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# Efficient Yellow-Green Organic Light-Emitting Diodes Based on Sublimable Cationic Iridium Complexes

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#### Abstract

Three new yellow-emitting cationic iridium complexes have been prepared, and the photophysical and electrochemical properties have been investigated. These cationic iridium complexes have excellent thermal stability and can be thermally vacuum-sublimed as phosphorescent dyes for the fabrication of efficient organic light-emitting diodes. The devices based on these complexes give yellow-green electroluminescences with Commission Internationale de L'Eclairage coordinates of (0.38, 0.58), (0.37, 0.58), (0.38, 0.58). The maximum current efficiencies of devices based on these complexes are

20.2, 23.7 and 21.5 cd  $A^{-1}$  that corresponds to maximum external quantum efficiencies of 6.3 %, 6.8 % and 6.5 %, respectively.

Keywords: Organic light-emitting diode; Sublimable; Cationic iridium complex;

Yellow-green light emission; 4,5-Diazafluorene; Bis-carbazole

#### **1. Introduction**

In the recent years, phosphorescent cyclometalated iridium(III) complexes have attracted more and more interest in the field of optoelectronics due to their high quantum efficiency, short lifetime of triplet excited states and broad range of emission colors [1]. Iridium(III) complexes can be divided into two classes: (i) the neutral complexes with molecular formula [Ir(C^N)<sub>3</sub>] [2-4] or [Ir(C^N)<sub>2</sub>(L^X)] (C^N and L^X stand for cyclometalated ligand and anionic ancillary ligand, respectively) [5-8] and (ii) cationic iridium(III) complexes  $[Ir(C^N)_2(N^N)]^+$  containing neutral bidentate ancillary ligands [9]. The former class of iridium(III) complexes have high quantum yields and their emission wavelengths and excited-state lifetimes can be tuned by changing the cyclometalated ligands. Most of the OLEDs based on these complexes were fabricated by vacuum deposition due to their good volatility. As for the latter case, the ionic character makes them quite soluble in polar solvents, which enable solution process to form the film for solid-state light-emitting electrochemical cells (LECs) containing only a single emissive layer [10]. LECs offer several advantages such as very simple device architectures, being independent of the thickness of the active layer and being used with air-stable electrodes. However, these devices suffer from a slow response and severe excited-state quenching in the active layers compared with conventional OLEDs [11-14].

Therefore, they are indeed difficult to be used in full-color flexible panel displays which require fast switching. Such drawbacks in LECs can be significantly suppressed by doping the phosphors in the polymer host materials as the emissive layer as well as using an extra functional layer in solution-processed OLEDs. Consequently, by using cationic iridium(III) complexes as emissive phosphors, blue, red, green, yellow and near-infrared OLEDs have been realized [15-20]. Most of these kind of devices commonly exhibit low luminance and efficiency due to the inferior compatibility of cationic iridium complex guest with hydrophobic polymer hosts, which could hinder the development of their widespread applications. It is expected that the performance of OLEDs based on cationic iridium complexes can be significantly relieved as the dopants are deposited by a vacuum-evaporable method. However, the intrinsic ionic nature of cationic iridium complex can result in their poor volatility and severe thermal degradation during vacuum evaporation. The volatility of cationic iridium complexes can be improved by enhancing molecular structural rigidity. Wong et al. reported OLEDs with sublimable cationic iridium complexes with rigid pyridinylfluorene derivatives as dopants, which gave yellow light emission with a maximum luminance efficiency of 20 cd  $A^{-1}$  and a quantum efficiency of 7 % [19]. As far as we know, other than the foregoing accounts there were no other reports on OLEDs based on cationic iridium dopants by thermally vacuum-sublimed method.

In this work, three novel cationic iridium complexes were synthesized by using 2phenylpyridine as the main ligand and bis-carbazole substituted 4,5-diazafluorene derivatives as the ancillary ligand. The bipolar ancillary ligands comprise two electrondonating carbazole units and an electron-accepting 4,5-diazafluorene group, and were even used as hosts for highly efficient blue phosphorescent OLEDs [21]. Such cationic iridium complexes have excellent thermal stability and can be thermally evaporated under vacuum without significant decomposition in phosphorescent OLED fabrication.

