy-type triplet emitters with either 2-naphthylthiazole-type²³ or 2-phenylthiazole-type²⁵ ligands. It has been shown that the phosphorescence color of the complexes can be tuned by the substitution position of the thiazole unit on the naphthalene²³ and the fluorine group attached to the ligands.²⁵ Furthermore, substitution position of the thiazole unit can also exert great influence on the EL efficiencies of

the naphthylthiazole-type phosphorescent Ir^{III}/Pt^{II} emitters.²³ In addition, the functional groups, such as triphenylamine (TPA)²⁴ and carbazole,²⁶ have also been combined with thiazole to prepare novel thiazole-based ligands, which have chelated with Ir^{III} center to develop functionalized phosphorescent emitters with attractive EL performances. All of these results indicate the great potential of the thiazole-based phosphorescent emitters in the field of OLEDs. Unfortunately, they are relatively rare and generally with the heteroleptic configuration.

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Due to the inherent electronic features associated with thiazole unit, thiazole-based phosphorescent Ir^{III} emitters typically exhibit bathochromic effect in phosphorescent wavelength with respect to that of their pyridine-based analogues.^{24,26} So, they generally emit orange/yellow phosphorescence, which can be coupled with blue emission to construct white organic light-emitting diodes (WOLEDs) of complementary colors.²⁴ The thiazole-based phosphorescent Ir^{III} emitters bearing TPA functional group have been applied to complementary color WOLEDs showing decent EL efficiencies.²⁴ However, the white EL spectra for the concerned WOLEDs vary markedly under different driving voltages to lead to great variation of both Commission Internationale de L'Eclairage (CIE) coordinates and color rendering index (CRI).²⁴ Some WOLEDs with single emission layer also show the voltage-dependent white EL spectra.^{27,28} In addition, there is a trade-off issue between the luminous efficiency and color quality for white emission from WOLEDs. This means that the trichromatic WOLEDs with red, green and blue (R-G-B) emitters typically have a better color quality but lower EL efficiency.¹⁵ All these issues are really undesirable for the practical application of WOLEDs as new energy-saving lighting sources. So, it is indeed necessary to develop new thiazole-based phosphorescent emitters with diverse properties and structures to cope with the critical problems in the field of OLEDs, especially those associated with WOLEDs. So, in this paper, two homoleptic phosphorescent

thiazole-based ppy-type Ir^{III} emitters have been developed to furnish not only highly efficient monochromic OLEDs, but also to address the optimized trade-off in solution-processed WOLEDs with single doped emission layer.

Experimental Section

Spectroscopy

UV/Vis spectra were recorded with a Shimadzu UV-2250 spectrophotometer. The steady-state photoluminescent (PL) properties of the complexes were measured with Edinburgh FLS920 fluorometers. The phosphorescence quantum yields (Φ_P) were determined in degassed CH₂Cl₂ solution at 298 K against the *fac*-[Ir(ppy)₃] standard ($\Phi_P = 0.40$).²⁹ The lifetimes were measured with a single photon counting spectrometer from Edinburgh Instruments (FLS-920) with a picosecond pulse LED excitation source. The data analysis was conducted by iterative convolution of the luminescence decay profile with the instrument response function using the software package provided by Edinburgh Instruments. DSC was performed with a NETZSCH DSC 200 PC unit under a nitrogen flow at a heating rate of 10 °C min⁻¹. TGA was conducted with a NETZSCH STA 409C instrument under nitrogen with a heating rate of 20 °C min⁻¹. Fast Atom Bombardment (FAB) mass spectra were recorded with a Finnigan MAT SSQ710 system.

Cyclic voltammetry studies

Electrochemical measurements were performed using a Princeton Applied Research 2273A potentiostat. Cyclic voltammetry (CV) of the sample solutions was performed at a scan rate of 100 mV s⁻¹ using a glassy carbon working electrode, a platinum counter electrode, and a platinum-wire reference electrode. The solvent was deoxygenated acetonitrile, and the supporting electrolyte was 0.1 m [nBu_4N][BF₄]. Ferrocene (Fc) was added as a calibrant after

each set of measurements, and all potentials reported were quoted with reference to the ferrocene/ferrocenium (Fc/Fc⁺) couple. The HOMO energy level was obtained by using the equations $E_{\text{HOMO}} = -(E_a + 4.8) \text{ eV}.^{30}$ However, the LUMO energy level was determined from $E_{\text{LUMO}} = (E_g + E_{\text{HOMO}})$ eV (E_g : optical band gap derived from the absorption onset in UV UV/Vis spectra).

Synthesis

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All reactions were conducted under a nitrogen atmosphere and no special precautions were required during workup. Solvents were carefully dried and distilled from appropriate drying agents prior to use. Commercially available reagents were used without further purification unless otherwise stated. All reactions were monitored by TLC with Merck pre-coated aluminum plates. Flash column chromatography was carried out using silica gel (200–300 mesh). [Ir(acac)₃], organic boric acid and 2-bromothiazole were purchased from Sigma-Aldrich. Organic ligands L1 and L2 were prepared by our published strategy.²⁵ The red phosphorescent emitter Ir-G1 was obtained from our laboratory and its preparation detail was provided in our previous paper.³¹

Typical procedure for synthesizing complexes Ir-3Tz1F and Ir-3Tz2F

Under a N₂ atmosphere, the corresponding organic ligand (3.5 equiv.) and $[Ir(acac)_3]$ (1.0 equiv.) were added to glycerol. The resulting mixture was stirred at *ca.* 220 °C for 10 h. After completion of the reaction, 1.0 M aqueous hydrochloric acid was added to the solution, resulting in precipitation of the colored crude product which was filtered, washed with water and dried at 100 °C under vacuum. The purification of the product was made by silica gel column chromatography eluting with CH₂Cl₂/hexane (2:1, v/v). The concerned complex was obtained as a yellow solid.

