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# Near-Infrared Emission of Di-nuclear Iridium Complexes with

# hole/electron transporting bridging and Their Monomer in

## Solution-Processed Organic Light-Emitting Diodes

Zhaoran Hao<sup>a</sup>, Min Li<sup>a</sup>, Yajun Liu<sup>a</sup>, Yafei Wang<sup>a,c</sup>, Guohua Xie<sup>b</sup>\*, Yu Liu<sup>a,c</sup>\*

# **Graphical abstracts**



Two dinuclear iridium (III) complexes D-Ir-Caz and D-Ir-OXD grafting hole or electron transporting  $\pi$ -conjugated bridges, and their corresponding monomer Mono-Ir were successfully synthesized and characterized. Under photo-excitation, all these complexes exhibit similar NIR emission peaked at approximately 698 nm in CH<sub>2</sub>Cl<sub>2</sub>. Due to a lower degree of spin-orbit coupling (SOC) in a system with centrosymmetric environment at the ancillary ligand, both dinuclear iridium (III) complexes D-Ir-Caz and D-Ir-OXD exhibited a much lower luminescence quantum yields ( $\Phi_L$ ) in comparison with their corresponding monomer complex Mono-Ir. Furthermore, the Mono-Ir-based device shows a EQE of 1.29% at 3.5 mA/cm<sup>2</sup>, while D-Ir-Caz- and D-Ir-OXD-based devices suffer relatively lower efficiencies of 0.27% and 0.41% accompanied with a negligible efficiency roll-off.

# Near-Infrared Emission of Dinuclear Iridium Complexes with hole/electron transporting bridging and Their Monomer in Solution-Processed Organic Light-Emitting Diodes

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Abstract: To obtain efficient near-infrared (NIR) emitting materials, a novel iridium (III) complex based on a triphenylamine functionalized pyridylpyrene ligand, namely, Mono-Ir, as well as its two corresonding dinuclear iridium (III) complexes possessing  $\pi$ -conjugated bridging linkages of hole-transporting carbazole (Caz) unit or electron-transporting 2,5-diphenyl-1,3,4-oxadiazole (OXD) unit, namely D-Ir-Caz and D-Ir-OXD, were successfully synthesized and characterized. Under photo-excitation, similar phosphorescence spectrum were obtained for the three complexes with intense NIR emission peak at approximately 698 nm and emission wavelength ranging from 650-900 nm. Also, in their single-emissive-layer OLEDs with a device structure of ITO/PEDOT:PSS/TFB/CBP:PBD:complexes/TmPyPB/Liq/Al, NIR similar electroluminescent (EL) emission peaked at 698 nm with a shoulder at 762 nm were obtained. The Mono-Ir-based device showed an external quantum efficiency (EQE) of 1.29% at low current density of 3.5 mA  $\text{cm}^{-2}$ , while a relatively lower efficiency of 0.27% for the D-Ir-Caz-based device and 0.41% for the D-Ir-OXD-based device, accompanied with negligible efficiencies roll-off at high current densities were achieved, respectively. The better device performance should be achieved when coupled with electron transporting bridging, especially at high currents.

Keywords: Cyclometalated dinuclear iridium (III) complexes; Near-infrared; Organic light-emitting diodes; Synthesis

#### **1. Introduction**

Since the pioneer work by Tang and Vanslyke in 1980s<sup>1</sup>, great progress have been made on developing high-efficiencies visible organic light-emitting diodes (OLEDs), where has potential applications in low cost, efficient, flexible full-color displays and lighting panels, et al <sup>2-8</sup>. As an extension of visible light, near-infrared (NIR) organic luminescent materials (700-2500 nm) also have emerging applications in night-vision displays, medical diagnosis, sensor, optical communication, et al 9-11. However, as for their device performance, NIR materials always suffer low efficiencies and sharp efficiencies roll-off at high currents, which should always be attributed to their decreased energy gap<sup>12,13</sup> and long excited-state lifetimes, and that commonly occurs in square-planar Pt(II)-porphyrin phosphors <sup>14</sup>. Furthermore, in persuit of increasing emission wavelength, many materials are always characterized by their strong donor/acceptor (D/A) or conjugate rigid plane structure, which are easily prone to fluorescence quenching that caused by close molecular packing <sup>15</sup>. Hence, it is still a tough issue for the design of high-efficient NIR emitters for OLEDs application.

