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Iridium-based Emitters Containing Pendant Triphenylene Moieties for Blue Green OLEDs with Improved Efficiency upon Thermal Annealing

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Abstract

Two new cyclometalated iridium complexes with non-conjugated triphenylene

moieties attached to the ancillary ligand, namely YF3 and YF4, are reported. Both iridium complexes presented intense blue green emission both in solution ($\Phi_{PL} \sim$ 0.37-0.5) and in solid state. High hole mobility of 0.001 cm²/V·s was obtained for YF4 annealed film, evidenced by the space-charge-limited-current method. This result is among the highest hole mobility for a cyclometalated iridium complex. Organic light-emitting diodes employing these iridium complexes as the dopant were fabricated. The influence of the annealing temperature of both the emitting layer and the host matrix on the devices performance was explored. Interestingly, YF4-based device with the annealing temperature of 60 °C shows the best performance with a maximum current efficiency of 15.6 cd/A and external quantum efficiency of 6.8% compared to 1.5 cd/A and 0.8% for the non-annealed device.

Introduction

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Phosphorescent organic light-emitting diodes (OLEDs) have been the focus of

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intense research for the next-generation display due to their high efficiency, low cost and potential large-area.¹⁻⁵ Over the past two decades, cyclometalated iridium complexes have been widely used as the emitter in electroluminescent devices due to their relatively short lifetime of triplet excited state, high emission efficiency and tunable emission color.⁶⁻⁹ To date, various strategies for the design of high-efficiency iridium complexes have been demonstrated. One particular approach is to functionalize the complex with conjugated charge transfer unit such as fluorene, carbazole or triphenylamine, which can achieve good charge transporting and charge recombination properties in devices.¹⁰⁻¹⁴ For example, triarylborane¹⁵⁻¹⁹ and triphenylamine^{11,20} have been widely incorporated into iridium complex owing to their strong electron-accepting and electron-donating properties. Yet, the charge mobility displayed by these phosphorescent materials is usually still low in the region of 10^{-5} cm²/V·s. In addition, the direct functionalization of the cyclometalated ligand results in large changes in optoelectronic properties compared to the non-functionalized parent complexes.

An alternative design to limit the impact of the charge transporting groups on the optoelectronic properties of the complexes is to functionalize the ancillary ligand,^{21,22} especially when non-conjugated linkages are used.^{23,24} For example, Wang and coworkers synthesized a series of iridium complexes where the ancillary ligand (acetylacetone derivative) bears carbazole-/oxadiazole units.²³ The non-doped OLEDs utilizing these iridium complexes as the emitter exhibited a maximum luminous efficiency of 25.5 cd/A. Recently, we introduced a biphenyl mesogenic unit onto an

acetylacetonate ancillary ligand through a flexible spacer.²⁵ The resulting iridium complexes possessed the same optical property as their parent complex while they showed a smectic liquid crystalline phase induced by the peripheral biphenyl derivative. Furthermore, these iridium complexes exhibited high hole-mobility up to 0.004 cm²/V·s, which is the highest hole mobility reported for iridium complexes.²⁵ These results indicate that modifying the ancillary ligand is an attractive strategy to tune the properties of the complexes beyond the sole photophysical properties.

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Triphenylene is a polycyclic aromatic hydrocarbon widely used in the field of discotic liquid crystals because of its appealing charge transporting characteristics.^{26,27} It was therefore conceived that the introduction of triphenylene unit on cyclometalated iridium complexes would result in interesting optical properties with high charge mobility. Although some researches on OLEDs with triphenylene derivatives have been reported,²⁸⁻³⁰ integrating a triphenylene moiety onto the ancillary ligand of iridium complexes has not yet been explored. Herein, we report the synthesis and characterization of two novel iridium complexes bearing an acetylacetone (acac) ligand monosubstituted- and bisubstituted with mesogenic triphenylene units, abbreviated YF3 and YF4. The photophysical properties and electroluminescent properties were systematically investigated. As expected, YF4 annealed film showed a high hole mobility up to 0.001 cm²/Vs, which is among the highest hole mobility reported for an iridium complex. Interestingly, when used as an emitter in an electroluminescent device, YF4 exhibited much improved performance with a maximum current efficiency of 15.6 cd/A and a maximum external quantum

efficiency of 6.8% after thermal annealing of the emissive layer.