# 2. Experimental

#### 2.1. General experiments

All reactants and solvents were used as received, and were purified or dried by standard methods when required. All reactions were monitored using precoated thinlayer-chromatography plates (0.20 mm with fluorescent indicator UV254). <sup>1</sup>H NMR spectra were recorded on a JEOL JNMECA600 NMR spectrometer with tetramethylsilane [Si(CH<sub>3</sub>)<sub>4</sub>] as the internal standard. Mass spectrometry (MS) was performed with an Esquire-LC\_00136 mass spectrometer. Elemental analysis for carbon, hydrogen, and nitrogen was determined on an Exeter Analytical CE-440 elemental analyzer. The dimeric iridium(III) intermediate  $[(ppy)_2Ir(\mu-Cl)]_2$  and diimine ligands ECAF (9,9-bis(9-ethylcarbazol-3-yl)-4,5-diazafluorene), EHCAF (9,9-bis(9ethylhexylcarbazol-3-yl)-4,5-diazafluorene) and PCAF (9,9-bis(9-phenylcarbazaol-3yl)-4,5-diazafluorene) were prepared according to the literature procedure [21, 22]. Absorption spectra were recorded with a UV-vis spectrophotometer (Agilent 8453) and photoluminescent (PL) spectra were recorded with a fluorospectrophotometer (Jobin Yvon, FluoroMax-3). The excited state lifetimes of the complexes were measured on a transient spectrofluorimeter (Edinburgh Instruments, FLSP920) with a time-correlated single-photon counting technique. Absolute PL quantum efficiency at room temperature were measured with an absolute photoluminescence quantum yield measurement system (Hamamatsu, C9920-02). Cyclic voltammetry was performed on a Princeton Applied Research potentiostat/galvanostat model 283 voltammetric analyzer in DMF solutions  $(1 \times 10^{-3} \text{ M})$  at a scan rate of 100 mV s<sup>-1</sup> with a platinum plate as the working electrode,

a silver wire as the pseudo-reference electrode, and a platinum wire as the counter electrode. The supporting electrolyte was  $n-Bu_4NPF_6$  (0.1 M) and ferrocene was selected as the internal standard. The solutions were bubbled with argon for 10 min before measurements.

## 2.2. Fabrication and characterization of OLEDs

Indium-tin-oxide (ITO) substrates with sheet resistance of 10  $\Omega$  sq<sup>-1</sup> were sufficiently cleaned using chemical and UV-ozone methods before the deposition of the organic layers. The poly-(3,4-ethylenedioxythiophene:poly-(styrene sulfonate) (PEDOT:PSS) layer was spin-coated onto the ITO substrate in air and baked at 120 °C for 30 min. The transporting material of TCTA (4,4',4''-tri(9-carbazoyl)triphenylamine) film (15 nm) was then deposited on the hole-injecting layer. The phosphor (10 wt%) and CBP (4,4'bis(9H-carbazol-9-yl)biphenyl) host were co-evaporated to form 30 nm emitting layer from two separate sources. Then, TmPyPb (1,3,5-tri[(3-pyridyl)-phen-3-yl]benzene) (50 nm), LiF (0.5 nm), and Al (100 nm) were evaporated, respectively. The organic layers were laminated in the above sequence under  $6 \times 10^{-4}$  Pa at a rate of 0.5 - 1 Å s<sup>-1</sup> without breaking vacuum between each vacuum-deposition process. The layer thickness was monitored in situ using a quartz crystal oscillator. The luminance-voltage-current density characteristics were measured with a PR655 spectrometer and a Keithley 2400 programmable voltage-current source. The current efficiency and external quantum efficiency characteristics were calculated from electrical parameters, electroluminescent (EL) spectra and luminance. All measurements of the devices were carried out in ambient atmosphere without further encapsulations.