Classical phosphorescent transition metal materials are available to exhibit high luminescence quantum efficiencies and narrow energy gap, resulting from their triplet emissive character through strong spin orbit coupling in the presence of heavy metal. Therefore, materials based on the Pt <sup>14,16-20</sup>, Ir <sup>21-24</sup>, or Os <sup>26</sup> complexes are of particular relevance in NIR applications. Of these, Pt complexes have shown record external quantum efficiencies (EQE) up to 8.8~24% with peak emission in the range of 650~800 nm <sup>14,19-20</sup>. However, most of these platinum systems are constructed by square-planar configuration, and the accompanying easy aggregation and relatively long phosphorescence lifetime always generate noticeable efficiency roll-offs at high current density <sup>27</sup>.

As another major category in phosphorescent transition metal materials, Ir(III) complexes exhibit typical octahedral configuration and relatively short triplet lifetime, which is favor for their efficiency stabilities in OLEDs <sup>21,24</sup>. Besides, in a C^N bidentate cyclometalated system, spin-orbit coupling (SOC) seems to be more efficient for octahedral d<sub>6</sub> Ir complexes than that for square-planar d<sub>8</sub> Pt complexes  $^{28}$ . These materials always exhibit slightly reduced device efficiencies at high currents, besides, their EQEs can reach up to as high as 3.4% at 702 nm<sup>21</sup>, 3.1% at 714 nm<sup>22</sup>, and 4.5% at 760 nm<sup>24</sup>, respectively. Qiao etc, reported a cationic iridium emitter based on benzophthalazine in solution-processed NIR OLED, and shows negligible efficiency roll-off even over a wide range of currents of 1-100 mA cm<sup>-2 23</sup>. On the basis of the foregoing work, recently, their group designed a neutral homoleptic iridium material, which may has the highest EQEs in the Ir complexes, of that 4.5% at 760 nm with small efficiency roll-off remaining of 3.5% at 100 mA cm<sup>-2 24</sup>. Similarly, Kesarkar etc, demonstrated a kind of benzothiophenyl-isoquinolinate-based Ir complexes with different  $\beta$ -diketonate ancillary ligands, and obtained a remarkable EQE of 3.07% in a solution processed OLED with negligible efficiency roll-off <sup>22</sup>.

Through the introduction of triphenylamine appendices at the peripheral side of the pyridylpyrene (PyPyr) ligand <sup>29</sup> to extend the  $\pi$ -conjugation, an effectively narrow

energy gap with longer emission wavelength was achieved in a new complex Mono-Ir. This material exhibit an efficient NIR emission peaked at 698 nm with a vibronic shoulder, while the spin-coated OLEDs achieved a maximum external quantum efficiency of 1.29%. Besides, carbazole and oxadiazole derivatives usually exhibt high hole-transporting and electron-injecting abilities, and are ideal component in constructing OLEDs materials <sup>30</sup>. To gain an insight into the performance change of materials that have these functional group act as bridging linkages, two dinuclear iridium (III) complexes incorporating a hole-transporting carbazole (Caz) or an electron-transporting oxadiazole (OXD) bridging unit were also designed and synthesized, namely D-Ir-Caz and D-Ir-OXD, respectively. The synthetic routes of the three complexes are shown in Scheme 1. Their thermal, electrochemical, and optophysical properties were also investigated. The strategy is focused on the introduction of the bulky structure to suppress molecular aggregation and provide with efficient hole/electron transporting abilities in device. It is interesting that the similar PL spectra were obtained in the three iridium (III) complexes. However, much lower luminescence quantum yields were detected in the dinuclear iridium (III) complexes. We think that it should be caused by a lower degree of spin-orbit coupling (SOC) in a system with centrosymmetric environment at the ancillary ligand. Therefore, the D-Ir-Caz- and D-Ir-OXD-based devices suffer relatively lower efficiencies of 0.27% and 0.41%, along with negligible efficiency roll-off values.

#### 2. Experimental section

#### 2.1. Materials and Synthesis

All reagents were purchased from Aldrich and Acros Inc. Tetrahydrofuran (THF) was distilled over sodium before used. The other reagents were directly used without further purification. All reactions were performed under nitrogen atmosphere and were monitored by thin-layer chromatography. As shown in Scheme 1, both dinuclear iridium (III) complexes D-Ir-Caz and D-Ir-OXD with hole-transporting carbazole- or electron-transporting oxadiazole bridging, as well as their corresponding monomer complex Mono-Ir were designed and synthesized, respectively. Both the ligand *t*-BuTPAPyPyr and the target dinuclear iridium (III) complexes were obtained simply through Suzuki coupling reactions which are similarly to the previous reports <sup>16,18</sup>. The yields of dinuclear iridium (III) complexes are low due to steric hindrance, and the reaction environment was carried out in two kinds of large polarity solvents. The target iridium (III) complexes were synthesized according to the literature procedures <sup>21-24</sup>. *t*-BuPyr-B was prepared followed by the literature reported <sup>31</sup>.