Ir-3Tz1F: Yield: 31%. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.50 (dd, J = 8.4 Hz, 5.6 Hz, 3H, Ar), 7.11 (d, J = 3.2 Hz, 3H, Ar), 6.80 (d, J = 3.6 Hz, 3H, Ar), 6.62-6.57 (m, 3H, Ar), 6.48 (d, J = 2.4 Hz, 3H, Ar). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 177.20, 165.33, 162.81, 159.45, 159.39, 139.48, 136.74, 126.03, 125.93, 122.80, 122.63, 116.61, 107.98, 107.74. ¹⁹F NMR (376 MHz, CDCl₃): δ (ppm) –110.36 (s, 3F). FAB-MS: m/z = 727 [M]⁺. C₂₇H₁₅F₃IrN₃S₃: calcd. C 44.62, H 2.08, N 5.78; found C 44.48, H 2.12, N 5.69.

Ir-3Tz2F: Yield: 27%. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.30 (dd, J = 3.2 Hz, 3H, Ar), 6.89 (t, J = 1.6 Hz, 3H, Ar), 6.46 (dd, J = 8.8 Hz, 17.2Hz, 3H, Ar), 6.38 (dd, J = 2Hz, 9.2 Hz, 3H, Ar). ¹³C NMR (100MHz, CDCl₃): δ (ppm) 176.16, 164.71, 159.93, 159.87, 139.87, 137.75, 126.92, 126.82, 121.75, 121.59, 120.25, 108.09, 107.85. ¹⁹F NMR (376 MHz, CDCl₃): δ (ppm) –106.50 (d, 1F), –108.91 (d, 1F). FAB-MS: m/z = 781 [M]⁺. C₂₇H₁₂F₆IrN₃S₃: calcd. C 41.53, H 1.55, N 5.38; found C 41.37, H 1.39, N 5.27.

OLED fabrication and measurements

The pre-cleaned ITO glass substrates were treated with ozone for 20 min. The thin MoO₃ layer was deposited on the surface of ITO glass to form a 4 nm-thick hole-injection layer. Then, 50 nm-thick layer of CBP with 15 nm local doping zone was constructed to serve as both hole-transporting and emission layers. After that, TPBi (40 nm), LiF (1 nm) and Al cathode (100 nm) were successively evaporated. For the fabrication of WOLEDs, the PEDOT:PSS was firstly deposited on the treated ITO glass by spin-coating strategy. Then, the coated ITO glass was dried at *ca*. 100 °C for 1 h. The chloroform solution containing host materials and emitters was spin coated with a concentration of *ca*. 10 mg/mL. After drying at *ca*. 50 °C for 0.5 h, other functional layers of TPBi (40 nm), LiF (1 nm) and Al cathode (100 nm) were successively evaporated. All the evaporation processes were conducted at a base pressure less than 10^{-6} Torr.

The EL spectra and CIE coordinates were measured with a PR650 spectra colorimeter. The J-V-L curves of the devices were recorded by a Keithley 2400/2000 source meter and the luminance was measured using a PR650 SpectraScan spectrometer. All the experiments and measurements were carried out under ambient conditions.

Computational details

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Density functional theory (DFT) calculations using the B3LYP were performed for all the Ir^{III} complexes and their geometries were obtained by theoretical optimization during the computation. The basis set used for C, H, F, N and O atoms was 6-31G while effective core potentials with a LanL2DZ basis set were employed for S and Ir atom.^{32,33} The energies of the excited states of the complexes were computed by time-dependent (TD) DFT (TD-DFT) based on all the ground-state geometries. All calculations were carried out using the Gaussian 09 program.³⁴ Mulliken population analyses were performed using MullPop.³⁵ Frontier molecular orbitals obtained from the DFT calculations were plotted using the Molden 3.7 program.³⁶

Results and Discussion

Synthesis and Characterization

The synthetic procedure for the thiazole-based homoleptic Ir^{III} ppy-type phosphorescent emitters is shown in Scheme 1. In order to prepare the complexes, organic ligands L1 and L2 should be synthesized firstly via Suzuki cross-coupling reaction between 2-bromothiazole and the corresponding fluorinated phenyl boronic acid with Pd(PPh₃)₄ as the catalyst. With the aim to tune the maximum phosphorescent wavelength of the complexes, fluorine substituent has been introduced to the organic ligands. All the ligands can be easily obtained in good yields over 80%. After obtaining the organic ligands, the two homoleptic phosphorescent Ir^{III} complexes were prepared according to the well-established one-pot strategy by the cyclometalation of

 $[Ir(acac)_3]$ (acac: acetylacetone anion) with the corresponding organic ligands in glycerol at *ca*. 220 °C.^{4,23,24} The homoleptic Ir^{III} complexes were purified by silica-gel chromatography in high purity as air-stable yellow powders.

In the ¹H NMR spectra of the two homoleptic Ir^{III} complexes, only one set of signals assigned to the protons of the three thiazole-based ligands, corresponding to the *fac*-isomers, were obtained for both **Ir-3Tz1F** and **Ir-3Tz2F**. In the ¹⁹F NMR spectrum of **Ir-3Tz1F**, the single resonance peak at *ca*. –110.36 ppm indicates the only -F group on the chelated phenyl ring of the thiazole-based ligand. For **Ir-3Tz2F**, the two sets of double resonance peaks at *ca*. –106.50 ppm and –108.91 ppm in its ¹⁹F NMR spectrum are consistent with the fluoro-substitution pattern of its ligand as well.



