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# Red to Blue Emitting Cationic Iridium Complexes with 2-phenyl-4-dimethylaminopyridine as the Cyclometalating Ligand: Synthesis, Characterization and Electroluminescent Devices

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# Abstract

2-Phenyl-4-dimethylaminopyridine (dmappy) with high  ${}^{3}\pi$ - $\pi^{*}$  triplet energy is, for the first time, employed as the cyclometalating ligand for constructing cationic iridium complexes with tunable emission properties. Three complexes, namely,  $[Ir(dmappy)_2(bpy)]PF_6$  $[Ir(dmappy)_2(pzpy)]PF_6$ (1), (2)and  $[Ir(dmappy)_2(dma-pzpy)]PF_6$  (3), have been designed and synthesized (bpy = 2, 2-(1*H*-pyrazol-1-yl)pyridine 2'-bipyridine, and dma-pzpy pzpy = = 4-dimethylamino-2-(1*H*-pyrazol-1-yl)pyridine), photophysical and their and electrochemical properties have been comprehensively investigated. By using

ancillary ligands with increasing electron-richness (bpy  $\rightarrow$  pzpy  $\rightarrow$  dmapzpy), complexes 1-3 emit red, green and blue light, respectively. Theoretical calculations reveal that for complexes 1 and 2, the light emission stems predominantly from the charge-transfer states (Ir/dmappy  $\rightarrow$  bpy or pzpy), whereas for complex 3, the light emission originates mainly from the dmappy-centered  ${}^{3}\pi$ - $\pi^{*}$  state. In the doped film, fluorine-free complex 3 affords comparable emission color, luminescent efficiency and excited-state lifetime to the typical blue-emitting, neutral iridium complex FIrpic that uses fluorinated ligands. Single-layer, solution-processed organic light-emitting diodes based on complex 3 affords blue electroluminescence (EL) peaked at 472 nm, with the EL color competing with that from FIrpic and the peak current efficiency (12.6 cd A<sup>-1</sup>) being among the highest reported for single-layer, solution-processed blue OLEDs based on ionic iridium complexes.

Keywords: cationic iridium complex; color-tuning; blue; organic light-emitting diode

# **1. Introduction**

Phosphorescent cationic iridium complexes have drawn growing research interest in the past decade, due to their intrinsic ionic nature, high phosphorescent efficiency, tunable emission color and rich redox properties. For these desirable features, they have been widely employed as functional agents in biological imaging [1,2], sensing [1,2], photocatalysis [3] and optoelectronic devices [4-7], to mention but a few. In particular, they have been widely used as emitting materials in light-emitting electrochemical cells (LECs) or as dopants in solution-processed organic light-emitting diodes (OLEDs) [4,6-9], which, as efficient emissive thin-film devices, have emerged as promising candidates for next-generation solid-state lighting or display applications.

Huge efforts have been devoted to tune the emission properties of cationic iridium complexes, which is realized by control of both cyclometalating ( $C^{\Lambda}N$ ) and ancillary  $(N^{\Lambda}N)$  ligands [4,6,7,10]. The earliest reported phosphorescent cationic iridium complex,  $[Ir(ppy)_2(bpy)]PF_6$ , with 2-phenylpyridine (Hppy) as the C<sup>A</sup>N ligand and 2,2'-bipyridine (bpy) as the N<sup> $\Lambda$ </sup>N ligand, emits orange-red light [11,12]. To shift the light emission toward blue, the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) needs to be widened [10,13,14]. To this end, various approaches have been adopted [6,10]. For instance, electron-withdrawing groups (such as F, -CF<sub>3</sub>, -SF<sub>5</sub>) have been attached at the phenyl ring of ppy to stabilize the HOMO [15-17] and electron-donating groups (such as dimethylamino) have been attached at the pyridine ring of bpy to destabilize the LUMO [18]; moreover, electron-rich N<sup> $\Lambda$ </sup>N ligands, such 2-(1H-pyrazo1-1-yl)pyridine (pzpy) and as 4-dimethylamino-2-(1H-pyrazo1-1-yl)pyridine (dma-pzpy), have been developed to destabilize significantly the LUMO [19-22]. For cationic iridium complexes, it has been unveiled that along with the emission blue-shift, the character of the emitting triplet state could change. For example, for orange-emitting  $[Ir(ppy)_2(bpy)]PF_6$ , the emitting triplet state exhibits mixed metal-to-ligand charge-transfer (<sup>3</sup>MLCT) (Ir→ bpy)/ligand-to-ligand charge-transfer ( ${}^{3}LLCT$ ) (ppy $\rightarrow$ bpy) character [12,23], whereas

for the blue-green-emitting [Ir(ppy)<sub>2</sub>(pzpy)]PF<sub>6</sub>, the emitting triplet state shows mixed <sup>3</sup>MLCT (Ir  $\rightarrow$  ppy)/<sup>3</sup> $\pi$ - $\pi^*$  (ppy-centered) character [19,23]. For the latter complex, the emission is mainly controlled by the <sup>3</sup> $\pi$ - $\pi^*$  state of the ppy C<sup>A</sup>N ligand. Therefore, C<sup>A</sup>N ligands with high <sup>3</sup> $\pi$ - $\pi^*$  triplet energy are preferred for constructing cationic iridium complexes with blue-shifted light emission.

It is noted that attaching electron-donating alkoxyl groups at the *para* position of the pyridine ring in ppy can effectively enhance the  ${}^{3}\pi$ - $\pi^{*}$  triplet energy of the ligand [22,24]. With a stronger electron-donating dimethylamino group at the *para* position of the pyridine ring, 2-phenyl-4-dimethylaminopyridine (dmappy) possesses even higher  ${}^{3}\pi$ - $\pi^{*}$  triplet energy and thus, is a suitable C<sup>A</sup>N ligand for color-tuning toward blue for cationic iridium complexes. Moreover, dmappy contains no fluorine substitutions, which is beneficial for constructing blue-emitting iridium complexes, because fluorine substitutions decrease the thermal and electrochemical stability of the complexes [25,26]. To our knowledge, dmappy has so far not been examined as the C<sup>A</sup>N ligand for cationic iridium complexes, especially for blue-emitting ones.