# 2.2. Apparatus and Procedures

<sup>1</sup>H and <sup>13</sup>C NMR spectra were measured with a Bruker Dex-400 NMR instrument using CDCl<sub>3</sub> as a solvent. Mass spectra (MS) were recorded on a Bruker Autoflex MALDI-TOF instrument using dithranol as a matrix. The thermogravimetric analysis (TGA) was undertaken using a NETZSCH STA449 measurement under nitrogen atmosphere at a heating rate of 20 °C min<sup>-1</sup>. The ultraviolet-visible (UV-vis) absorption and photoluminescence (PL) spectra of the compound were recorded on a Varian Cray 50 and Perkin-Elmer LS50B luminescence spectrometer, respectively. The optical band gap (E<sub>g</sub>) energy level was estimated from the onset of the absorption

edge. Excited-state lifetimes were recorded at excitation wavelengths of 440 nm for three complexes on FLS920 with time-corrected single-photon-counting (TCSPC) measurement, while the low temperature phosphorescence spectra were obtained on an Edinburgh FLS920 Spectrometer at 77 K in DCM solution. The  $\Phi_p$  values of complexes in degassed DCM solutions were measured with tris(2,2'-bipyridine) ruthenium(II) ( $\Phi_p$ =0.062 in acetonitrile solution at 298 K) as the standard. The equation of  $\Phi_s = \Phi_r(\eta_s^2 A_r I_s/\eta_r^2 A_s I_r)$  was used to calculate the fluorescence quantum yields where  $\Phi_s$  is the quantum yield of the sample,  $\Phi_r$  is the quantum yield of the reference,  $\eta$  is the refractive index of the solvent, A<sub>s</sub> and A<sub>r</sub> are the absorbance of the sample and the reference at the wavelength of excitation, and  $I_s$  and  $I_r$  are the integrated areas of emission bands <sup>32</sup>. Cyclic voltammetry (CV) measurements were performed on a CHI600E electrochemical workstation with platinum as the working electrode, platinum wire as the counter electrode, and KCl saturated Ag/AgCl as the reference electrode at a 100 mV s<sup>-1</sup> scanning rate. Tetrabutylammonium hexafluorophosphate (Bu<sub>4</sub>NPF<sub>6</sub>, 0.10 M) was used as the supporting electrolyte in acetonitrile solvent. Standard ferrocenium/ferrocene (Fc<sup>+</sup>/Fc) system was used to calibrate the experiment data.

#### 2.3. Device fabrication.

The OLEDs structure employed in this study is ITO/PEDOT:PSS (30 nm)/TFB (10 nm)/CBP:PBD:complexes (60:30:10, 40 nm)/TmPyPB (40 nm)/Liq (1 nm)/Al (100 nm), where PEDOT is poly(3,4-ethylenedionythiophene) and PSS is poly(styrenesulfonic acid) (Batron-P 4083, purchased from Bayer AG). The ITO

surface was pre-cleaned in an ultrasonic solvent bath, and dried in an oven at 120 °C for more than 3 h, then treated with UV ozone for 15 min. After that, the substrates were transferred to the spin-coating process, and then different functional layers (PEDOT: PSS layer and transporting layer and emissive layer) were sequentially spin-coated onto the substrates and were dried in vacuum. Then the samples were transferred to the deposition system, and TmPyPB and Liq/Al layers were sequentially deposited onto the substrate by thermal deposition in the vacuum of  $10^{-6}$ Torr. The emitting layer consisted of the host of CBP:PBD and dopant of the complex. The dopant concentration was 10 wt %. The electroluminescent (EL) spectra were measured by a PR650 spectrometer. The current density-voltage-brightness (J-V-R) features of the OLEDs were measured with a Keithey 2400 Source meter and Konica Minolta chromameter CS-200 with a calibrated silicon photodiode. The EQEs values were calculated from the current densities, current efficiencies, and the corresponding EL spectra. All measurements were carried out at room temperature under ambient conditions.