Scheme 1 Synthetic sketches for the thiazole-based phosphorescent Ir^{III} complexes Ir-3Tz1F and Ir-3Tz2F.

Thermal and Photophysical Properties

The thermal properties of the thiazole-based phosphorescent Ir^{III} complexes had been

characterized by both thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) under a nitrogen flow. The TGA results show the obvious decomposition process occurs at ca. 380 °C for Ir-3Tz1F and 365 °C for Ir-3Tz2F (Table 1 and Figure S1a in Electronic Supplementary Information (ESI)), which is much higher than their heteroleptic counterparts.²⁵ However, it seems that slight decomposition of Ir-3Tz2F begins at *ca.* 160 °C (Figure S1a), indicating its poorer stability with respect to that of Ir-3Tz1F. This might be ascribed to the higher molecular activity of Ir-3Tz2F induced by the multiple highly polar C-F bonds.³⁷ The DSC traces for the homoleptic thiazole-based Ir^{III} complexes indicate the high glass-transition temperatures (T_{o}) of ca. 215 °C for **Ir-3Tz1F** (Table 1 and Figure S1b). However, it appears that Ir-3Tz2F exhibits one exothermic process at *ca*. 165 °C and an endothermic process at *ca*. 220 °C, respectively (Figure S1b). With respect to the TGA curve for Ir-3Tz2F (Figure S1a), the former exothermic process should be induced by the slight decomposition of Ir-3Tz2F. Similar to that of Ir-3Tz1F, the glass-transition event occurring at *ca.* 220 °C for Ir-3Tz2F can be related to the distortion of the whole rigid molecular skeleton.

Both of the homoleptic thiazole-based Ir^{III} complexes show two distinct absorption bands in their UV-Vis spectra (Figure 1 and Table 1). The high-energy strong UV absorption bands before 310 nm should be induced by the spin-allowed $S_1 \leftarrow S_0$ transitions of the organic ligands. On the contrary, the weaker and low-energy absorption located beyond 310 nm can be assigned to charge transfer (CT) transitions in both singlet and triplet states. Obviously, the energy level for the CT absorption bands falls in the order of **Ir-3Tz1F** < **Ir-3Tz2F** (Figure 1).

Upon UV light irradiation at 360 nm, both of the homoleptic thiazole-based Ir^{III} complexes emit strong phosphorescence in CH₂Cl₂ (Figure 1 and Table 1). Their photoluminescence (PL) spectra display double-peak pattern (Figure 1). Clearly, the high-energy phosphorescent

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emission bands (*ca.* 529 nm for **Ir-3Tz1F** and 507 nm for **Ir-3Tz2F**) exhibit unstructured line-shape, while the low-energy ones (*ca.* 555 nm for **Ir-3Tz1F** and 533 nm for **Ir-3Tz2F**) show well-structured line-shape (Figure 1 and Table 1). The triplet/phosphorescent character of these emission bands have been supported by the long lifetime in the order of microsecond for the associated excited states.



Fig. 1 UV-vis and photoluminescence (PL) spectra for the homoleptic thiazole-based phosphorescent Ir^{III} complexes.

Table 1 Photophysical and thermostability data for the homoleptic thiazole-based Ir^{III} complexes.

Absorption	Emission	${{oldsymbol{\Phi}_{\mathrm{P}}}^{c}}$	${ au_{ m P}}^d$	$T_{\rm d}/T_{\rm g}$
$\lambda_{abs} (nm)^{a}$	$\lambda_{em} (nm)^{b}$		(µs)	(°C)
298 K	298 K			
249 (4.67), 281 (4.67), 303 (4.57),	525, 555	0.29	0.73 (525 nm),	380/215
364 (4.14), 402 (3.92), 434 (3.83)			1.61 (555 nm)	
270 (4.71), 283 (4.66), 295 (4.59),	508, 533	0.28	1.20 (507 nm),	365/220
343 (4.20), 382 (4.01), 418 (3.51)			1.33 (533 nm)	
	Absorption λ_{abs} (nm) ^{<i>a</i>} 298 K 249 (4.67), 281 (4.67), 303 (4.57), 364 (4.14), 402 (3.92), 434 (3.83) 270 (4.71), 283 (4.66), 295 (4.59), 343 (4.20), 382 (4.01), 418 (3.51)	$\begin{array}{llllllllllllllllllllllllllllllllllll$	AbsorptionEmission $\Phi_{\rm P}^{\ c}$ $\lambda_{\rm abs} (\rm nm)^{\ a}$ $\lambda_{\rm em} (\rm nm)^{\ b}$ 298 K298 K298 K298 K249 (4.67), 281 (4.67), 303 (4.57), 525, 5550.29364 (4.14), 402 (3.92), 434 (3.83)270 (4.71), 283 (4.66), 295 (4.59), 508, 5330.28343 (4.20), 382 (4.01), 418 (3.51)508, 5330.28	$\begin{array}{c cccc} Absorption & Emission & \varPhi_{P}{}^{c} & \tau_{P}{}^{d} \\ \lambda_{abs} \left(nm\right)^{a} & \lambda_{em} \left(nm\right)^{b} & (\mu s) \\ \hline 298 \ K & 298 \ K & \\ \hline 249 \ (4.67), \ 281 \ (4.67), \ 303 \ (4.57), & 525, 555 & 0.29 & 0.73 \ (525 \ nm), \\ 364 \ (4.14), \ 402 \ (3.92), \ 434 \ (3.83) & 1.61 \ (555 \ nm) \\ 270 \ (4.71), \ 283 \ (4.66), \ 295 \ (4.59), & 508, 533 & 0.28 & 1.20 \ (507 \ nm), \\ 343 \ (4.20), \ 382 \ (4.01), \ 418 \ (3.51) & 1.33 \ (533 \ nm) \\ \hline \end{array}$