Herein, we report three red to blue emitting cationic iridium complexes with dmappy C<sup>A</sup>N ligands, namely, [Ir(dmappy)<sub>2</sub>(bpy)]PF<sub>6</sub> (1), [Ir(dmappy)<sub>2</sub>(pzpy)]PF<sub>6</sub> (2) and [Ir(dmappy)<sub>2</sub>(dma-pzpy)]PF<sub>6</sub> (3) (Scheme 1). By using N<sup>A</sup>N ligands with increasing electron-richness (bpy  $\rightarrow$  pzpy  $\rightarrow$  dmapzpy), complexes 1-3 afford red, green and blue light emission, respectively. Theoretical calculations reveal that from complexes 1 and 2 to complex 3, the emitting triplet state changes from mixed <sup>3</sup>MLCT (Ir $\rightarrow$ N<sup>A</sup>N)/<sup>3</sup>LLCT (dmappy $\rightarrow$ N<sup>A</sup>N) to mixed <sup>3</sup>MLCT (Ir $\rightarrow$ dmappy)/<sup>3</sup> $\pi$ - $\pi^*$ 

(dmappy-centered). In the lightly doped film, fluorine-free blue-emitting complex 3 affords comparable emission properties to the typical blue-emitting, neutral iridium complex FIrpic that uses fluorinated ligands [27]. Single-layer, solution-processed OLEDs using the complexes as dopants have been fabricated. The blue OLED based on complex 3 affords comparable electroluminescence (EL) color to that based on FIrpic and its efficiency (12.6 cd  $A^{-1}$ ) is among the highest reported for single-layer, solution-processed blue OLEDs based on ionic iridium complexes [20,22,28-33].

# 2. Experimental

**General experiments.** All reactants and solvents, unless otherwise stated, were purchased from commercial sources and used as received. <sup>1</sup>H-NMR spectra were recorded on a BRUKER 400/500 NMR spectrometer with Si(CH<sub>3</sub>)<sub>4</sub> as the internal standard. Mass spectrometry was conducted with a LTQ-ORBITRAP-ETD mass spectrometer. Elemental analysis was determined on an EA3000 elemental analyzer (Eurovector, Italy). Thermogravimetric analysis (TGA) was performed on a simultaneous thermal analyzer (SDTQ650) with a temperature increasing rate of 10 <sup>o</sup>C/min under a nitrogen atmosphere. Absorption and photoluminescence (PL) spectra were recorded with a UV-vis spectrophotometer (Agilent 8453) and a fluorospectrophotometer (Jobin Yvon, FluoroMax-3), respectively. The PL transient lifetimes were measured on a transient spectrofluorimeter (Edinburgh Instruments, FLSP920) with a time-correlated single-photon counting technique. The photoluminescent quantum yields (PLQYs) (excited at 380 nm) in degassed CH<sub>3</sub>CN

were measured with Ru(bpy)<sub>3</sub>Cl<sub>2</sub> ( $\Phi_p = 0.028$  in water) as the standard for complex 1 and quinine sulfate ( $\Phi_p = 0.545$  in 1 M H<sub>2</sub>SO<sub>4</sub>) as the standard for complexes 2 and 3. The PLQYs in thin films were measured with an absolute PLQY measurement system (Hamamatsu C11347) equipped with an integrating sphere. Cyclic voltammetry was performed on a LK1100 voltammetric analyzer in CH<sub>2</sub>Cl<sub>2</sub> solution ( $10^{-3}$  M) for oxidation and in *N*,*N*-dimethylformamide (DMF) solution ( $10^{-3}$  M) for reduction at a scan rate of 100 mV s<sup>-1</sup>, with a glass-carbon working electrode, a Ag wire reference electrode and a Pt wire counter-electrode. Tetrabutylammonium hexafluorophosphate (0.1 M) and ferrocene were used as the supporting electrolyte and the internal standard, respectively. The solutions were degassed with argon before measurements. **Synthesis.** The ligands pzpy and dma-pzpy were synthesized according to reported procedures [19,22].

Synthesis of 4-chloro-2-phenylpyridine. Phenylboronic acid (3.0 g, 25 mmol), 2,4-dichloropyridine (3.7 g, 25 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.87 g, 0.75 mmol) and K<sub>2</sub>CO<sub>3</sub> (10.4 g, 75 mmol) were dissolved in 1,2-dimethoxyethane/H<sub>2</sub>O (70/30 mL). The mixture was stirred at 90 °C under a nitrogen atmosphere for 18 h. After being cooled to room temperature, the mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> ( $3 \times 50$  mL). The organic phase was washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and purified by column chromatography on silica gel with petroleum ether/CH<sub>2</sub>Cl<sub>2</sub> (5:1) as the eluent, yielding a light yellow oil (3.1 g, 16.9 mmol).Yield: 65%. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz,  $\delta$ [ppm]):  $\delta$  8.59 (d, *J* = 5.3 Hz, 1H), 8.00-7.95 (m, 2H), 7.74 (d, *J* = 1.8 Hz, 1H),

7.52–7.42 (m, 3H), 7.24-7.27 (m, 1H). HRMS (ESI, m/z): 190.0407 [M+H]<sup>+</sup> (calc. 190.0418).

Synthesis of dmappy. 4-chloro-2-phenylpyridine (2.8 g, 15 mmol), dimethyllamine hydrochloride (12.2 g, 150 mmol) and sodium hydroxide (6.0 g, 150 mmol) were dissolved in DMF/H<sub>2</sub>O (50/25 mL). The mixture was stirred at room temperature for 30 minutes and then potassium carbonate (4.1 g, 30 mmol) was added. The mixture was further stirred at 130 °C for 10 h in a sealed tube. After being cooled to room temperature, the mixture was extracted with  $CH_2Cl_2$  (80 mL). The organic phase was washed with brine, dried over anhydrous  $Na_2SO_4$  and purified by column chromatography on silica gel with  $CH_2Cl_2/CH_3OH$  (50:1) as the eluent, yielding a white solid (2.4 g, 12.1 mmol).Yield: 81%. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 500 MHz,  $\delta$ [ppm]): 8.37 (d, J = 6.4 Hz, 1H), 8.00 – 7.94 (m, 2H), 7.53 – 7.42 (m, 3H), 6.89 (d, J = 2.6 Hz, 1H), 6.56 (dd, J = 6.5, 2.5 Hz, 1H), 3.15 (s, 6H). HRMS (ESI, m/z): 199.1215 [M+H]<sup>+</sup> (calc. 199.1230).

*Synthesis of*  $[Ir(dmappy)_2Cl]_2$ . The chloro-bridged iridium dimer  $[Ir(dmappy)_2Cl]_2$  was prepared by refluxing  $IrCl_3.nH_2O$  and dmappy (2.5 eq.) in 2-ethoxyethanol/water (3:1) under nitrogen[34,35]. The precipitate was collected, dried under vacuum and used without further purification.