#### 2.3. Syntheses

The ancillary ligands ECAF, EHCAF and PCAF were synthesized from a reported procedure [21]. All reactions were performed under argon. Solvents were carefully dried and distilled from appropriate drying agents prior to use.

Synthesis and Structural Characterization of  $[Ir(ppy)_2(ECAF)]PF_6$  (1): The dichloro-bridged diiridium complex  $[(ppy)_2Ir(\mu-Cl)_2Ir(ppy)_2]$  (0.35 g, 0.33 mmol) and ECAF ancillary ligand (0.42 g, 0.76 mmol) were dissolved in 2-methoxyethanol (10 mL). The mixture was then refluxed at 150 °C for 15 h under an argon atmosphere to form a clear yellow solution. After cooling to room temperature, an aqueous solution of NH<sub>4</sub>PF<sub>6</sub> (0.87 g in 20 mL deionized water) was slowly added into the reaction mixture under stirring, resulting in a yellow suspension. The suspension was then filtrated and the resulting precipitate was washed with deionized water and dried under vacuum at 70 °C for 12 h. The crude product was purified by column chromatography on silica gel (200–300 mesh) with  $CH_2Cl_2$ /acetone (10:1) as the eluent, yielding a yellow powder (0.62 g, 0.52 mmol). Yield: 79%. mp: > 300 °C. IR (KBr, cm<sup>-1</sup>): 1564, 1236, 1121, 844, 751, 618, 559. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>,  $\delta$ ): 8.10 (d, J = 7.8 Hz, 2H), 7.88 (dd, J = 9.6 Hz and 9.0 Hz, 4H), 7.84 (s, 2H), 7.79 (d, J = 5.4 Hz, 2H), 7.75 (t, J = 7.8 Hz, 2H), 7.70 (d, J = 5.4 Hz, 2H), 7.64 (d, J = 7.8 Hz, 2H), 7.50–7.47 (m, 2H), 7.43 (t, J = 7.8 Hz, 2H), 7.38 (dd, J = 8.4 Hz and 7.8 Hz, 4H), 7.31–7.29 (m, 2H), 7.16 (t, J = 7.2 Hz, 2H), 7.08 (dd, J = 7.2 Hz and 6.0 Hz, 2H), 6.99 (dd, J = 7.8 Hz and 7.2 Hz, 2H), 6.90 (dd, J = 7.8 Hz and 7.2 Hz, 2H), 6.42 (d, J = 7.8 Hz, 2H), 4.34–4.30 (m, 4H), 1.39 (t, J = 7.2 Hz, 6H). MS (MALDI-TOF) [m/z]: 1055.3 (M – PF<sub>6</sub>)<sup>+</sup>. Anal. found: C 61.10, H 3.87, N 6.95. Anal. Calcd for C<sub>61</sub>H<sub>46</sub>N<sub>6</sub>PF<sub>6</sub>Ir: C 61.04, H 3.86, N 7.00.

Synthesis and Structural Characterization of  $[Ir(ppy)_2(EHCAF)](PF_6)$  (2): The synthesis of complex 2 is similar to that of complex 1, except that ECAF was replaced