^{*a*} Measured in CH₂Cl₂ at a concentration of 10⁻⁵ M, and log ε values are shown in parentheses. ^{*b*} Measured in CH₂Cl₂ at a concentration of 10⁻⁵ M. ^{*c*} In degassed CH₂Cl₂ relative to *fac*-[Ir(ppy)₃] ($\Phi_{\rm P} = 0.40$), $\lambda_{\rm ex} = 360$ nm. ^{*d*} Measured in degassed CH₂Cl₂ solutions at a sample concentration of *ca*. 10⁻⁵ M, and the excitation wavelength was set at 355 nm for all the samples at 298 K.

In order to interpret the photophysical results aforementioned of these homoleptic thiazole-based phosphorescent Ir^{III} complexes, DFT calculations have been carried out and the

results are shown in Figure 2 and Table 2. The DFT calculation results indicate that the lowest-energy transitions correspond to HOMO \rightarrow LUMO (H \rightarrow L) transitions with non-zero oscillator strengths for the S₁ states of the two homoleptic thiazole-based Ir^{III} complexes. However, transitions HOMO \rightarrow LUMO (H \rightarrow L), HOMO \rightarrow LUMO+1 (H \rightarrow L+1), the HOMO-2 \rightarrow LUMO (H-2 \rightarrow L) and HOMO-2 \rightarrow LUMO+1 (H-2 \rightarrow L+1) represent features of their T_1 states (Table 2), which are responsible for the phosphorescence in the two homoleptic thiazole-based Ir^{III} complexes. As indicated by the noticeably different contribution to the HOMO/HOMO-2 and LUMO/LUMO+1 from the metal d_{π} orbitals (Table 2 and Figure 2), the lowest-energy excited states S₁ and T₁ show obvious metal-to-ligand charge transfer (MLCT) features. In addition, the intra-ligand charge transfer (ILCT) features from phenyl ring to the thiazole unit can also be seen according to the distribution patterns of the critical transitions corresponding to the characters of the lowest-energy excited states S_1 and T_1 (Figure 2). Hence, it can be concluded that the S₁ and T₁ states associated with the two homoleptic thiazole-based Ir^{III} complexes should consist of mixed MLCT and ILCT states. So, the weak CT absorption bands in the UV-Vis spectra of Ir-3Tz1F and Ir-3Tz2F are induced by singlet and triplet MLCT states (¹MLCT and ³MLCT) as well as those of ILCT states (¹ILCT and ³ILCT).

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Owing to the large contribution form the metal d_{π} orbitals to both HOMO and HOMO-2 of the homoleptic thiazole-based Ir^{III} complexes (Figure 2 and Table 2), the molecular orbitals (MO) of the organic ligands and metal center are mixed effectively to induce strong spin–orbit coupling effects. So, triplet absorption bands with the feature of both ³MLCT and ³ILCT, which induce the phosphorescent emission at 298 K (Figure 1). According to the established relationship between T₁ character and line-shape of phosphorescent spectra for Ir^{III} complexes,^{3,4} the high-energy broad and featureless phosphorescent band of the homoleptic thiazole-based Ir^{III}

complexes can be assigned the radiative decay of the ³MLCT states, while the low-energy sharp phosphorescent band should come from the emissive decay of the ligand-centered ³ILCT states (Figure 1) due to its vibronic fine structure observed at low temperature of 77 K (Figure S1c). Owing to the close energy-levels for ³MLCT and ³ILCT states (Figure 1), there should be a competition between their radiative decay processes. So, Ir-3Tz1F and Ir-3Tz2F exhibit dual emission bands (Figure 1), typically observed in ppy-type Ir^{III} phosphorescent complexes.^{3,4} Similar to those of their analogues in the literature,^{23,24} the HOMO and HOMO-2 for both **Ir-3Tz1F** and **Ir-3Tz2F** are mainly located on the d_{π} orbitals of Ir^{III} center and the π orbitals of the phenyl rings. Hence, introducing strongly electron-withdrawing -F group to the phenyl ring will stabilize the HOMO and HOMO-2 and lower their energy levels, which should increase the energy associated with the transitions corresponding to the T_1 states and elevate their energy level. Hence, Ir-3Tz1F should possess T1 states with lower energy level to induce phosphorescence with longer wavelength with respect to that of Ir-3Tz2F, which has been shown by the PL spectra of the homoleptic thiazole-based Ir^{III} complexes (Figure 1 and Table 1). So, there is a good consistence between the experimental results and theoretical calculations.