Reaction conditions: a) 1-bromooctane, K_2CO_3 , KI, acetone, reflux, overnight; b) FeCl₃, H_2SO_4 , RT, 3 h; c)1,6-dibromohexane, K_2CO_3 , KI, acetone, reflux, overnight; d) acetylacetone, NaH, *n*BuLi, THF, 0°C to RT, overnight; e) LG1 or LG2, TABOH, CH₂Cl₂, MeOH, reflux, overnight.

Scheme 1 Synthetic route for YF3 and YF4

Experimental

General information

Pyrocatechol and all reagents were purchased from Aldrich and VWR and used as received. All reactions and manipulations were carried out under Ar atmosphere with the use of standard inert atmosphere techniques. ¹H NMR spectra were measured in CDCl₃ solution on a Bruker DPX (300 MHz and 400 MHz) NMR spectrometer with tetramethylsilane (TMS) as the internal standard. Mass spectra (MS) were recorded on a Bruker Autoflex TOF/TOF (MALDI-TOF) instrument using dithranol as a matrix. Thermogravimetric analysis (TGA) was carried out with a NETZSCH STA449 from 25 °C to 600°C at a 20 °C/min heating rate under N₂ atmosphere. Differential scanning calorimetry (DSC) was measured at the phase transition temperature with a rate of 10 °C/min on the first heating circle and 10 °C/min on the first cooling process. UV-vis absorption spectroscopy was measured by Shimadzu UV-265 spectrometer at room temperature. Emission spectra were recorded on RF-5301 PC (Perkin Elmer) at room temperature in dichloromethane (solutions 10^{-5} M) degassed by Ar. Time-resolved fluorescence lifetime measurements were carried out by using a time-correlated single photon counting lifetime spectroscopy system, Hamamatsu Quantaurus-Tau C11567-01. The quality of the fit has been judged by the fitting parameters such as χ^2 (<1.2) as well as the visual inspection of the residuals. Cyclic voltammetry were measured by an electrochemical analyzer (CHI660) in degassed CH₂Cl₂ solution with (Bu₄N)PF₆ as electrolyte. A platinum disk was used as the working electrode. The platinum wire was served as the counter electrode and Ag/Ag⁺ was used as the reference electrode. Ferrocenium/ferrocene was considered as the internal reference compound.

Hole mobility

The hole mobilities of both iridium complexes were estimated using the space-charge limited current (SCLC) method. Hole mobility was measured using the space charge limited current method with a diode configuration of ITO/PEDOT:PSS (40 nm)/iridium complex (50 nm)/MoO₃ (10 nm)/Ag (100 nm) for hole mobility and the results were fitted by space charge limited form. The rotate speed for PEDOT:PSS and activity layer are 4000 rmp/min and 600 rmp/min, respectively. All devices were measured at room temperature and an annealed temperature (150 °C for 30 min). The SCLC is described by: $J = (9/8)\varepsilon_0\varepsilon_{\tau}\mu(V^2/d^3)$, where *J* is the current density, *d* is the film thickness of the active layer, μ_0 is the hole mobility, ε_r is the relative dielectric constant of the transport medium, ε_0 is the permittivity of free space (8.85 × 10⁻¹² F m⁻¹), *V* is the internal voltage in the device.²⁵

Devices fabrication and characterization

All devices employing YF3 or YF4 as the dopant were fabricated by solution-processed approach. In these OLEDs, ITO was treated with the same procedures of our previous reports.³¹ PEDOT:PSS was spin coated onto ITO substrate with a 30 nm thick layer, which is utilized as the smooth layer and hole inject layer. The blend of mCP and OXD-7 (or the neat mCP) was used as the host matrix. TmPyPB is the electron transporting layer with 40 nm in thickness. Liq and Al are used as the composite cathode. In order to explore the effect of temperature on the device performance, the activity emitter was treated with annealing at 60 °C and 80 °C. EL spectra were recorded using a spectroradiometer, Photo-Research PR735. The

features of current and brightness versus applied voltage were obtained by combining a Keithley 2400 and the spectroradiometer. The external quantum efficiency (EQE) was calculated from the luminance, current density, and EL spectrum, assuming a Lambertian distribution. The device configurations are as follows:

Device A: ITO/PEDOT:PSS (30 nm)/mCP:OXD-7:YF3 or YF4 (70:20:10, RT, 40 nm)/TmPyPB (40 nm)/Liq(2 nm)/Al (100 nm)