Synthesis of  $Ir[(dmappy)_2(bpy)]PF_6$  (1). [Ir(dmappy)\_2Cl]<sub>2</sub> (286 mg, 0.23 mmol) and bpy (80 mg, 0.51 mmol) were dissolved in CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH (10/10 mL).The mixture was refluxed overnight under a nitrogen atmosphere and then cooled to room temperature. To the solution, NH<sub>4</sub>PF<sub>6</sub> (375 mg, 2.3 mmol) was added. The mixture

was stirred at room temperature for 2 h and the solvent was removed under vacuum. The remaining solid was washed with water and dried under vacuum. The solid was purified by column chromatography on silica gel (200-300 mesh) with CH<sub>2</sub>Cl<sub>2</sub>/acetone as the eluent, vielding a red solid (123 mg, 0.14 mmol). Yield: 30%. <sup>1</sup>H-NMR (DMSO- $d_6$ , 500 MHz,  $\delta$ [ppm]): 8.84 (d, J = 8.2 Hz, 2H), 8.23 (td, J = 8.0, 1.4 Hz, 2H), 7.94 – 7.82 (m, 4H), 7.70–7.64 (m, 2H), 7.25 (d, J = 2.5 Hz, 2H), 6.98 – 6.92 (m, 4H), 6.86 (t, J=7.5 Hz, 2H), 6.42 – 6.38 (m, 2H), 6.34 (d, J = 7.4 Hz, 2H), 3.08 (s, 12H). HRMS (ESI, m/z): 743.2487 [M-PF<sub>6</sub>]<sup>+</sup> (calc. 743.2469). Anal. found: C, 48.59; H, 3.97; N, 9.41. Anal. calcd for C<sub>36</sub>H<sub>34</sub>F<sub>6</sub>IrN<sub>6</sub>P: C, 48.70; H, 3.86; N, 9.47. Synthesis of  $Ir[(dmappy)_2(pzpy)]PF_6$  (2). Complex 2 was synthesized with a similar procedure to that for complex 1, except that bpy was replaced by pzpy, yielding a yellow solid. Yield: 35%. <sup>1</sup>H-NMR (DMSO- $d_6$ , 500 MHz,  $\delta$ [ppm]): 9.26 (d, J = 3.0 Hz, 1H), 8.49 (d, J = 8.5 Hz, 1H), 8.30 (td, J=8.0, 1.5 Hz, 1H), 7.88 - 7.80 (m, 2H), 7.67 (dd, J = 5.5, 1.0 Hz, 1H), 7.54–7.49 (m, 1H), 7.28–7.23 (m, 2H), 7.22 (d, J = 2.0 Hz, 1H), 7.12 (d, J = 7.0 Hz, 1H), 7.09 (d, J = 7.0 Hz, 1H), 6.97 – 6.87 (m, 3H), 6.85 (td, J = 7.4, 1.3 Hz, 1H), 6.80 (td, J = 7.4, 1.3 Hz, 1H), 6.47 (dd, J = 7.0, 2.9 Hz, 1H), 6.44 (dd, J = 7.0, 2.9 Hz, 1H), 6.37–6.32 (m, 2H), 3.12–3.08 (m, 12H). HRMS (ESI, m/z): 732.2385  $[M-PF_6]^+$  (calc. 732.2421). Anal. found: C, 46.42; H, 3.86; N, 11.10. Anal. calcd for C<sub>34</sub>H<sub>33</sub>F<sub>6</sub>IrN<sub>7</sub>P: C, 46.57; H, 3.79; N, 11.18.

Synthesis of  $Ir[(dmappy)_2(dma-pzpy)]PF_6$  (3). Complex 3 was synthesized with a similar procedure to that for complex 1, except that bpy was replaced by dma-pzpy, yielding a light yellow solid. Yield: 28%. <sup>1</sup>H-NMR (CD<sub>3</sub>CN, 500 MHz,  $\delta$ [ppm]): 8.68

(d, J = 3 Hz, 1H), 7.74–7.68 (m, 2H), 7.28 (d, J = 7.0 Hz, 1H), 7.21 (d, J = 6.5 Hz, 1H), 7.18–7.11(m, 4H), 7.03 (d, J = 2.5 Hz, 1H), 6.96–6.84 (m, 2H), 6.86–6.77 (m, 2H), 6.69–6.66 (m, 1H), 6.50 (dd, J = 7.0, 2.5Hz, 1H), 6.43–6.31(m, 4H), 3.13–3.09 (m, 18H). HRMS (ESI, m/z): 775.2809  $[M-PF_6]^+$  (calc. 775.2843). Anal. found: C, 46.89; H, 4.24; N, 12.11. Anal. calcd for  $C_{36}H_{38}F_6IrN_8P$ : C, 47.00; H, 4.16; N, 12.18.

**X-ray crystallography.** The single-crystal X-ray experiments were conducted on a Rigaku CCD Saturn 724+deffractometer equipped with graphite monochromatized Mo K $\alpha$  radiation. Direct phase determination led to the positions of all non-hydrogen atoms which were subjected to anisotropic refinement. All hydrogen atoms were produced theoretically and rode on their parent atoms in the final refinement. All computations were conducted using the SHELXTL program. Single crystal structures of complexes 1 and 2 were deposited to Cambridge Crystallographic Data Centre (CCDC) with deposition numbers of 1887889 and 1887890, respectively.

Theoretical calculations. For calculations on the ground and excited electronic states, density functional theory (DFT) at the B3LYP level was employed [36,37]. "Double- $\xi$ " quality basis sets were used for C, H and N (6-31G\*\*) and the Ir (LANL2DZ). An effective core potential (ECP) replaces the inner core electrons of iridium, leaving the outer core  $(5s)^2(5p)^6$  electrons and the  $(5d)^6$  valence electrons of Ir(III). The geometries of singlet ground states (S<sub>0</sub>) were fully optimized with the C1 symmetry. The lowest-lying ten triplets were calculated at the optimized S<sub>0</sub> geometries with the time-dependent DFT (TD-DFT) approach. The geometries of the triplet excited states were fully optimized at the spin-unrestricted B3LYP level with a spin multiplicity of 3.

All the calculations were performed in the presence of solvent (CH<sub>3</sub>CN). Solvent effects were considered within the self-consistent reaction field (SCRF) theory adopting the polarized continuum (PCM) model [38]. All calculations were conducted with Gaussian 09 software package [39]. The geometries of selected triplet states were directly compared with the  $S_0$  geometries by using the VMD program [40]. The root mean square displacement/deviation (RMSD) values between the two geometries were given by the VMD program.

Fabrication and characterizations of OLEDs. Indium-tin-oxide (ITO) substrates with a sheet resistance of 15  $\Omega/\Box$  were sufficiently cleaned in detergent and then in deionized water, and treated with UV-zone before use. The PEDOT: PSS layers were deposited onto the ITO substrates in air and baked at 200 °C for 10 minutes. The substrates coated with PEDOT: PSS were transferred into a nitrogen-filled glove box, in which the emissive layers were spin coated on top of PEDOT:PSS from 1,2-dichloroethane solution. The films were baked at 80 °C for 30 minutes and then transferred into a vacuum chamber, where LiF and Al were evaporated at 0.1–0.2 Å/s and 5–8 Å/s, respectively. The devices were characterized with a Keithley 4200 semiconductor characterization system. The EL spectra were recorded with a Photo Research PR705 spectrophotometer under ambient conditions.