with EHCAF, yielding a yellow powder. Yield: 81%. mp: > 300 °C. IR (KBr, cm<sup>-1</sup>): 1559, 1463, 1116, 838, 753, 619, 555. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>,  $\delta$ ): 8.15 (d, J = 7.8 Hz, 2H), 7.91–7.87 (m, 4H), 7.81–7.73 (m, 8H), 7.65 (d, J = 7.8 Hz, 2H), 7.55–7.53 (m, 2H), 7.44 (dd, J = 8.4 Hz and 7.2 Hz, 2H), 7.38–7.33 (m, 6H), 7.18 (dd, J = 8.4 Hz and 7.2 Hz, 2H), 7.06 (dd, J = 7.2 Hz and 5.4 Hz, 2H), 7.01 (dd, J = 7.8 Hz and 7.2 Hz, 2H), 6.92 (dd, J = 7.8 Hz and 7.2 Hz, 2H), 6.43 (d, J = 7.8 Hz, 2H), 4.17–4.09 (m, 4H), 2.05–1.98 (m, 2H), 1.39–1.24 (m, 16H), 0.91–0.88 (m, 6H), 0.85–0.82 (m, 6H). MS (MALDI-TOF) [m/z]: 1223.5 (M – PF<sub>6</sub>)<sup>+</sup>. Anal. found: C 64.03, H 5.19, N 6.10. Anal. Calcd for C<sub>73</sub>H<sub>70</sub>N<sub>6</sub>PF<sub>6</sub>Ir: C 64.07, H 5.16, N 6.14.

Synthesis and Structural Characterization of  $[Ir(ppy)_2(PCAF)](PF_6)$  (3): The synthesis of complex **3** is similar to that of complex **1**, except that ECAF was replaced with PCAF, yielding a yellow powder. Yield: 81%. mp: > 300 °C. IR (KBr, cm<sup>-1</sup>): 1565, 1454, 1115, 845, 757, 616, 557. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>,  $\delta$ ): 8.15 (d, J = 7.8 Hz, 2H), 7.96 (d, J = 7.8 Hz, 2H), 7.90–7.87 (m, 4H), 7.79 (d, J = 5.4 Hz, 2H), 7.75–7.72 (m, 4H), 7.64 (d, J = 7.8 Hz, 2H), 7.59–7.54 (m, 6H), 7.51 (d, J = 7.2 Hz, 4H), 7.45 (dd, J = 7.8 Hz and 7.2 Hz, 2H), 7.40–7.35 (m, 6H), 7.29–7.27 (m, 2H), 7.22–7.23 (m, 2H), 7.04–6.98 (m, 4H), 6.92–6.89 (m, 2H), 6.42 (d, J = 7.8 Hz, 2H). MS (MALDI-TOF) [m/z]: 1151.3 (M – PF<sub>6</sub>)<sup>+</sup>. Anal. found: C 63.89, H 3.54, N 6.52. Anal. Calcd for C<sub>69</sub>H<sub>46</sub>N<sub>6</sub>PF<sub>6</sub>Ir: C 63.93, H 3.58, N 6.48.

# 2.4. Quantum Chemical Calculations

Density functional theory (DFT) calculations using the B3LYP functional were performed. "Double- $\xi$ " quality basis sets were employed for the C, H and N (6-31G\*\*) [23] and the Ir (LANL2DZ) [24]. An effective core potential (ECP) replaces the innercore electrons of Ir leaving the outer core 5s<sup>2</sup>5p<sup>6</sup> electrons and the 5d<sup>6</sup> valence electrons of Ir(III). The solvent effect of  $CH_2Cl_2$  was taken into consideration using a conductorlike polarizable continuum model (C-PCM). All of the calculations were performed with Gaussian 03 software pakage [25].

## 3. Results and discussion

## 3.1. Synthesis and Structural Characterization

Scheme 1 shows the synthesis of the three cationic iridium complexes. The ancillary ligands ECAF, EHCAF and PCAF were easily synthesized from 4,5-diazafluoren-9-one and carbazole derivatives by using Eaton's reagent as the catalyst and condensing agent [21]. Complexes **1**, **2** and **3** were then routinely synthesized with yields of 79%, 81% and 81%, respectively, by reacting dimeric iridium(III) intermediate  $[(ppy)_2Ir(\mu-Cl)_2Ir(ppy)_2]$  with ancillary ligands, followed by a counter ion-exchange reaction from Cl<sup>-</sup> to PF<sub>6</sub><sup>-</sup> [26]. The three complexes were structurally characterized by <sup>1</sup>H NMR (Fig. S1–S3 in the SI), ESI (electron spray ionization) mass spectroscopy (Fig. S4–S6 in the SI) and elemental analysis.