Device B: ITO/PEDOT:PSS (30 nm)/mCP:OXD-7: YF3 or YF4 (70:20:10, 80°C, 40 nm)/TmPyPB (40 nm)/Liq(2 nm)/Al (100 nm)

Device C: ITO/PEDOT:PSS (30 nm)/mCP:YF3 or YF4 (90:10, RT, 40 nm)/TmPyPB (40 nm)/Liq(2 nm)/Al (100 nm)

Device D: ITO/PEDOT:PSS (30 nm)/mCP: YF3 or YF4 (90:10, 60°C, 40 nm)/TmPyPB (40 nm)/Liq(2 nm)/Al (100 nm)

Synthesis of 3,6,7,10,11-pentakis(octyloxy)triphenylen-2-ol (2)

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Compound 1 (12.0 g, 36 mmol) and 3-4 drops H_2SO_4 was added to dry CH_2Cl_2 . Then, FeCl₃ (17.4 g, 108 mmol) was added and the reaction mixture was stirred at room temperature for 3.5 h. The reaction mixture was poured into MeOH and the mixture left in freezer overnight. The solid was collected by filtrate and purified with column chromatography using hexane/ethyl acetate = 35:1 (*V/V*) as the eluent. A grey white solid (3.0 g, 28.6 %) was achieved. ¹H NMR (CDCl₃ 300 MHz): δ 7.96 (s, 1H), 7.82 (d, *J* = 4.8 Hz, 4H), 7.76 (s, 1H), 5.92 (s, 1H), 4.28-4.18 (m, 10H), 1.97-1.92 (m, 10H), 1.58-1.32 (m, 52H), 0.93-0.89 (m, 15H). MS (MALDI-TOF) m/z (M•Na⁺): calcd. for C₅₈H₉₂O₆, 907.7; found, 907.7.

Synthesis of 2-(6-bromohexyloxy)-3,6,7,10,11-pentakis(octyloxy)triphenylene (3)

A mixture of compound 2 (3.0 g, 3.39 mol), 1,6-dibromohexane (3.0 g, 12.3 mol) and K₂CO₃ (2.4 g, 17.0 mol) was dissolved in acetone (300 mL). The mixture was refluxed for 48 h under Ar. After cooling to room temperature, the reaction mixture was poured into water and extracted with CH₂Cl₂. The organic layer was collected, washed with water and dried with MgSO₄. The solvent was removed under vacuum and the residual will be purified with column chromatography using hexane/ethyl acetate = 35:1 (*V/V*) as the eluent. A light yellow solid was obtained (2.6 g, 73%). ¹H NMR (CDCl₃ 300 MHz): δ 7.83 (s, 6H), 4.23 (d, *J* = 6.3 Hz, 12H), 3.45 (t, *J* = 6.6 Hz, 2H), 2.0-1.89 (m, 12H), 1.59-1.56 (m, 12H), 1.39-1.28 (m, 44H), 0.90 (t, *J* = 6.6 Hz, 15H). ¹³C NMR (100 MHz, CDCl₃): δ 148.98, 123.56, 107.37, 69.72, 33.74, 32.73, 31.85, 29.48, 27.99, 26.20, 25.40, 22.69, 14.11.

General procedures for synthesis of ancillary ligands LG1 and LG2

Acetylacetone (1 eq) was added carefully to the stirred suspension of the sodium hydride (1.2 eq) in THF (5 ml) at 0°C. The resultant mixture was stirred for 30 min. at 0°C. Butyllithium (2.2 eq) was added dropwise over 30 min. to the stirred mixture at 0°C. After 30min., a solution of compound 3 (2.2 eq) in THF (5 ml) was added dropwise to the solution at 0°C. The reaction mixture was stirred for 2 hours at 0°C and for overnight at RT, after which it was quenched with aqueous ammonium chloride. The mixture was acidified with concentrated hydrochloric acid to pH = 1 and the aqueous phase was separated and extracted with CH₂Cl₂. The combined organic layers were washed with brine and dried with anhydrous Na₂SO₄, and the

solvent was evaporated in vacuo. The crude product was simply purified by column chromatography on silica (CH_2Cl_2 -Methanol) to give the mixture of LG1 and LG2 as a yellow solid (0.1 g, 12.2 %). It is failed to separate them and the mixture was used to next step.