#### 2.4. Synthesis

2.4.1. Synthesis of 7-tert-butyl-1-(5-bromopyridine-2-yl)pyrene (t-BuPyrPy)

A mixture of 7-tert-butyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyrene (0.86 g, 2.2 mmol), 2,5-dibromopyridine (0.63 g, 2.7 mmol), aqueous Na<sub>2</sub>CO<sub>3</sub> (4.5 M, 5 mL), and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.05 g, 0.045 mmol) in 30 mL THF was flushed with N<sub>2</sub> while stirring at reflux temperature for 24 h. After cooled to RT, the mixture was extracted with  $CH_2Cl_2$  and the combined organic layer was dried over MgSO<sub>4</sub>. The solvent was

removed by rotary evaporation and the residue was passed through a flash silica gel column using PE-DCM (*V/V*, 2/1) as the eluent, then recrystallized using hexane to afford a yellowish solid (0.48 g, 52 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.94 (s, 1H), 8.34 (d, *J* = 9.2 Hz, 1H), 8.25 (d, *J* = 10.1 Hz, 3H), 8.09 (t, *J* = 7.8 Hz, 4H), 8.03 (d, *J* = 8.3 Hz, 1H), 7.66 (d, *J* = 8.3 Hz, 1H), 1.59-1.54 (m, 9H). MALDI-TOF MS (m/z) for C<sub>43</sub>H<sub>34</sub>N<sub>2</sub>. Calcd: 413.078; Found, 414.112.

2.4.2. Synthesis of N,N-diphenyl-4-(2-(1-tert-butyl-pyrene-7-yl)-pyridine-5-yl)benzene amine (t-BuPyrPyTPA)

A mixture of compound 5 (0.62 g, 1.5 mmol), N,N-diphenyl-4-(4,4,5,5tetramethyl-1,3,2-dioxaborolan-2-yl)benzenamine (0.72 g, 1.9 mmol), aqueous Na<sub>2</sub>CO<sub>3</sub> (5 M, 10 mL), and Pd(PPh<sub>3</sub>)<sub>4</sub> (35 mg, 0.03 mmol) was added into 30 mL dry THF under N<sub>2</sub> atmosphere. The reaction was heated at reflux for 24 h under stirring. After cooled to RT, the mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> and the combined organic layer was dried over MgSO<sub>4</sub>. The solvent was removed by rotary evaporation and the residue was passed through a flash silica gel column using PE-DCM (V/V, 2/1) as the eluent, then recrystallized using acetone to afford a yellow solid (0.45 g, 55 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.10 (s, 1H), 8.49 (d, J = 9.4 Hz, 1H), 8.23 (dd, J = 20.7, 12.6 Hz, 4H), 8.13 (s, 1H), 8.10 (s, 1H), 8.06 (d, J = 7.9 Hz, 2H), 7.81 (d, J = 8.0 Hz, 1H), 7.60 (d, *J* = 8.3 Hz, 2H), 7.32 (t, *J* = 7.7 Hz, 4H), 7.21 (dd, *J* = 15.6, 8.1 Hz, 6H), 7.09 (t, J = 7.2 Hz, 2H), 1.60 (s, 9H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  157.77, 149.26, 148.17, 147.80, 147.59, 135.32, 134.23, 133.96, 131.38, 131.18, 130.90, 129.44, 128.57, 128.23, 128.11, 127.81, 127.31, 125.53, 125.15, 124.85, 124.64, 123.68, 123.41, 123.22, 122.65, 122.34, 35.25, 31.96. MALDI-TOF MS (m/z) for C<sub>43</sub>H<sub>34</sub>N<sub>2</sub>. Calcd: 578.272; Found, 578.237.