	Contribution	Contribution	Largest coefficient in	Largest coefficient in	Oscillator
Compound	of metal d_{π} orbitals ^{<i>a</i>}	of metal d_{π} orbitals ^{<i>a</i>}	the CI expansion of	the CI expansion of the	strength (f) of
Compound			the T_1 state ($S_0 \rightarrow T_1$)	S_1 state ($S_0 \rightarrow S_1$	the $S_0 \rightarrow S_1$
			excitation energy) ^b	excitation energy) ^b	transition
			$H \rightarrow L: 0.34777$		
			24.2%		
			$H \rightarrow L+1: 0.22311$	$H \rightarrow L: 0.67760$	
	HOMO-2: 21.3%	LUMO+1: 3.4%	10.0%	91.8%	
Ir-3Tz1F			$H-2 \rightarrow L: 0.25445$	$H \rightarrow L+1: 0.15807$	0.0407
	HOMO: 37.1%	LUMO: 1.5%	12.9%	5.0%	
			$H-2 \rightarrow L+1: 0.25584$	(402 nm)	
			13.1%		
			(489 nm)		
			$H \rightarrow L: 0.30468$		
			18.6%		
			$H \rightarrow L+1$: -0.21271	$H \rightarrow L: 0.66742$	
	HOMO-2: 23.9%	LUMO+1: 3.6%	9.05%	89.1%	
Ir-3Tz2F			$H-2 \rightarrow L: 0.30397$	$H \rightarrow L+1: -0.18832,$	0.0420
	HOMO: 38.1%	LUMO: 1.6%	18.5%	7.1%	
			$\text{H-2} \rightarrow \text{L+1:} -0.27530$	(381 nm)	
			15.2%		
			(470 nm)		

Table 2 Contribution of the metal d_{π} orbitals to the key frontier molecular orbitals together with the TD-DFT calculation results.

^{*a*} Data were obtained by exporting DFT results with the software AOMix.

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^b H→L represents the HOMO to LUMO transition. CI stands for configuration interaction.



Fig. 2 Key frontier molecular orbitals corresponding to the important transition processes in (a) **Ir-3Tz1F** and (b) **Ir-3Tz2F**

Electrochemical Characterization

The electrochemical properties of the two homoleptic thiazole-based Ir^{III} complexes were investigated by cyclic voltammetry (CV) calibrated with ferrocene as the internal standard under a nitrogen atmosphere. Both of the complexes show a reversible oxidation couple (E_a) at ca. 0.61 V for Ir-3Tz1F and 0.72 V for Ir-3Tz2F (Table 3). With two -F groups on the phenyl ring of the ligand, the oxidation potential of Ir-3Tz2F moves markedly to the more positive region due to the stabilization effect to the HOMOs induced by the -F groups (vide infra). The reduction potentials (E_c) for the two complexes are located at ca. -2.56 V for Ir-3Tz1F and -2.14 V for Ir-3Tz2F (Table 3). From the MO patterns of the thiazole-based Ir^{III} complexes, it can be seen clearly that the phenyl rings of the organic ligands also give large contribution to their LUMOs (Figure 2). As a result, introducing more -F groups with strongly electron-withdrawing ability to the phenyl rings of the organic ligands should lower the LUMO levels of the thiazole-based Ir^{III} complexes and make them easier to be reduced. So, Ir-3Tz2F possesses E_c at the less negative potential region with respect to Ir-3Tz1F (Table 3). The irreversibility for the reduction process of the complexes can be ascribed to its character that is more susceptible to other environmental factors. The irreversible reduction processes of the two complexes during the cathodic sweep make their LUMO levels poorly reliable based on electrochemistry measurements. Therefore, we calculated their LUMO levels from the optical gap (E_g) .

	en prop e rne			Cype compression
Compound	$E_{\rm a}({\rm V})$	$E_{\rm c}$ (V)	HOMO $(eV)^{c}$	LUMO $(eV)^d$
Ir-3Tz1F	0.61 ^{<i>a</i>}	-2.56^{b}	-5.41	-3.01
Ir-3Tz2F	0.72^{a}	-2.14^{b}	-5.52	-3.43

Table 3 Redox properties of the thiazole-based Ir^{III} ppy-type complexes.

^{*a*} Reversible. The value was set as $E_{1/2}$. ^{*b*} Irreversible. The value was derived from the cathodic peak potential. ^{*c*} HOMO levels were calculated according to the equation HOMO = $-(4.8 + E_a)$. ^{*d*} LUMO levels were obtained from the optical gap E_g .

Electrophosphorescent Characterization

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The electrophosphorescent properties of **Ir-3Tz1F** and **Ir-3Tz2F** were characterized by phosphorescent OLEDs (PhOLEDs) with the configuration of ITO/MoO₃ (4 nm)/CBP (35 nm)/Ir x wt.-%:CBP (15 nm)/TPBi (40 nm)/LiF:Al (1:100 nm). Figure 3 depicts the structures for both the multi-layer OLEDs made by vacuum deposition and the chemicals involved in the fabrication of devices. In order to reduce interfaces in the device and benefit EL performances, the doped 4,4'-*N*,*N*'-dicarbazolebiphenyl (CBP) layer serve as both hole-transporting layer and emission layer. In order to optimize the EL efficiencies, doping-level dependent experiments were also carried out in the range of 6 to 10 wt.-%.



Fig. 3 General configuration for PhOLEDs made from **Ir-3Tz1F** and **Ir-3Tz2F** together with molecular structures of the relevant compounds used in these devices.



Fig. 4 EL spectra for the optimized devices A2 and B2 at ca. 8 V.