General procedures for iridium complexes YF3 and YF4

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A mixture of cyclometalated ligand (dfppy) (2.5 eq) and $IrCl_3 \cdot 3H_2O$ (1 eq) in the 2-ethoxylethanol (15 mL) and water (5 mL) was heated to 100 °C for 16 h. After cooling; the precipitate was collected and washed with water and hexane. The solid was used to the next step without any further purification. A mixture of LG-1 (or LG-2) (2.2 eq), TBAOH (2.2 eq) and $CH_2Cl_2/MeOH$ (V/V = 7:3) was added into the solution of the dimer (1 eq) and CH_2Cl_2 . The reaction mixture was stirred at 40 °C for overnight. After cooling to room temperature, the solution was removed by evaporator and the residue was purified by silica gel chromatography (CH_2Cl_2) to get the target iridium complexes.

YF3. Yellow glassy material, yield: 35.1 %. ¹H NMR (300 MHz, CDCl₃): δ 8.44-8.41 (m, 2H), 8.25-8.21 (m, 2H), 7.85 (s, 6H), 7.80-7.72 (m, 2H), 7.20-7.12 (m, 2H), 6.37-6.29 (m, 2H), 5.72 (dd, *J* = 8.7 Hz, 2.4 Hz, 1H), 5.72 (dd, *J* = 8.7 Hz, 2.4 Hz, 1H), 5.65 (dd, *J* = 8.7 Hz, 2.4 Hz, 1H), 5.24 (s, 1H), 4.26-4.19 (m, 12H), 2.03-1.89 (m, 12H), 1.82 (s, 3H), 1.61-1.54 (m, 12H), 1.42-1.25 (m, 48H), 0.89 (t, *J* = 3 Hz, 15H). ¹³C NMR (100 MHz, CDCl₃): δ 188.53, 185.09, 151.70, 149.05, 148.15, 137.90, 128.61, 123.60, 122.51, 121.52, 115.21, 107.41, 100.37, 97.24, 69.76, 41.46, 31.87, 29.51, 28.84, 27.01, 26.22, 22.71, 14.13. MS (MALDI-TOF) m/z (M⁻):

C₉₁H₁₂₁F₄IrN₂O₈, 1638.87; found, 1662.0 (Na⁺).

YF4. Yellow glassy material, yield: 22.3 %. ¹H NMR (300 MHz, CDCl₃): δ 8.41 (dd, *J* = 5.7 Hz, 0.9 Hz, 2H), 8.22 (d, *J* = 8.4 Hz, 2H), 7.83 (s, 12H), 7.77-7.71 (m, 2H), 7.16-7.11 (m, 2H), 6.36-6.28 (m, 2H), 5.71 (dd, *J* = 8.7 Hz, 2.4Hz, 2H), 5.22 (s, 1H), 4.25-4.19 (m, 24H), 2.06-1.81 (m, 20H), 1.61-1.52 (m, 24H), 1.39-1.26 (m, 100H), 0.88 (t, *J* = 4.2 Hz, 30H). ¹³C NMR (100 MHz, CDCl₃): δ 188.87, 152.40, 149.32, 148.40, 138.14, 123.89, 122.77, 121.72, 115.71, 107.70, 100.24, 96.14, 70.051, 41.84, 32.16, 29.80, 27.38, 26.51, 23.0, 14.42. MS (MALDI-TOF) m/z (M⁻): C₁₅₅H₂₂₃F₄IrN₂O₁₄, 2605.64; found, 2606.17.

Results and discussion

Synthesis and structure

The synthetic routes for the ancillary ligands and the iridium complexes are shown in **Scheme 1**. Compound **1** was prepared from pyrocatechol according to a previous report.³² For intermediate **2**, a multi-step synthetic route is usually carried out,³³ which is costly and time-consuming. Herein, an improved one step reaction of intermediate **1** using H_2SO_4 and FeCl₃ in CH₂Cl₂ afforded **2** in 28 % yield.³⁴ The precursor **3** was obtained via etherification between intermediate **2** and 1,6-dibromohexane in good yield.

The ancillary ligands were prepared via one-pot alkylation between acetylacetone and the precursor **3** using NaH and *n*-BuLi in dry THF with low yield (10-23%).^{23,25} Both mono- and dialkylated compounds were observed with the monoalkylated ligand

(LG1) being the major species compared to the bialkylated ligand (LG2), which is attributed to increased steric effect of the pendent unit limiting the dialkylation. However, they could not be separated and were used directly as a mixture in the complexation reaction. Then, the cyclometalated iridium complexes were prepared from di- μ -chlorodiiridium-(III) dimer [(C^N)₄Cl₂Ir] and ancillary ligands (LG1 and LG2), in which the (C^N)₄Cl₂Ir was synthesized according to previous reports.²² Finally, the target iridium complexes were purified and characterized by ¹H NMR, ¹³C NMR and TOF-MS (ESI†). Both iridium complexes have good solubility in organic solvent, such as CH₂Cl₂ and hexane.