## 3. Results and discussion

#### 3.1. Synthesis and structural characterizations



Scheme 1. Synthesis of complexes 1-3.

Scheme 1 depicts the synthetic routes to dmappy and complexes 1-3. Dmappy was previously synthesized by a Pd(0)-catalyzed Suzuki coupling reaction between phenylboronic acid and 2-iodo-4-dimethylaminopyridine with just a moderate yield of 46%; moreover, the synthesis of the intermediate 2-iodo-4-dimethylaminopyridine required a complex procedure including the use of n-butyllithium [35]. In this work, dmappy was readily synthesized by a nucleophilic substitution reaction between 4-chloro-2-phenylpyridine and dimethylamine with a high yield of 81% (Scheme 1). The intermediate 4-chloro-2-phenylpyridine was conveniently prepared by a Suzuki coupling reaction between phenylboronic acid and 2,4-dichloropyridine (Scheme 1).

Complexes 1-3 were prepared by cleaving the chloro-bridged iridium dimer,  $[Ir(dmappy)_2Cl]_2$ , with the N<sup>A</sup>N ligand, followed by an anion-exchanging reaction from Cl<sup>-</sup> to PF<sub>6</sub><sup>-</sup>. Chemical structures of all the complexes were verified by NMR spectroscopy, high-resolution mass spectrometry and elemental analysis (see Experimental). Thermal stability of complexes 1-3 was characterized by thermogravimetric analysis (Fig. S1), which shows that complexes 1-3 exhibit high decomposition temperature (5% weight loss) of 380, 330 and 305 °C, respectively.



**Figure 1.** Single crystal structures of complexes 1 and 2. Thermal ellipsoids were drawn at 30% probability.  $PF_6^-$  counter anions, solvent molecules and all hydrogen atoms were omitted for clarity.

Single crystals of complexes 1 and 2 were grown from solution and characterized

by X-ray experiments. Fig. 1 depicts the determined single-crystal structures. Pertinent bond lengths and ligand bite angles are presented in Table S1 in the supporting information. The geometries of the iridium centers are distorted octahedrons with the two dmappy ligands adopting C, C-cis and N, N-trans configurations. The Ir-C, Ir-N bond lengths and the ligand bite angles fall within those found in analogous complexes [19,22]. It is noted that the C-N bonds (1.32–1.36 Å) connecting the dimethylamino groups and the pyridine rings in the dmappy ligands resemble the typical C=N double bond (1.35 Å), which indicates that the nitrogen atoms of the dimethylamino groups are in conjugation with the pyridine rings, *i.e.*, they donate their lone-pair electrons to the pyridine rings. For this reason, the dmappy ligand bear higher  ${}^{3}\pi - \pi^{*}$  triplet energy than the ppy ligand [22,24].



Figure 2. Absorption and PL spectra of complexes 1-3 in CH<sub>3</sub>CN solution.

	Absorption $\lambda$ [nm] ( $\epsilon$ [×10 <sup>4</sup> M <sup>-1</sup> cm <sup>-1</sup> ]) <sup>a</sup>	Emission at room temperature						PL at	Electrochemi-	
		CH <sub>3</sub> CN <sup>b</sup>			2 wt.% in PMMA <sup>c</sup>			77 k	cal data <sup>e</sup>	
		PL [nm]	$\Phi_{\rm em}$ (t[µs])	$k_{\rm r}, k_{\rm nr}$ [10 <sup>5</sup> s <sup>-1</sup> ]	PL [nm]	$\Phi_{\rm em}$ ( $\tau$ [µs])	$k_{r}, k_{nr}$ [10 <sup>5</sup> s <sup>-1</sup> ]	[nm] d	E <sub>ox</sub> [V]	E <sub>red</sub> [V]
1	486 (0.09)	620	0.03	1.8, 57	582	0.50	6.6, 6.6	563	0.61	-1.85
	405 (0.48)		(0.17)			(0.76)				
	383 (0.97)									
	270 (6.15)									
2	450 (0.08)	526	0.12	1.8, 14	491	0.65	3.8, 2.0	453,	0.59	-2.32 ir
	407 (0.35)		(0.65)			(1.72)		483		
	382(1.03)						2			
	269 (6.50)									
3	446 (0.04)	464,	0.04	3.6, 87	465,	0.76	4.8, 1.4	459,	0.53	-2.62 <sup>ir</sup>
	402 (0.40)	489	(0.11)		489	(1.59)		491		
	380 (1.08)									
	266 (7.76)									

 Table 1. Photophysical and electrochemical data of complexes 1-3.

<sup>a</sup> In CH<sub>3</sub>CN solution (10<sup>-5</sup> M). <sup>b</sup> In degassed CH<sub>3</sub>CN solution (10<sup>-5</sup> M). <sup>c</sup> Films coated on quartz substrates. <sup>d</sup> In CH<sub>3</sub>CN glass at 77 K. <sup>e</sup> Potentials were recorded *versus*  $Fc^+/Fc$ ; the superscript "ir" denotes irreversible reduction processes.

Fig. 2 depicts the absorption and PL spectra of complexes 1-3 in CH<sub>3</sub>CN solution. Detailed photophysical characteristics were summarized in Table 1. As shown in Fig. 2, complexes 1-3 exhibit strong absorption bands in the ultra-violet region (below 350 nm), which arise from the spin-allowed ligand-centered  ${}^{1}\pi$ - $\pi^{*}$  transitions, and relatively weak absorption bands (above 350 nm) that extend to the visible region, which can be tentatively assigned to  ${}^{1}MLCT/{}^{3}MLCT$ ,  ${}^{1}LLCT/{}^{3}LLCT$  and ligand-centered  ${}^{3}\pi$ - $\pi^{*}$  transitions [11,41,42]. The spin-forbidden triplet transitions become partially permitted owing to the strong spin-orbital coupling endowed by the heavy iridium atoms.

In degassed CH<sub>3</sub>CN solution, complexes 1-3 emit red, green and blue light with

the emission peaks at 620, 526 and 464 nm, respectively, with their emission spectra spanning nearly the entire visible spectrum (Fig. 2). As shown in Fig. 2, complexes 1 and 2 afford featureless and broad PL spectra, which indicates that their light emission comes predominantly from charge-transfer (CT) states, whereas complex 3 affords a structured and narrowed PL spectrum, which indicates that its light emission originates mainly from a ligand-centered  ${}^{3}\pi$ - $\pi^{*}$  state. Apparently, the blue-shift of light emission is accompanied with the change of the character of emitting triplet state from dominant  ${}^{3}$ CT to ligand-centered  ${}^{3}\pi$ - $\pi^{*}$ . The underlying mechanism for this character change will be discussed in theoretical calculations.