After applying proper voltage, all the devices emit intense electrophosphorescence with the maxima at *ca*. 520, 552 nm for devices **A1–A3** and *ca*. 512, 532 nm for devices **B1–B3** (Figure 4, Table 4 and Figure S2). The current density (*J*)–voltage (*V*)–luminance (*L*) curves for the concerned devices are shown in Figure 5 and Figure S3 in ESI, while the relationship between

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EL efficiencies and current density for the devices are presented in Figure 6 and Figure S4. From Table 4, it can be clearly seen that device A2 with 8 wt.-% doping level of Ir-3Tz1F shows the best EL ability. The device A2 doped with Ir-3Tz1F exhibits impressive EL performances with a low turn-on voltage of 3.0 V, a maximum luminance (L_{max}) of 25957 cd m⁻ ² at 8.3 V, a peak external quantum efficiency (η_{ext}) of 15.8%, a luminance efficiency (η_L) of 56.2 cd A⁻¹ and a power efficiency (η_p) of 50.2 lm W⁻¹ (Table 4, Figures 5 and 6). Among the devices doped with Ir-3Tz2F, the device B2 shows the best EL properties. It can be turned on at ca. 3.2 V and its light output can reach 27605 cd m^{-2} at 9.4 V with peak EL efficiencies of 8.0%, 26.7 cd A^{-1} and 20.1 lm W^{-1} (Table 4, Figures 5 and 6). Clearly, the EL capacity of Ir-3Tz1F is higher than that of Ir-3Tz2F (Table 4 and Figure 6). This result can be ascribed to the following reasons: 1) The triplet energy level (E_1) of Ir-3Tz2F is ca. 2.45 eV, which is quite close to that of CBP host (ca. 2.62 eV). The small difference between their triplet energy levels would effectively enhance the possibility of endothermic back energy transfer from the emissive triplet states of Ir-3Tz2F to the nonemissive triplet states of CBP host. Obviously, the undesired back energy transfer process would adversely affect the EL performance of Ir-3Tz2F. 2) According to the TGA results (Figure S1), Ir-3Tz2F inclines to show slight decomposition at lower temperature. It should induce contamination in the emission layer of the device doped with Ir-3Tz2F to lower its EL efficiencies. Hence, Ir-3Tz1F exhibits much better EL performance than that Ir-3Tz2F.

From the EL results of the monochromic PhOLEDs aforementioned, the optimized devices can be turned on at low voltages of *ca*. 3.0 V (Table 4). Even at a high luminance of 1000 cd m⁻², the optimized device **A2** can still furnish decent EL efficiencies of 13.5%, 53.5 cd A⁻¹ and 42.1 lm W⁻¹ (Table 4 and Figure 6). Recently, the heteroleptic thiazole-based Ir^{III} analogues

have been developed to show maximum EL efficiencies of 23.62 cd A^{-1} , 7.87% and 13.46 lm W^{-1} with CBP host in PhOLEDs fabricated by vacuum deposition.²⁵ The functionalized thiazole-based Ir^{III} phosphorescent emitter with TPA group have furnished attractive EL efficiencies of 39.97 cd A^{-1} , 14.82% and 34.95 lm W^{-1} .²⁴ In addition, high EL efficiencies of 30.84 cd A^{-1} , 12.88% and 26.17 lm W^{-1} have been achieved by the Ir^{III} complexes bearing 2-phenylthiazole-type ligand. The heteroleptic thiazole-based Ir^{III} phosphorescent emitters with picolinic acid derivatives as ancillary ligands can bring EL efficiencies of 10.98 cd A^{-1} , 6.08% and 6.89 lm W^{-1} in solution-processed OLEDs.²⁶ Compared with the high EL performances ever achieved by thiazole-based Ir^{III} phosphorescent emitters aforementioned, the great potential of these two homoleptic complexes in achieving high device efficiencies can be clearly seen.

Device	Phosphorescent	$V_{\rm turnon}$	Luminance L	η_{ext}	$\eta_{ m L}$	$\eta_{ m p}$	λ_{\max}
	dopant	(V)	$(cd m^{-2})$	(%)	$(cd A^{-1})$	$(lm W^{-1})$	$(nm)^{d}$
A1	Ir-3Tz1F (6 wt%)	3.0	21756 (9.5) ^{<i>a</i>}	14.1 (3.7) ^{<i>a</i>}	49.8 (3.8)	44.9 (3.2)	520, 552
				14.0 ^b	49.5	42.0	(0.37,0.58)
				13.5 ^c	47.0	35.0	
A2	Ir-3Tz1F (8 wt%)	3.0	25957 (8.3)	15.8 (3.5)	56.2 (3.5)	50.2 (3.5)	520, 552
				15.2	55.8	49.8	(0.37,0.59)
				15.0	53.5	42.1	
A3	Ir-3Tz1F (10 wt%)	2.7	22496 (8.9)	13.0 (3.5)	45.7 (3.5)	40.8 (3.5)	520, 552
				12.7	45.0	38.1	(0.36,0.58)
				12.0	42.1	31.1	
B1	Ir-3Tz2F (6 wt%)	3.1	24803 (10.5)	6.1 (5.4)	20.1 (5.4)	13.8 (3.8)	512, 532
				5.4	17.5	13.1	(0.32,0.56)
				5.0	19.6	12.2	
B2	Ir-3Tz2F (8 wt%)	3.2	27605 (9.5)	8.0 (4.8)	26.7 (4.6)	20.1 (3.5)	512, 532
				7.1	21.6	19.6	(0.31,0.58)
				7.9	26.5	18.7	
B3	Ir-3Tz2F (10 wt%)	3.3	26760 (10.0)	7.4 (5.4)	24.6 (5.4)	17.1 (3.5)	512, 532
				6.2	20.5	15.0	(0.32,0.58)
				7.2	24.0	16.0	

Table 4 Maximum EL performance for all the PhOLEDs based on the homoleptic thiazole-based Ir^{III} complexes.

^{*a*} Maximum values of the devices. Values in parentheses are the voltages at which they were obtained. ^{*b*} Values collected at 100 cd m⁻². ^{*c*} Values collected at 1000 cd m⁻². ^{*d*} Values were collected at 8 V and CIE coordinates (x, y) are shown in parentheses.



Fig. 5 Current density (J)-voltage (V)-luminance (L) curves for the optimized devices A2 and B2.