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Fig. 1 ¹H NMR (400 MHz, CDCl₃, room temperature) spectra of **YF3** (A) and **YF4** (B)

YF3 and **YF4** were successfully separated via thin-layer chromatography, and can be clearly distinguished by ¹H NMR spectroscopy. In **YF4**, the protons on triphenylene are 12H (a'), while the protons on triphenylene unit are 6H (a) in **YF3**

(Fig. 1). Additionally, a singlet resonance with 3H at 1.82 ppm is observed in YF3, assigning to the methyl on acac moiety. Furthermore, a series of multiplets in the range of 8.22-8.44 ppm and two different doublet-doublet signals in 5.64-5.74 ppm are presented in YF3, indicating that the asymmetric structure leads to different chemical environments of protons on the cyclometalating ligand. In additional, ¹³C NMR and TOF-MS also proved YF3 and YF4 were separated well (ESI†). Both iridium complexes present good thermal properties measured by TGA (ESI†). The decomposed temperatures of 5wt% are 332 °C and 343 °C for YF-3 and YF-4, respectively. However, YF-3 and YF-4 did not display visible phase transition between 50 °C to 250 °C, evidenced by DSC (ESI†), pointing to glassy materials with low transition temperatures.

Photophysical property



Fig. 2. UV-vis absorption spectra of YF3 and YF4 in CH₂Cl₂ solution at room temperature

 Table 1 photophysical data of iridium complexes

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	^a Absorption /nm (ε/10 ⁵ M ⁻¹ cm ⁻¹)	$\lambda_{ m em}$ /nm	${}^{d} \boldsymbol{\varPhi}_{\mathrm{PL}}$	^e τ /μs	$f_{k_{\rm r}}/10^5 {\rm s}^{-1}$	${}^{g}k_{\rm nr}/10^5~{\rm s}^{-1}$
YF3	260 (0.97), 268 (1.19), 278 (1.56), 307 (0.46) 344 (0.15), 389 (0.05), 435 (0.03)	^{<i>b</i>} 482 ^{<i>c</i>} 483,509	0.50	1.07	4.67	4.68
YF4	260 (1.40), 268 (1.75), 278 (2.38), 307 (0.66), 345 (0.16), 388 (0.05),437 (0.03)	^{<i>b</i>} 482 ^{<i>c</i>} 483, 509	0.37	1.06	3.49	5.94
^{<i>a,b,d,e</i>} The data was collected in CH ₂ Cl ₂ at room temperature under Ar. ^{<i>c</i>} Emission was measured in neat film at room temperature. ^{<i>f</i>} Radiative decay rate $K^{\text{r}} = \Phi_{\text{PI}}/\tau$. ^{<i>g</i>} Non-radiative decay rate $K^{\text{nr}} = \tau^{-1} - K^{\text{r}}$.						

The UV-vis absorption spectra measured in CH_2Cl_2 solution (10^{-5} M) at room temperature are depicted in **Fig. 2**, and the corresponding data are summarized in **Table 1**. Intense absorption peaks centered at 279 nm with high molar extinction coefficient ($\epsilon \sim 10^5 \text{ M}^{-1} \text{ cm}^{-1}$) are observed for YF3 and YF4, generated from the S₀-S₄ transition of the triphenylene.³⁵ The weaker absorption bands ($\sim 10^3 \text{ M}^{-1} \text{ cm}^{-1}$) from 320 nm to ~ 470 nm are attributed to the mixture of singlet and triplet metal-to-ligand charge transfer and ligand centered transitions (¹MLCT, ³MLCT, ³LC) involving the cyclometalating ligand and the iridium center.³⁶ Due to the two triphenylene units, YF4 shows clearly increased absorption intensity in the range of 250-320 nm compared to YF3.