#### 3.2. Thermal stability

The thermal stability of emitters is very important for efficient OLEDs. The decomposition temperatures of complexes 1, 2 and 3 were determined from the thermogravimetric analysis (TGA) curves under a nitrogen atmosphere. As shown in Fig. 1, these iridium complexes were very stable under a N<sub>2</sub> atmosphere and no significant weight loss was seen below 300 °C. Presumably, because they have two bulky carbazoles and a robust 4,5-diazafluorene core that completely surround the  $Ir^{3+}$  ions, weaker interactions between adjacent iridium molecules tend to increase the thermal stability of these ionic complexes. From the TGA curves it can be observed that the decomposition temperature (5% loss of weight) are 365 °C for 1, 320 °C for 2 and

410 °C for **3**, respectively, indicating that the complexes are suitable for application in OLEDs by vacuum-deposition method.

# 3.3. Photophysical Properties

The absorption and PL spectra of complexes **1**, **2** and **3** in CH<sub>2</sub>Cl<sub>2</sub> ( $5 \times 10^{-5}$  M) are shown in Fig. 2, and detailed photophysical characterizations are collected in Table 1. The strong and broad absorption bands in the ultra-violet up to around 360 nm are attributed to spin-allowed intraligand <sup>1</sup>LC ( $\pi \rightarrow \pi^*$ ) transition of cyclometalated main ligands and ancillary ligands. The relatively weak absorption bands from 360 nm extending to the visible region are assigned to excitations to <sup>1</sup>MLCT (metal-to-ligand charge-transfer), <sup>1</sup>LLCT (ligand-to-ligand charge-transfer), <sup>3</sup>MLCT, <sup>3</sup>LLCT, and ligandcentered (LC) <sup>3</sup> $\pi \rightarrow \pi^*$  transitions. The spin-forbidden <sup>3</sup>MLCT, <sup>3</sup>LLCT, and <sup>3</sup>LC  $\pi \rightarrow \pi^*$ transitions gain considerable intensity by mixing with the higher-lying <sup>1</sup>MLCT transition through spin-orbit coupling (SOC) endowed by the heavy iridium atom [22, 27]. No distinct difference is observed in absorption profiles for the complexes **1**, **2** and **3**, indicating the similar electronic and vibrational structures of the ground states (S<sub>0</sub>) and the first excited states (S<sub>1</sub>).

As depicted in Fig. 2, complexes 1, 2 and 3 exihibit yellow light emission (peaks at ca. 580 nm) in degassed  $CH_2Cl_2$  solutions at room temperature. Compared with their PL spectra in solutions, the PL spectra of complexes 1, 2 and 3 in neat films are slightly blue-shifted. In contrast, these complexes emit efficient yellow-green light with peaks at 540, 536 and 540 nm, respectively, in 5% (by weight) doped poly(methyl methacrylate) (PMMA) films. The large hypsochromic shift originates from the change of the local environment of the complex, as previously observed for the similar cationic iridium complexes [28, 29]. Generally, for mixed-ligand cationic iridium complexes,

three excited states contribute to the observed light emission, that is, LC  ${}^{3}\pi \rightarrow \pi^{*}$ ,  ${}^{3}$ MLCT, and  ${}^{3}$ LLCT [30-32]. At room temperature, the three complexes display broad and almost featureless emission spectra in CH<sub>2</sub>Cl<sub>2</sub> solutions and in films, which indicates that the emissive excited states have predominantly characters of  ${}^{3}$ MLCT or  ${}^{3}$ LLCT other than LC  ${}^{3}\pi \rightarrow \pi^{*}$ , as the latter always show vibronically structured emission spectra [30, 32]. At 77 K in 2-MeTHF matrix, the emission spectra of the complexes **1**, **2** and **3** are largely blueshifted (with peaks at 502, 503 and 504 nm, respectively) and structured, which indicates that, at low temperatures, considerable LC  ${}^{3}\pi \rightarrow \pi^{*}$  character develops in the emissive excited states of the complexes [30, 32, 33].