Fig. 6 Relationship between EL efficiencies and current density for the optimized devices (a) **A2** and (b) **B2**.

Both PL and EL spectra (Figures 1 and 4) of the two homoleptic thiazole-based Ir^{III} complexes display double-peak pattern, which can furnish emission bands in different wavelength regions. So, these phosphorescent emitters should show advantage to fabricate WOLEDs. Furthermore, our previous WOLEDs with thiazole-based Ir^{III} phosphorescent emitters bearing TPA functional group show undesired voltage-dependent white EL spectra.²⁴ Hence, it is necessary to construct highly efficient WOLEDs with these phosphorescent emitters to show stable white EL spectra. Considering the high EL efficiencies as one of the preferential

parameters for WOLEDs, **Ir-3Tz1F** with higher EL performances has been chosen to fabricate WOLEDs using the cheap and convenient solution-process technique. The configuration of the solution-processed WOLEDs is shown in Figure 7. Besides **Ir-3Tz1F**, the well-known blue phosphorescent **FIrpic** and the pure-red phosphorescent **Ir-G1** have been employed to fulfill Red-Green-Blue (R-G-B) WOLEDs. All the three phosphorescent emitters are co-doped in PVK and OXD-7 to form the emission layer by simple spin-coating strategy. In order to optimize the EL performances, the ratio among the three phosphorescent emitters have been tuned in the trichromatic WOLEDs.



Device Emission layer component

 W1
 PVK (63 wt.-%):OXD-7 (27 wt.-%):Ir dopant (10 wt.-%) (FIrpic:Ir-3Tz1F:Ir-G1 = 40.0:1.40:0.40)

 W2
 PVK (63 wt.-%):OXD-7 (27 wt.-%):Ir dopant (10 wt.-%) (FIrpic:Ir-3Tz1F:Ir-G1 = 40.0:1.40:0.25)

 W3
 PVK (63 wt.-%):OXD-7 (27 wt.-%):Ir dopant (10 wt.-%) (FIrpic:Ir-3Tz1F:Ir-G1 = 40.0:1.24:0.26)

Fig. 7 Structure for the phosphorescent WOLEDs based on **Ir-3Tz1F** together with both energy diagram and molecular structures of the relevant compounds used in these devices.

For device **W1** with weight ratio for **FIrpic** (Blue, B), **Ir-3Tz1F** (Green, G) and **Ir-G1** (Red, R) (B-G-R ratio) of 40:1.4:0.4, its EL spectra under low driving voltage show red-emission dominated pattern (Figure 8a). With increasing driving voltage, blue and green EL bands are enhanced to furnish more balanced EL pattern (Figure 8a). It is clear that both the EL spectra and CIE coordinates of device **W1** are quite unstable with the variation of driving voltage (Table

5, Figures 8a and 9). The voltage-dependent EL spectra in device W1 can be explained as follows. From the energy-level diagram involved in these WOLEDs, it can be seen clearly that the red emitter Ir-G1 possesses high HOMO level due to the electron-rich TPA group to furnish strong hole-trapping ability (Figure 7). Hence, the injected holes in the emission layer can be easily trapped by Ir-G1. At the same time, the LUMO level of Ir-G1 is very close to that of **FIrpic** and **Ir-3Tz1F**. So, the charge carriers in small number injected at low driving voltage are easy to recombine on Ir-G1 molecules to enhance red EL band in the EL spectra. This situation will greatly reduce the chance of charge recombination on FIrpic and Ir-3Tz1F molecules and weaken the EL bands from **FIrpic** and **Ir-3Tz1F**. In addition, the inevitable cascade energy transfer processes from FIrpic to Ir-3Tz1F and then to Ir-G1 also enhance the red EL band. Hence, device W1 exhibits red-emission dominated EL spectra at low driving voltages. However, with increasing driving voltage, too many charge carriers injected into the emission layer to be consumed by the Ir-G1 molecules due to its low content in the emission layer. A lot of remaining charge carriers can recombine on FIrpic and Ir-3Tz1F molecules to substantially enhance the blue and green EL bands (Figure 8a) and the cascade energy transfer processes cannot effectively weaken the blue and green EL bands due to the low content of Ir-G1. Hence, device W1 exhibits voltage-dependent EL spectra (Figure 8a). From the discussion above, it is clear that the red emitter Ir-G1 can play a critical role in inducing the undesired voltage-dependent EL spectra.

In order to weaken the effect of the red emitter **Ir-G1** in inducing unstable white EL spectra, the most feasible way is to reduce the content of red emitter **Ir-G1** in the emission layer. Based on this idea, device **W2** with B-G-R ratio of 40:1.4:0.25 in its emission layer has been constructed. Encouragingly, both the EL spectra and CIE coordinates of device **W2** can be

maintained very stable in a wide driving voltage range (Figures 8b, 9 and Table 5). The much lower content of **Ir-G1** in the emission layer of device **W2** will effectively eliminate its negative effect on the charge carrier recombination on **FIrpic** and **Ir-3Tz1F** molecules as well as the cascade energy transfer processes. Accordingly, the EL spectra of device **W2** can be maintained very stable in a wide driving voltage range (Figure 8b).



Fig. 8 EL spectra for the WOLEDs at different driving voltages. (a) W1, (b) W2 and (c) W3



Fig. 9 Dependence of CIE coordinates of the solution-processed WOLEDs on driving voltages.