The PL spectra of complexes 1-3 in the frozen CH<sub>3</sub>CN glass at 77 K were measured, as shown in Fig. S2 in the supporting information. At 77 K, complex 1 exhibits an almost featureless PL spectrum that is largely blue-shifted by about 60 nm compared to the room-temperature PL spectrum, which agrees with the dominant <sup>3</sup>CT character assigned to the light emission of complex 1 [43]. At 77 K. complex 2 affords a structured PL spectrum peaked at 483 nm, which indicates the development of ligand-centered  ${}^{3}\pi$ - $\pi^{*}$  character in the low-temperature emission, in contrast with the dominant  ${}^{3}$ CT character in the room-temperature emission. It is thus suggested that the  ${}^{3}$ CT state and the ligand-centered  ${}^{3}\pi$ - $\pi^{*}$  state in complex 2 lie close in energy, the order of which depend on the local environment (such as temperature) [44]. At 77 K, complex 3 exhibits a highly structured PL spectrum that is slightly blue-shifted by about 5 nm compared to the room temperature PL spectrum, which agrees with the dominant ligand-centered  ${}^{3}\pi$ - $\pi^{*}$  character assigned to the light emission of complex 3.

In the degased CH<sub>3</sub>CN solution, complexes 1-3 afford PLQYs of 0.03, 0.12 and 0.04, respectively, and excited-state lifetimes of 0.17, 0.65 and 0.11 µs, respectively (Table 1). According to these PLQY and excited-state lifetime values, the radiative  $(k_r)$ and non-radiative (k<sub>nr</sub>) decay rates in the degassed CH<sub>3</sub>CN solution were calculated and summarized in Table 1. Complex 1 exhibits a normal  $k_r$  of  $1.8 \times 10^5 \ s^{-1}$  but quite a large  $k_{nr}$  of  $5.7 \times 10^6$  s<sup>-1</sup>. The large  $k_{nr}$  of red-emitting complex 1 can be explained by the energy gap law which predicts that a narrower energy gap leads to a larger  $k_{nr}$ [45-47]. Complex 2 exhibits  $k_r$  and  $k_{nr}$  of  $1.8 \times 10^5$  s<sup>-1</sup> and  $1.4 \times 10^6$  s<sup>-1</sup>, respectively. Compared to complex 1, green-emitting complex 2 exhibits a largely decreased  $k_{nr}$ , which agrees with the energy gap law. However, compared to typical green-emitting iridium complexes which show  $k_{nr}$  values in the order of  $10^5$  s<sup>-1</sup>, complex 2 still exhibits a relatively large  $k_{nr}$ . Blue-emitting complex 3 exhibits a  $k_r$  of  $3.6 \times 10^5$  s<sup>-1</sup> and a  $k_{nr}$  of  $8.7 \times 10^6$  s<sup>-1</sup> that is the largest among the series of complexes, which seems to disobey the energy gap law. The relatively large  $k_{nr}$  of complex 2 and the abnormally large  $k_{nr}$  of complex 3 indicate that there exist efficient non-radiative deactivation channels for the emitting triplet states of complexes 2 and 3 in the solution.

Emission properties of complexes 1-3 in the 2 wt. % doped poly(methylmethacrylate) (PMMA) films were measured, with the PL spectra presented in Fig. S3 in the supporting information and the photophysical data summarized in Table 1. In the PMMA film, complex 1 affords orange-red light emission with a featureless PL spectrum centered at 582 nm, a PLQY of 0.50 and an

excited-state lifetime of 0.76  $\mu$ s; complex 2 emits green-blue light with an almost featureless PL spectrum centered at 491 nm, a PLQY of 0.65 and an excited-state lifetime of 1.72  $\mu$ s; complex 3 emits blue light with a structured PL spectrum peaked at 465 nm, a PLQY of 0.76 and an excited-state lifetime of 1.59  $\mu$ s. The spectrum profiles indicate that in the lightly doped films, the emission of complexes 1 and 2 and the emission of complex 3 originate predominantly from the <sup>3</sup>CT states and the ligand-centered  ${}^{3}\pi$ - $\pi^{*}$  state, respectively, similar to those observed in the solution. It is worth noting that in the doped film, fluorine-free blue-emitting complex 3 exhibits comparable emission peak, PLQY and excited-state lifetime to the typical blue-emitting neutral iridium complex FIrpic that uses fluorinated C<sup>A</sup>N ligands [27]. In the doped PMMA film, FIrpic affords an emission peak at 468 nm with a PLQY of 0.89 and an excited state lifetime 1.7  $\mu$ s [48].

According to the PLQY and excited-state lifetime values, the  $k_r$  and  $k_{nr}$  values in the doped PMMA films were calculated and summarized in Table 1. Compared to those in the solution, the  $k_{nr}$  values in the PMMA films are significantly reduced, owing to the suppressed non-radiative deactivations in the solid rigid films. On the other hand, the  $k_r$  values are remarkably enhanced compared to those in the solution (Table 1). In general, for blue light emission with dominant ligand-centered  ${}^{3}\pi$ - $\pi^{*}$ character, the  $k_r$  value is usually small because of the reduced  ${}^{3}MLCT$  character in the emitting triplet state [49]. However, complex 3 still exhibits a relatively large  $k_r$  of 4.8  $\times 10^{5}$  s<sup>-1</sup>. This result agrees with the previous work on blue-emitting complexes using dma-pzpy N<sup>A</sup>N ligand, in which it was revealed that the highly electron-rich dma-pzpy ligand is capable of enhancing the  $k_r$  values of blue-emitting complexes[22]. Owing to the suppressed  $k_{nr}$  and enhanced  $k_r$ , complex 3 exhibits relatively high PLQY and short excited-state lifetime in the doped film, which benefits its application as dopants in OLEDs.

 $(\mathsf{True}) \mathsf{True} (\mathsf{True}) \mathsf{True} (\mathsf{True})$ 

#### 3.3. Electrochemical properties

Figure 3. Cyclic voltammograms of complexes 1-3 in solution.

Electrochemical properties of complexes 1-3 were measured by cyclic voltammetry in solution. Fig. 3 depicts the cyclic voltammograms. Complexes 1-3 all show reversible oxidation processes, with oxidation potentials at 0.61, 0.59 and 0.53 V, respectively. With these oxidation potentials, the HOMO levels of complexes 1-3 were calculated to be -5.41, -5.39 and -5.33 eV, respectively. Complexes 1-3 show similar HOMO levels (within 0.08 eV), although the trend is that the HOMO level is slightly destabilized from complex 1, to 2 and to 3.