In degassed CH<sub>2</sub>Cl<sub>2</sub> solutions, complexes **1**, **2** and **3** give photoluminescent quantum yields (PLQY,  $\Phi$ ) of 0.32, 0.28 and 0.33, respectively, which are slightly larger than that of yellow light-emitting iridium complex [Ir(ppy)<sub>2</sub>(dtb-bpy)]PF<sub>6</sub> (0.24 in degassed CH<sub>3</sub>CN solutions) [34]. The excited-state lifetimes ( $\tau$ ) of complexes **1**, **2** and **3** in degassed CH<sub>2</sub>Cl<sub>2</sub> solutions (0.62, 0.61 and 0.60 µs, respectively) are similar to that of [Ir(ppy)<sub>2</sub>(dtb-bpy)]PF<sub>6</sub> (0.557 µs in degassed CH<sub>3</sub>CN solutions) [34]. The lack of vibronic structure in the phosphorescence spectra and the relatively short calculated radiative lifetimes ( $\tau_{rad} = \tau/\Phi$ ) indicate that these complexes emit from the charge-transfer excited state [33, 35].

Unlike previously reported [26], the PLQY values of 1, 2 and 3 in thin films are 0.32, 0.37 and 0.48, respectively, and are slightly larger than those in CH<sub>2</sub>Cl<sub>2</sub> solutions. This could be attributed to the steric hindrance of the ancillary ligands and molecules can be well dispersed in the neat films. In sharp contrast to the PLQYs in solutions and neat films, the doped films of complexes 1, 2 and 3 in PMMA exhibit significantly better PLQYs of 0.74, 0.72 and 0.78, respectively, accompanied by a remarkable increase of

excited state lifetimes. This enhancement in quantum yield and excited state lifetime plausibly result from the great restriction of rotations and vibrations in rigid polymer [12].

#### 3.4. Electrochemical Properties and Theoretical Calculations

The electrochemical behavior of these iridium complexes was measured in deoxygenated *N*,*N*-Dimethylformamide (DMF) solutions containing 0.1 M tetra(n-butyl)ammonium hexafluorophosphate (n-Bu<sub>4</sub>NPF<sub>6</sub>) as the supporting electrolyte by cyclic voltammetry (Fig. 3). During the anodic scan at the rate of 100 mV s<sup>-1</sup>, all of these complexes show the same first oxidation ( $E_{onset}^{ox}$ ) wave at about 0.90 V, which is almost identical to those of the ppy-based (ppy = 2-phenylpyridine) cationic iridium complexes [15, 16, 26]. It is confirmed that the oxidation occurred mainly at the iridium metal center. On the basis of the onset potential of  $E_{onset}^{ox}$  and the absorption edge data, the energy levels of the highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) can be estimated from the empirical formulae:  $E_{HOMO} = -e(E_{onset}^{ox} + 4.4)$  and  $E_{LUMO} = E_{HOMO} + E_g$  (where  $E_g$  is the optical energy gap obtained from the absorption threshold) [36, 37]. The HOMO (-5.3 eV for complexes **1**, **2** and **3**) and LUMO (-2.9 eV for complexes **1**, **2** and **B** locating in the same positions.

DFT calculations at the B3LYP/(6-31G<sup>\*\*</sup> +LANL2DZ) level were carried out to gain more insight into the photophysical and electrochemical properties of complexes 1, 2 and 3. Fig.4 displays the atomic orbital composition of HOMOs and LUMOs for complexes 1, 2 and 3. As expected, the HOMO orbitals of all complexes were composed of a mixture of Ir  $d\pi$  orbitals and phenyl  $\pi$  orbitals distributed among the

cyclometalated ligands, which are similar to those of other ppy-based iridium complexes [16, 26]. However, their LUMO orbitals were mainly dominated by the bipyridine units of the ancillary ligands ECAF, EHCAF and PCAF. This result, together with the electrochemical properties, refers that the introduction of the substituents in the ancillary ligands have no signicant effects on the frontier molecular orbitals of these complexes.