			WOLEDs	
		W1	W2	W3
		B-G-R ratio = 40:1.4:0.4	B-G-R ratio = 40:1.4:0.25	B-G-R ratio = 40:1.24:0.26
$V_{\text{turn-on}}$ (V)		3.7	3.4	3.5
Luminance $L (cd m^{-2})^a$		9300	12052	11890
$\eta_{\rm ext}$ (%	́о) ^а	16.4	14.8	16.5
$\eta_{\rm L}$ (cd A	$(A^{-1})^{a}$	31.3	34.6	33.4
$\eta_{\rm p}(\ln V)$	$(V^{-1})^{a}$	25.5	31.8	30.6
CIE/CRI	4 V	(0.40, 0.43) / 78	(0.33, 0.47) / 70	(0.35, 0.45) / 79
	5 V	(0.39, 0.43) / 81	(0.33, 0.47) / 68	(0.35, 0.45) / 80
	6 V	(0.38, 0.43) / 82	(0.32, 0.47) / 66	(0.35, 0.45) / 79
	7 V	(0.38, 0.44) / 83	(0.32, 0.47) / 67	(0.34, 0.45) / 78
	8 V	(0.37, 0.44) / 83	(0.32, 0.47) / 67	(0.34, 0.45) / 78
	9 V	(0.37, 0.43) / 83	(0.32, 0.46) / 67	(0.34, 0.45) / 78
	10 V	(0.36, 0.43) / 82	(0.32, 0.46) / 68	(0.34, 0.45) / 78
	11 V	(0.36, 0.43) / 82	(0.32, 0.46) / 69	(0.34, 0.44) / 78

Table 5 EL performance for all the solution-processed WOLEDs based on Ir-3Tz1F.

^a Maximum values

Typically, red emitters exhibit relatively lower EL efficiencies. Hence, compared with those of device **W1**, the EL efficiencies of device **W2** are improved due to the lower content of **Ir-G1** (Table 5, Figures S5 and S6). Device **W2** can furnish peak EL efficiencies of 34.6 cd A^{-1} , 14.8% and 31.8 lm W^{-1} (Figures S5 and S6), representing very attractive EL performances ever

achieved by solution-processed R-G-B WOLEDs. Despite the high EL efficiencies and stable white EL spectra, device W2 displays relatively unbalanced white EL spectra with low red-light component. As a result, white light emitting from device W2 possesses low color rendering index (CRI) of generally < 70 (Table 5). Clearly, device W2 shows green-dominated white EL spectra. Hence, one of the most feasible ways to achieve balanced white EL spectra is to reduce the content of Ir-3Tz1F in the emission layer. From the EL behaviors of both W1 and W2, higher content of **Ir-G1** can obviously increase the red-light component in the white light EL spectra and reduce the EL efficiencies as the same time. So, the reasonable strategy for achieving the optimized trade-off among stable balanced white EL spectra, high EL efficiency and CRI is reducing the content of **Ir-3Tz1F** in the emission layer as well as slightly increasing the Ir-G1 content. Hence, device W3 with B-G-R ratio of 40:1.24:0.26 has been fabricated. From the EL performances, it can be seen that device W3 can achieve a maximum luminance of 11890 cd m^{-2} (Figure 10 and Table 5). Importantly, device W3 shows much balanced stable white EL spectra with CRI of about 80 than device W2 while maintaining high EL efficiencies of 33.4 cd A^{-1} , 16.5% and 30.6 lm W^{-1} (Figure 11 and Table 5), nearly identical to device W2. Hence, excellent trade-off among stable balanced white EL spectra, high EL efficiency and CRI has been successfully fulfilled in device W3. Thiazole-based Ir^{III} phosphorescent complexes have been rarely introduced into WOLEDs. We had prepared orange phosphorescent thiazole-based Ir^{III} complexes with TPA functional group to construct WOLEDs through both vacuum deposition and solution-processing strategies.²⁴ The highest EL efficiencies of the concerned WOLEDs were 22.72 cd A⁻¹, 9.06% and 17.28 lm W⁻¹. In addition, white EL spectra of the devices exhibited serious voltage-dependent characters with the highest CRI of ca. 72.²⁴ To the best of our knowledge, device W3 represents the state-of-the-art WOLED made from





Fig. 10 Current density (J)-voltage (V)-luminance (L) curves for the optimized device W3.



Fig. 11 Relationship between EL efficiencies and current density for the optimized device W3.

Conclusions

Two homoleptic thiazole-based cyclometalated Ir^{III} phosphorescent complexes have been successfully developed. Their thermal stability, photophysical properties, electrochemistry and EL performances have been carefully investigated. Owing to their advanced photophysical and electrochemical features, the phosphorescent homoleptic thiazole-based Ir^{III} emitters exhibit

high EL efficiencies in monochromic PhOLEDs with η_{ext} of 15.8%, η_{L} of 56.2 cd A⁻¹ and η_{p} of 50.2 lm W⁻¹. Importantly, excellent trade-off between stable balanced white EL spectra and high EL efficiency has been successfully realized in solution-processed trichromatic WOLEDs based on these homoleptic thiazole-based Ir^{III} phosphorescent emitters. The optimized solution-processed WOLED with three primary colors can show very attractive EL efficiencies of 33.4 cd A⁻¹, 16.5% and 30.6 lm W⁻¹ while maintaining both high CRI of *ca.* 80 and very stable white EL spectra in a wide voltage range. All these decent results should represent the top-ranking EL performances ever achieved by thiazole-based Ir^{III} phosphorescent emitters, indicating their great potential in the field of PhOLEDs.

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Optimized trade-off among high EL efficiency, stable CIE and high CRI has been achieved in solution-processed WOLEDs with homoleptic thiazole-based Ir^{III} phosphorescent complexes showing high EL capability.