Under the excitation wavelength of 400 nm, the iridium complexes present similar emission spectra both in solution and neat film (**Fig. 2**). All emission profiles show intense bluish-green emission with the maximum emission peak at about 482 nm and a shoulder at 509 nm. Employing FIrpic as the reference compound,³⁷ YF3 and YF4 present the high PL quantum yields (Φ_{em}) of 0.5 and 0.37 in degassed CH₂Cl₂, respectively. The excited state lifetimes of 1.07 µs and 1.06 µs were measured for YF3 and YF4 at room temperature (**Fig. 2** insert, **Table 1**). Consequently both the radiative

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and non-radiative rate constants are calculated to be in the 10^5 s⁻¹ range, similar to the corresponding acetylacetonate complexes. Additionally, both iridium complexes are luminescent in the solid state (ESI[†]). It is particularly interesting for YF3 and YF4 as blue emitters generally suffer significantly from red-shifted emission when in the bulk. Additionally, the PL property of pristine film and annealing film were preliminary explored. Taking YF3 as an example (ESI[†]), the emission intensity of annealing film is obviously weak than that of the pristine film, accompanied with \sim 2 nm red shift for the annealing film. Correspondingly, the emission efficiency of the pristine film is better than that of the annealing film.

Electrochemical property

Table 2 Electrochemical data of iridium complexes

	$^{a}E_{red}/V$	^b E ^{opt} _{gap} /eV	$^{c}E_{\text{LUMO}}/\text{eV}$	$^{d}E_{\mathrm{HOMO}}/\mathrm{eV}$			
YF3	-1.31	2.77	-3.49	-6.26			
YF4	-1.34	2.79	-3.46	-6.25			
^a the data were recorded by CV in CH ₂ Cl ₂ solution; ^b the data were recorded at the crossing point of							
UV-vis spectra and emission spectra; ${}^{c}E_{LUMO} = -(4.8 + E_{red}) \text{ eV}; {}^{d}E_{HOMO} = (E^{opt}_{gap} - E_{LUMO}) \text{ eV}.$							

The electrochemical property of both YF3 and YF4 were evaluated by cyclic voltammetry in CH₂Cl₂ solution (ESI[†]), and the relevant data are listed in **Table 2**. The irreversible reduction waves rather than oxidation waves were detected for YF3 (V_{onset} : -1.31 V; vs. Fc/Fc⁺; the same below) and YF4 (-1.34 V). According to the reduction potential, the lowest unoccupied molecular orbitals levels (E_{LUMO}) of YF3

and YF4 are calculated to be -3.49 eV and -3.46 eV, respectively, via the empirical formula of $E_{\text{LUMO}} = -(4.8 + E_{\text{red}}) \text{ eV}$.³⁸ Based on the optical band-gap (**Table 2**) and the value of E_{LUMO} , the highest occupied molecular orbital levels (E_{HOMO}) were evaluated to be -6.26 eV and -6.25 eV. Notably, negligible effect on the electrochemical property of both iridium complexes was found due to the non-conjugation of triphenylene unit in ancillary ligand.

Hole mobilities

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Fig. 3 The curves of current densities-voltage of hole-only devices based on the annealed films of YF3 and YF4. The solid lines represent the fit using a model of single carrier SCLC with field-independent mobility.

As high charge mobility is expected from triphenylene derivatives, we evaluated the hole mobilities of these iridium complexes *via* SCLC method. Both iridium complexes show the hole mobilities of 2.5×10^{-6} (YF3) and 7.7×10^{-4} (YF4) cm²/V·s in the pristine film. After thermal annealing, greatly enhanced hole mobilities were obtained for both iridium complexes. Interestingly, YF4 annealed film displays the hole mobility up to 0.001 cm²/V·s (**Fig. 3**), which is among the highest report for the hole mobilities of iridium complex.

Electroluminescent properties



Fig. 4 EL spectra of YF3 and YF4 collected at 10 V

To evaluate the electroluminescent properties of both iridium complexes, the OLEDs with different architectures (see experimental part) have been fabricated, in which YF3/or YF4 were used as the dopant. Both the blend of mCP and OXD-7 and neat mCP are chosen as the host matrix. Due to the enhanced hole mobility in the annealed film, the effect of annealed emitter layer on device performance was also explored.

All devices based on YF3 dopant show almost identical EL spectra with the maximum emission at 483 nm (**Fig. 4**), matching perfectly with the PL emission in solution. This phenomenon implies that the EL emission is dominant from the iridium complex. Additionally, no emission from the host matrix was detected, even for the annealed emissive layer, implying efficient energy transfer from the host to the dopant. YF4-based devices display similar EL spectra to YF3-based devices, except for some high-energy emission observed in devices B and D (**Fig. 4**, annealed emissive layer).