As shown in Fig. 3, complex 1 shows a reversible reduction process, with the reduction potential at -1.85 V, whereas complexes 2 and 3 exhibit irreversible reduction processes, with the peak reduction potentials at -2.32 and -2.62 V, respectively. From these reduction potentials, the LUMO levels of complexes 1-3 were calculated to be -2.95, -2.48 and -2.18 eV, respectively. From complex 1, to 2 and to 3, the LUMO level is stepwisely destabilized by a large extent (0.30–0.47 eV) [19,22]. As a result, the energy gap is largely enlarged from complex 1, to 2 and to 3, which consists with the gradual blue-shift of light emission experimentally observed.





**Figure 4.** Optimized S<sub>0</sub> geometries and surface distributions ( $|\Psi| = 0.025$ ) and energy levels of HOMO (lower images) and LUMO (upper images) orbitals calculated for complexes 1-3.

To gain deep insight into the photophysical and electrochemical properties of the complexes, theoretical calculations on the complexes were conducted (see Experimental). Fig. 4 depicts the optimized geometries of the ground states ( $S_0$ ) and surface distributions and energy levels of the HOMO and LUMO orbitals. Those of other molecular orbitals were presented in Table S2 in the supporting information. The geometrical parameters of the optimized  $S_0$  states were summarized in Table S3 in the supporting information. The calculated bond lengths and ligand bite angles agree well with those observed in the single-crystal structures (Tables S1 and S3).

As shown in Fig. 4, the HOMO orbitals reside predominantly on the iridium ions and the phenyl rings of the dmappy ligands, while the LUMO orbitals distribute almost exclusively over the N<sup> $\Lambda$ </sup>N ligands. From complex 1, to 2 and to 3, the HOMO level exhibits only a slight change (within 0.08 eV) but the LUMO level is gradually destabilized by a large extent of about 0.4 eV, which agrees with the electrochemical measurements. Because the LUMO resides on the N<sup> $\Lambda$ </sup>N ligand, increasing the electron-richness of the N<sup> $\Lambda$ </sup>N ligand from bpy, to pzpy and to dmapzpy results in the stepwise destabilization of the LUMO level, which agrees with previous studies on complexes using electron-rich N<sup> $\Lambda$ </sup>N ligands [19,22].

As shown in Table S2, for complexes 1-3, the HOMO-1 and HOMO-2 reside on the pyridine rings and dimethylamino groups of the dmappy ligands and the iridium ions, while the HOMO-3 distributes predominantly over the entire dmappy ligands. For complexes 1 and 2, the LUMO+1 resides mainly over the N<sup>A</sup>N ligands, while the LUMO+2 and LUMO+3 distribute mainly over the dmappy ligands. For complex 3, the LUMO+1 and LUMO+2 reside predominantly over the dmappy ligands, while the LUMO+3 resides mainly on the pyridine ring of the dma-pzpy ligand.

	State	$E_{\mathrm{T}}$	Dominant Excitation	Character
		(eV) <sup>a</sup>	b	
1	$T_1$	2.39	$H \rightarrow L (97\%)$	<sup>3</sup> MLCT (Ir→bpy)/ <sup>3</sup> LLCT (dmappy→bpy)
	$T_2$	2.65	H-1 →L (84%)	<sup>3</sup> MLCT (Ir→bpy)/ <sup>3</sup> LLCT (dmappy→bpy)
	$T_3$	2.69	H-2 →L (90%)	<sup>3</sup> MLCT (Ir→bpy)/ <sup>3</sup> LLCT (dmappy→bpy)
2	$T_1$	2.83	$H \rightarrow L (97\%)$	<sup>3</sup> MLCT (Ir→pzpy)/ <sup>3</sup> LLCT (dmappy→pzpy)
	$T_2$	2.94	H→ $L$ +2 (44%),	<sup>3</sup> MLCT (Ir $\rightarrow$ dmappy)/ <sup>3</sup> $\pi$ - $\pi^*$ (dmappy-centered)
			H-3 →L+3 (18%)	
			$H \rightarrow L+1 (13\%)$	
	$T_3$	2.99	H→ $L$ +3 (40%),	<sup>3</sup> MLCT (Ir $\rightarrow$ dmappy)/ <sup>3</sup> $\pi$ - $\pi^*$ (dmappy-centered)
			H-3 →L+2 (23%)	
3	$T_1$	2.92	H→ $L$ +1 (59%),	<sup>3</sup> MLCT (Ir $\rightarrow$ dmappy)/ <sup>3</sup> $\pi$ - $\pi^*$ (dmappy-centered)
			H-3 →L+2 (15%)	
	$T_2$	2.98	H →L+2 (45%),	<sup>3</sup> MLCT (Ir $\rightarrow$ dmappy)/ <sup>3</sup> $\pi$ - $\pi$ <sup>*</sup> (dmappy-centered)
			H-3 →L+1 (23%)	
	<b>T</b> <sub>3</sub>	3.12	H →L (74%),	<sup>3</sup> MLCT(Ir→dmapzpy)/ <sup>3</sup> LLCT (dmappy→dmapzpy)
			H-1 →L (13%)	

 Table 2. Selected triplet states of complexes 1-3 calculated from the TDDFT approach.

<sup>a</sup> Excitation energies calculated for the triplet states. <sup>b</sup> H and L denote HOMO and LUMO, respectively; data in parentheses are the contributions of corresponding excitations; only excitations with contributions larger than 10% are listed.

To reveal the triplet-state character, TDDFT calculations were performed on the optimized S<sub>0</sub> geometries. Table 2 summarizes the characteristics of the first three triplet states of complexes 1-3. The character of the triplet states were concluded by analyzing the dominant transitions and the surface distributions of the molecular orbitals involved in the transitions. For complex 1, the T<sub>1</sub>, T<sub>2</sub> and T<sub>3</sub> states all exhibit mixed <sup>3</sup>MLCT (Ir  $\rightarrow$  bpy)/<sup>3</sup>LLCT (dmappy  $\rightarrow$  bpy) character, *i.e.*, pure <sup>3</sup>CT

character. For complex 2, the T<sub>1</sub> state exhibits mixed <sup>3</sup>MLCT (Ir  $\rightarrow$  pzpy)/<sup>3</sup>LLCT (dmappy  $\rightarrow$  pzpy) character, *i.e.*, pure <sup>3</sup>CT character, whereas the T<sub>2</sub> and T<sub>3</sub> states exhibit mixed <sup>3</sup>MLCT (Ir  $\rightarrow$  dmappy)/<sup>3</sup> $\pi$ - $\pi^*$  (dmappy-centered) character. For complex 3, the T<sub>1</sub> and T<sub>2</sub> states exhibit mixed <sup>3</sup>MLCT (Ir  $\rightarrow$  dmappy)/<sup>3</sup> $\pi$ - $\pi^*$  (dmappy centered) character, whereas the T<sub>3</sub> state shows mixed <sup>3</sup>MLCT (Ir  $\rightarrow$  dmappy)/<sup>3</sup>LLCT (Ir  $\rightarrow$  dmappy)/