## 3.5. Electroluminescent Properties of OLED Devices

In order to evaluate the electroluminescent properties of these cationic iridium complexes, complexes **1**, **2** and **3** were used as doped emitters to fabricate OLEDs with the structure of ITO/PEDOT:PSS (40 nm)/TCTA(15 nm)/emitting layer (30 nm)/TmPyPb (50 nm)/LiF (0.5 nm)/Al (100 nm), in which PEDOT:PSS acts as hole-injecting layer, TCTA acts as hole-transporter, CBP acts as host, TmPyPb acts as electron-transporter, and LiF/Al as the electron-injection layer and cathode (Fig. 5). The optimized Ir(III) emitters with 10 wt% doped concentration in host material were used as the emitting layer. The device architecture, as well as molecular structure of the materials used are shown in Fig. 5.

Fig. 6 depicts the EL spectra of the OLEDs based on complexes 1, 2 and 3. Devices based on complexes 1, 2 and 3 emit yellow-green light with CIE coordinates of (0.38, 0.58), (0.37, 0.58), (0.38, 0.58), respectively. In the EL spectra, the emission from the host CBP disappears completely, indicating that the complete energy and/or charge transfer occurs from the host to the phosphors upon electrical excitation. In addition, the emission wavelength and profile of EL spectra of devices closely resemble those of PL spectra in PMMA film, indicating that phosphors 1, 2 and 3 were not decomposed during the vacuum thermal evaporation and electroluminescence originated from their

triplet excited states.

Fig. 7 shows the luminance-voltage-current density and current efficiency-current density-external quantum efficiency characteristics of the devices. Detailed electrical characteristics of the devices are summarized in Table 2. A maximum luminance  $(L_{max})$ of 8588 cd m<sup>-2</sup>, a maximum luminance efficiency ( $\eta_c$ ) of 20.2 cd A<sup>-1</sup> and an external quantum efficienty ( $\eta_e$ ) of 6.3 % for complex **1**, a  $L_{max}$  of 11850 cd m<sup>-2</sup>, a maximum  $\eta_c$ of 23.7 cd A<sup>-1</sup> and a  $\eta_e$  of 6.8 % for complex 2, and a  $L_{\rm max}$  of 10340 cd m<sup>-2</sup>, a maximum  $\eta_c$  of 21.5 cd A<sup>-1</sup> and a  $\eta_e$  of 6.5 % for complex 3 are achieved. As depicted in Fig. 7, the EL efficiencies of devices decrease gradually with a further increase of luminance. This phenomenon is the so-called EL efficiency roll-off and can be attributed to the triplet-triplet annihilation [38] originating from the long lifetime of triplet excited state and triplet-polaron quenching [39]. The EL efficiency roll-off effects in these devices are very mild, which should be attributed to the good carrier transport properties of the phosphorescent emitters with carbazole and 4,5-diazafluorene groups. The results suggest these complexes are good yellow-green phosphors and have potential applications in OLEDs. Ongoing novel cationic iridium(III) complexes with excellent thermal stability and corresponding device studies are currently in progress.

# 4. Conclusion

In conclusion, three novel cationic iridium complexes,  $[Ir(ppy)_2(ECAF)]PF_6$  (1),  $[Ir(ppy)_2(EHCAF)]PF_6$  (2) and  $[Ir(ppy)_2(PCAF)]PF_6$  (3), have been synthesized and fully characterized. Due to the excellent thermal stability, yellow-green OLEDs were fabricated by a vacuum-deposition method. Devices based on 1, 2 and 3 exibit the maximum current efficiencies of 20.2, 23.7 and 21.5 cd A<sup>-1</sup> and maximum external

quantum efficiencies of 6.3 %, 6.8 % and 6.5 % with the CIE coordinates of (0.38, 0.58), (0.37, 0.58), (0.38, 0.58), respectively.