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Importantly, the thermal annealing process has a distinct favorable effect on the EL

spectra of YF4, probably due to the presence of two triphenylenes per complex.



Fig. 5 *J-V-B* curves of iridium complexes-based devices A-D (\blacksquare : device A; \bullet : device B; $\blacktriangle \Delta$:

device C; $\mathbf{\nabla}$: device D)

The current density-voltage-brightness (*J-V-B*) characteristics of the devices are depicted in **Fig. 5**. YF4-based devices possess a lower turn on voltage (V_{on} , ca. 5 V) than that of YF3-based devices (ca. 6 V), which is attributed to the higher hole mobility of YF4. It appears that mCP:OXD-7 is a better host matrix than mCP in these devices (**Fig. 5 and Fig. 6**). For the EL devices of YF3, both the annealed emitters

exhibit much higher luminance than that of pristine film. The maximum brightness of 11380 cd/m^2 (12 V, 169 mA/cm²) was achieved in device B. In contrast, YF4 based devices show the highest luminance of 7237 cd/m² (9 V, 149 mA/cm²) in the device D, of which the emissive layer was annealed at lower temperature (60 °C). This result implies that the temperature plays a key role on the performance of YF4-based devices.

Table 3. The performances of devices A-D of YF3 and YF4

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	Туре	V _{on} (V)	Maximum efficiency			
			$L (cd/m^2)$	<i>CE</i> (cd/A)	<i>PE</i> (lm/W)	EQE (%)
YF3	device A	6	5333	8.6	2.9	3.5
	device B	6	11380	9.2	3.0	3.8
	device C	6.5	3694	16.1	5.9	6.6
	device D	6	10900	8.1	2.5	3.4
YF4	device A	5.5	4114	8.3	3.1	3.5
	device B	5.5	1280	1.5	0.6	0.8
	device C	6	2052	8.1	3.2	3.4
	device D	5	7237	15.6	7.5	6.8





Fig. 6 Current efficiency-current density characteristics of YF3 and YF4 based devices

For the pristine activated emitter, devices of YF3 presented a best performance of $\eta_{CE, max} = 16.1 \text{ cd/A}$, $\eta_{PE, max} = 5.9 \text{ lm/W}$ and $\eta_{exe, max} = 6.6 \%$ (device C), whereas devices of YF4 obtained the best EL performance of $\eta_{CE, max} = 8.3 \text{ cd/A}$, $\eta_{PE, max} = 3.1 \text{ lm/W}$, $\eta_{exe, max} = 3.5 \%$ (device A, Table 3). Notably, YF3-based devices with a pristine film have better performance than YF4-based devices, which is in agreement with their Φ_{PL} in solution. Inspired by the enhanced mobility in annealed film, we treated the emitter layer with thermal annealing (60 °C and 80 °C). It is worth noting that the devices showed an increased performance after annealing except device D of YF3. Especially, device D with YF-4 dopant achieved a sharply increased performance of $\eta_{CE, max} = 15.6 \text{ cd/A}$, $\eta_{PE, max} = 7.5 \text{ lm/W}$, $\eta_{exe, max} = 6.8 \%$ (device D). This exciting result could be ascribed to the enhanced charge transport in the annealed film, leading to better device performance. Therefore, this result would be in favor of designing the novel iridium complex for enhancing the device performance with annealed film.

Conclusions

Two novel iridium complexes bearing non-conjugated triphenylene units on the ancillary ligand have been successfully synthesized and characterized. Both iridium complexes showed intense blue green emission in solution and solid state. Their optical and electrochemical properties were similar to the parent complex (dfppy)₂Iracac due to the non-conjugated linkage between the iridium emission core and the triphenylene units. Interestingly, YF4 annealed film exhibited high hole mobility up to 0.001 cm²/Vs, which is among the highest hole mobility reported for a cyclometalated iridium complex. After thermal annealing of the emissive layer, the YF4-based device displayed largely enhanced performance with the maximum current efficiency of 15.6 cd/A and external quantum efficiency of 6.8%. This research demonstrated that introducing a proper functionalized unit on the ancillary ligand of iridium complex is an attractive strategy to improve the performance of electroluminescent devices.

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Table of Content



High hole mobility was obtained for iridium complex bearing triphenylene unit, and the annealing emitter shows the best device performance.