From Table 2, it can be observed that from complex 1, to 2 and to 3, the <sup>3</sup>MLCT  $(Ir \rightarrow N^{\Lambda}N)^{3}LLCT$  (dmappy  $\rightarrow N^{\Lambda}N$ ) state, *i.e.*, the pure <sup>3</sup>CT state, is destabilized in a stepwise manner  $(2.39 \rightarrow 2.83 \rightarrow 3.12 \text{ eV})$  because of the gradual destabilization of the LUMO residing on the N<sup>A</sup>N ligand, whereas the <sup>3</sup>MLCT (Ir  $\rightarrow$  dmappy)/<sup>3</sup> $\pi$ - $\pi^*$ (dmappy-centered) state (around 2.94 eV) remains almost unchanged. The gradual destabilization of the <sup>3</sup>CT state finally leads to the change of the energy level order between the two states (Table 2). For complexes 1 and 2, the <sup>3</sup>CT states (Ir/dmappy  $\rightarrow$  N<sup>A</sup>N) are the lowest-lying triple states that account for the light emission, while for complex 3, the <sup>3</sup>MLCT (Ir  $\rightarrow$  dmappy)/<sup>3</sup> $\pi$ - $\pi$ <sup>\*</sup> (dmappy-centered) state becomes the lowest-lying triplet state from which the light emission occurs. The assignments of the emitting triplet states consist with the character of light emission concluded from the photophysical characterizations (vide supra). It is worth noting that for complex 3, the <sup>3</sup>CT state (T<sub>3</sub>) and the <sup>3</sup>MLCT (Ir  $\rightarrow$  dmappy)/<sup>3</sup> $\pi$ - $\pi^*$  (dmappy-centered) state (T<sub>1</sub>/T<sub>2</sub>) lie close in energy (within 0.20 eV), which indicates that thermal population from the latter to the former is likely to occur [50-53].



**Figure 5.** Optimized geometries and unpaired-electron spin-density contours (0.002 e bohr<sup>-3</sup>) calculated for a)  $T_1$  of complex 1, b)  $T_1$  of complex 2, c)  $T_1$  of complex 3 and d)  $T_3$  of complex 3.

Table 3. Triplet energies (in eV) calculated for complexes 1-3.

complex	$T_1$	$T_3$	<sup>3</sup> MC	$\Delta E(^{3}MC-T_{1})$
1	2.23	_	3.06	0.83
2	2.69	_	3.07	0.38
3	2.80	2.96	3.06	0.26

To gain further insight into the character of triplet states, they were optimized with the spin-unrestricted DFT method (see Experimental). Fig. 5 depicts the geometries and spin-density distributions of the optimized triplet states. The geometrical parameters of the optimized triplet states were presented in Table S3 in the supporting information. As shown in Fig. 5, for the T<sub>1</sub> states of complexes 1 and 2 and the T<sub>3</sub> state of complex 3, the spin-densities distribute over the iridium ions, the phenyl rings of dmappy ligands and the entire N<sup>A</sup>N ligands, which match very well with the the topologies of HOMO and LUMO orbitals (Fig. 4) and agree with the <sup>3</sup>MLCT (Ir → N<sup>A</sup>N)/<sup>3</sup>LLCT (dmappy→N<sup>A</sup>N) character assigned to these states (Table 2). For the T<sub>1</sub> state of complex 3, the spin-density distributes over the iridium ion and one dmappy ligand, which consists with the <sup>3</sup>MLCT (Ir  $\rightarrow$  dmappy)/<sup>3</sup> $\pi$ - $\pi^*$  (dmappy-centered) character assigned to this state (Table 2).

Table 3 summarizes the triplet energies of the optimized triplet states. From complex 1, to 2 and to 3, the triplet energy of the  $T_1$  state (the emitting state) increases gradually from 2.23 to 2.69 and to 2.80 eV, which accords with the gradually blue-shifted light emission experimentally observed. For complex 3, the optimized  $T_1$  and  $T_3$  states still lie close in energy (within 0.16 eV), which further indicates that thermal population from the  $T_1$  to the  $T_3$  states could occur at ambient conditions [50-54].

Structural distortion between the excited and ground states usually results in a large temperature-independent non-radiative decay of the excited-state [45,55-58]. The geometries of the optimized triplet states were thus compared with those of  $S_0$  states (see Experimental), as shown in Fig. S4. For complex 1, the T<sub>1</sub> state exhibits a small structural distortion compared to the  $S_0$  state, with a small RMSD value of 0.102 (Fig. S4a). However, because of its narrow energy gap, complex 1 still shows quite a large non-radiative decay in the solution (Table 1). For complex 2, the T<sub>1</sub> state shows a considerably large structural distortion with respect to the S<sub>0</sub> state (Fig. S4b), with a relatively large RMSD value of 0.179, mainly because of the twist of the pzpy ligand on the T<sub>1</sub> state, as observed in similar complexes with pzpy-type N<sup>A</sup>N ligands [53,54]. For this relatively large structural distortion, complex 2 should show a relatively large non-radiative decay in the solution, which was indeed observed in the photophysical measurement (Table 1). For complex 3, the T<sub>1</sub> state exhibits a small

structural distortion compared to the  $S_0$  state (Fig. S4c), with a small RMSD value of 0.084; however, the  $T_3$  state shows a large structural distortion compared to the  $S_0$  state, with a large RMSD value of 0.258, mainly because of the remarkable twist of the dma-pzpy ligand (Fig. S4d) [53,54]. Therefore, for complex 3, the  $T_3$  state should be dominated by non-radiative decay. On the other hand, the  $T_3$  state could be thermally accessed by the  $T_1$  state; as a result, the  $T_1$  state could undergo additional non-radiative decay through thermal population to the  $T_3$  state [53,54], which partially explains the abnormally large non-radiative decay of complex 3 in the solution.

The metal-centered states ( ${}^{3}MC$ ) resulting from the d-d transitions in the iridium ions are well known non-radiative dark states in iridium complexes [49,59]. For complexes 1-3, their  ${}^{3}MC$  states were optimized and the optimized geometries and spin-density distributions were presented in Fig. S5. On the  ${}^{3}MC$  states, the Ir–N bonds between iridium and dmappy ligands are remarkably elongated by about 0.4 Å, which indicates bond ruptures and the de-coordination of the pyridine rings. The spin-densities distribute mainly on the iridium ions, consistent with the metal-centered character. As shown in Table 3, the  ${}^{3}MC$  state lies 0.83, 0.38 and 0.26 eV higher in energy than the T<sub>1</sub> state for complex 1, 2 and 3, respectively. For complex 1, the much higher-lying  ${}^{3}MC$  state should hardly affect the T<sub>1</sub> state and thus makes little contribution to the overall non-radiative decay. For complex 2, non-radiative decay through thermal population to the  ${}^{3}MC$  state cannot be precluded in the solution. For complex 3, it is very likely that non-radiative decay occurs through thermal population to the  ${}^{3}MC$  state which lies moderately higher in energy than the T<sub>1</sub> state.