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# **Supplementary material**

<sup>1</sup>H NMR and ESI-MS spectra of the synthesized complexes were presented. This material is available free of charge via the Internet.

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#### **Captions for Schemes and Figures**

Scheme 1. The synthetic route of iridium complexes 1–3.

Fig. 1. The TGA curves of complexes 1–3.

Fig. 2. Absorption and emission spectra of complexes 1 (a), 2 (b) and 3 (c).

Fig. 3. Cyclic voltammograms of complexes 1, 2 and 3 in DMF solutions  $(10^{-3} \text{ M})$ . Potentials were recorded versus Fc<sup>+</sup>/Fc.

Fig. 4. Molecular orbital surfaces of cationic iridium complexes. (a) LUMO orbital of complex 1. (b) HOMO orbital of complex 1. (c) LUMO orbital of complex 2. (d) HOMO orbital of complex 2. (e) LUMO orbital of complex 3. (f) HOMO orbital of complex 4. All the MO surfaces correspond to an isocontour value of  $|\Psi| = 0.02$ .

**Fig. 5.** Device architecture and chemical structures of the materials used in these OLEDs.

Fig. 6. EL spectra of the OLEDs based on complexes 1, 2 and 3 with 10 wt% doped concentration in host material.

**Fig. 7.** The current density-voltage-luminance (a) and current efficiency-current density-external quantum efficiency characteristics (b) of the devices based on complexes **1**, **2** and **3**.

**Captions for Tables** 

Table 1 Photophysical characteristics of complexes 1, 2 and 3.

Table 2 Electrical characteristics of devices based on complexes 1, 2 and 3.

			Emissio	Emission at 77 K <sup>[e]</sup>				
	$\lambda_{abs} [nm]^{[a]}$	Solution $\lambda \text{ [nm]}^{[b]}$	PMMA film λ[nm] <sup>[c]</sup>	$CH_2Cl_2\\_{[b]}$	$\frac{\Phi_{\rm em} \left[\tau \left[\mu s\right]\right]}{5 \text{ wt\% in}}$ PMMA <sup>[c]</sup>	Neat Film <sup>[d]</sup>	λ[nm]	τ[µs]
1	239/288/410	580	540	0.32 [0.62]	0.74 [0.93]	0.32 [0.54]	502	4.26
2	239/289/411	580	536	0.28 [0.61]	0.72 [0.96]	0.37 [0.58]	503	4.13
3	242/290/409	582	540	0.33 [0.60]	0.78 [0.92]	0.48 [0.56]	504	4.34

<sup>[a]</sup> In CH<sub>2</sub>Cl<sub>2</sub> solutions (1  $\times$  10<sup>-5</sup> M). <sup>[b]</sup> In degassed CH<sub>2</sub>Cl<sub>2</sub> solutions. <sup>[c]</sup> Doped films were made on quartz substrates with thicknesses of about 100 nm. <sup>[d]</sup> Neat films were made on quartz substrates with thicknesses of about 100 nm. <sup>[e]</sup> In 2-MeTHF matrix at 77 K.

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Devices	$V_{\text{turn-on}}(\mathbf{V})$	$L_{\rm max}$ /cd m <sup>-2 [a]</sup>	$\eta_{ m c}$ /cd $ m A^{-1}$ [a]	$\eta_{ m p}$ /lm ${ m W}^{ m 1~[a]}$	$\eta_{ m e}$ /% $^{[a]}$	$\lambda_{ m em}/ m nm$	CIE (x, y)					
D1	9.2	8588	20.2	4.87	6.3	540	(0.38, 0.58)					
D2	8.4	11850	23.7	5.32	6.8	540	(0.37, 0.58)					
D3	8.2	10340	21.5	5.63	6.5	540	(0.38, 0.58)					

<sup>[a]</sup> Maximum values of the devices.

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# Highlights

- > Sublimable cationic iridium complexes > Bis-carbazole substituted
- 4,5-diazafluorene ligand > Yellow-green organic light-emitting diodes