Therefore, for complex 3, thermal populations to the higher-lying non-radiative  $T_3$  and <sup>3</sup>MC states represent important non-radiative decay channels for the  $T_1$  state, which lead to the abnormally large non-radiative decay observed in the solution (Table 1). It is worth noting that in the doped film, these non-radiative decay channels should be remarkably suppressed because of the destabilization of the <sup>3</sup>CT state ( $T_3$ ) [41,42] and the suppression of geometry relaxation for the triplet states in the rigid matrix. As a result, in the doped PMMA film, complex 3 affords a remarkably suppressed non-radiative decay and a high PLQY (Table 1).





Figure 6. EL spectra of the OLEDs based on complexes 2 and 3.



Figure 7. Current-density and brightness *versus* voltage curves of the OLEDs based on complexes 2 and 3.

Table 4. Electrical characteristics of the OLEDs based on complexes 2 and 3.

Complex	Von	$B_{\rm max}$	η <sub>c,p</sub>	EQE <sub>p</sub>	$EL \lambda$	CIE
-	(V) <sup>a</sup>	$(cd m^2)^{b}$	$(cd A^{-1})^{c}$	(%) <sup>d</sup>	(nm)	(x,y)
2	6.7	13600	16.2	6.5	506	(0.27, 0.50)
3	6.8	7000	12.6	6.3	472, 488	(0.19, 0.35)

<sup>a</sup> Voltage required to reach 1 cd m<sup>-2</sup>. <sup>b</sup> The maximum brightness. <sup>c</sup> The peak current efficiency. <sup>d</sup> The peak external quantum efficiency.

Complex 1 shows limited solubility in organic solvents with low or medium polarity, which hinders its use in solution-processed OLEDs. Complex 2 and complex 3 show good solubility in organic solvents with medium polarity and also high PLQYs in the doped films (Table 1). They were thus used as dopants in single-layer, solution-processed OLEDs. The device structure is ITO/PEDOT: PSS (40 nm)/PVK: 30 wt.% OXD-7: 10 wt.% complex (90 nm) /LiF (1 nm)/Al (100 nm), where poly(*N*-vinylcarbazole) (PVK) was used as the hole-transporting host and

1,3-bis(5-(4-(*tert*-butyl)phenyl)-1,3,4-oxadiazol-2-yl)benzene (OXD-7) was doped into PVK to facilitate the electron-transport. The film morphologies of the emissive layers (PVK: OXD-7: complex) were characterized and the root-mean square roughness values for the (PVK: OXD-7: complex 2) and (PVK: OXD-7: complex 3) films ( $5 \times 5 \ \mu m^2$ ) are 0.75 and 0.72 nm, respectively, which indicates that the emissive layers have smooth surfaces. These smooth film surfaces agree with a previous study on similar (PVK:OXD-7: complex) films [60].

Fig. 6 and Fig. 7 depict the EL spectra and the current density and brightness versus voltage curves of the OLEDs, respectively. Detailed electrical characteristics were summarized in Table 4. The OLED based on complex 2 affords green-blue EL centered at 506 nm, with CIE (Commission Internationale de L'Eclairage) coordinates of (0.27, 0.50). The OLED based on complex 3 affords sky-blue EL peaked at 472 and 488 nm, with CIE (Commission Internationale de L'Eclairage) coordinates of (0.19, 0.35), which is comparable to that from the OLED based on FIrpic (EL<sub>peak</sub> = 474 nm, CIE=(0.17, 0.34)) [60]. The PL spectra of the light emitting layers show residual light emission around 400 nm originating from the PVK:OXD-7 host (Fig. S6), which indicates incomplete energy transfer from the host to the complex under photo-excitation. However, the EL spectra show no such residual light emission from the host, which indicates that in addition to the energy transfer, charge-trapping followed by direct exciton formation on the complex occurs under electrical excitation [61,62]. The energy level diagrams of the OLEDs reveal that complexes 2 and 3 behave as strong hole trappers due to their shallow HOMO levels (Fig. S7),

which consists with the EL measurements [61,62].

The OLEDs show relatively high turn-on voltages around 7.0 V, which should be ascribed to the large hole-injection barrier (0.6 eV) at the PEDOT:PSS/light-emitting layer interface and the hole-trapping effect of the dopant (Fig. S7). It has been shown that strong charge-trapping effects enhance remarkably the turn-on voltages of OLEDs. Here, complexes 2 and 3 exhibit strong hole-trapping in the light-emitting layers (Fig. S7), which should largely increase the turn-on voltages. The green-blue OLED based on complex 2 affords a maximum brightness of 13600 cd m<sup>-2</sup> and a peak current efficiency of 16.2 cd A<sup>-1</sup>. Those of the blue OLED based on complex 3 are 7000 cd m<sup>-2</sup> and 12.6 cd A<sup>-1</sup>, respectively. These efficiencies are among the highest reported for single-layer solution-processed OLEDs based on ionic iridium complexes [7,20,22,28-33,62], which indicates the great potential for the use of these complexes in electroluminescent devices.

# 4. Conclusion

Dmappy is for the first time adopted as the  $C^{\Lambda}N$  ligand to construct red to blue emitting cationic iridium complexes. By gradually increasing the electron-richness of the ancillary ligand, the emission color of the complex was finely tuned from red to blue, with the emission spectra spanning nearly the entire visible spectrum. The emission blue-shift was demonstrated to result from the gradual destabilization of the LUMO level and the emitting triplet state upon the variation of the ancillary ligand. With the highly electron-rich dmapzpy ancillary ligand, fluorine-free blue-emitting

complex 3 afforded comparable emission properties to the blue-emitting neutral iridium complex FIrpic in the doped film. Single-layer, solution-processed OLEDs based on complexes 2 and 3 afforded green-blue and blue EL, respectively, with the efficiencies being among the highest reported for similar devices based on ionic iridium complexes. The work reveals that dmappy with high  ${}^{3}\pi$ - $\pi$ \* triplet energy is a promising C<sup>A</sup>N ligand for constructing cationic iridium complexes with tunable emission properties for advanced applications.

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Highlights

- 2-phenyl-4-dimethylaminopyridine was tested as a main ligand for cationic Ir complex
- Color-tuning from red to blue was achieved by varying the ancillary ligand
- The blue-emitting complex showed comparable emission properties to FIrpic
- Single-layer solution-processed blue OLED afforded an efficiency of 12.6 cd  $A^{-1}$