2.4.3. Synthesis of Mono-Ir.

A mixture of t-BuPyrPyTPA (200mg, 0.33 mmol) and IrCl<sub>3</sub>·H<sub>2</sub>O (30 mg, 0.095 mmol) were dissolved in 2-ethoxyethanol/H<sub>2</sub>O (12mL/4 mL) (V/V) and heated at 100 °C for 24 h under N<sub>2</sub> atmosphere. The suspension was filtered and the red solid was washed with water and a small amount of methanol then dried under high vacuum. The product was directly thrown into the next step without any purification. The compounds Ir(t-BuPyrPyTPA)<sub>2</sub>(µ-Cl)<sub>2</sub> (128mg, 0.046 mmol), picolinic acid (147 mg, 1.2 mmol), and Na<sub>2</sub>CO<sub>3</sub> (100 mg) were suspended in 2-ethoxyethanol (25 mL) and stirred at 80 °C for 7 h under N<sub>2</sub> atmosphere. After cooled to RT, the mixture was directly poured into methanol and filtered, evaporated in vacuum to give a red solid, the residue was purified by silica gel column chromatography using PE-DCM (V/V, 2/1) as eluent to afford Mono-Ir as an orange red solid (85 mg, 60.9%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.29 (s, 1H), 8.84 (m, 4H), 8.39 (d, J = 7.8 Hz, 1H), 8.10(m, 8H), 7.98 (s, 1H), 7.91 (s, 1H), 7.86 (t, J = 7.6 Hz, 1H), 7.77 (d, J = 8.9 Hz, 1H), 7.70 (d, J = 8.9 Hz, 1H), 7.55 (d, J = 8.2 Hz, 2H), 7.47 (d, J = 8.8 Hz, 2H), 7.40 (d, J = 9.0 Hz, 1H), 7.28 (s, 3H), 7.08 (m, 24H), 6.81 (s, 1H), 1.53 (d, J = 7.8 Hz, 18H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 173.05, 167.66, 166.06, 152.60, 148.96, 148.65, 148.44, 147.81, 147.33, 146.30, 138.29, 137.92, 134.84, 134.47, 133.84, 131.86, 131.58, 130.23, 129.33, 129.30, 128.25, 127.76, 127.24, 126.91, 124.93, 123.79, 123.43, 123.25,

122.67, 122.15, 35.06, 31.91. MALDI-TOF MS (m/z) for C<sub>92</sub>H<sub>70</sub>IrN<sub>5</sub>O<sub>2</sub>. Calcd: 1469.516; Found, 1469.700.

#### 2.4.4. Synthesis of Mono-Ir-Br

Similar synthetic procedures was adopted to afford Mono-Ir-Br as an orange red solid (80 mg, 54.4%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.22 (s, 1H), 8.85 (m, 4H), 8.28 (d, *J* = 8.3 Hz, 1H), 8.08(m, 11H), 7.78 (d, *J* = 8.7 Hz, 1H), 7.71 (d, *J* = 8.6 Hz, 1H), 7.53 (m, 4H), 7.38 (d, J = 8.6 Hz, 1H), 7.29 (s, 3H), 7.12 (m, 23H), 6.77 (s, 1H), 1.53 (d, J = 10.1 Hz, 18H). MALDI-TOF MS (m/z) for C<sub>92</sub>H<sub>69</sub>BrIrN<sub>5</sub>O<sub>2</sub>. Calcd: 1547.426; Found, 1547.632.

#### 2.4.5. Synthesis of D-Ir-Caz

(200)0.13 А mixture of Mono-Ir-Br mmol). mg, 2,5-bis(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-1,3,4-oxadiazole (28 mg, 0.058 mmol), aqueous Na<sub>2</sub>CO<sub>3</sub> (5 M, 3 mL), and Pd(PPh<sub>3</sub>)<sub>4</sub> (5 mg, 0.004 mmol) was added into a mixture of 10 mL dry THF and DMF under N<sub>2</sub> atmosphere. The reaction was heated at 80 °C for 24 h under stirring. After cooled to RT, the mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> and the combined organic layer was dried over MgSO<sub>4</sub>. The solvent was removed by rotary evaporation and the residue was passed through a flash silica gel column using PE-DCM-THF (V/V/V, 1/1/0.04) as the eluent several times to afford an orange red solid (70 mg, 37.5 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ 9.29 (s, 1H), 8.82 (m, 4H), 8.43 (d, J = 8.0 Hz, 1H), 8.11 (m, 9H), 7.99 (d, J = 5.4 Hz, 2H), 7.89 (s, 1H), 7.71 (d, J = 8.8 Hz, 2H), 7.54 (d, J = 8.2 Hz, 2H), 7.42 (m, 3H), 7.16 (m, 14H), 7.01 (m, 11H), 6.90 (m, 2H), 6.66 (t, J = 8.5 Hz, 1H), 3.27 (s, 1H), 11

1.52 (s, 18H), 1.03 (m, 8H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  173.10, 167.67, 166.01, 150.79, 148.67, 148.33, 147.67, 147.61, 147.44, 147.41, 147.23, 147.19, 146.53, 141.48, 138.19, 137.82, 134.79, 134.51, 133.91, 131.88, 131.57, 130.28, 129.45, 129.40, 129.24, 129.12, 128.78, 128.70, 128.65, 128.24, 128.17, 127.72, 127.17, 127.00, 126.93, 124.85, 123.96, 123.92, 123.77, 123.55, 123.40, 123.34, 123.29, 123.05, 122.68, 122.61, 122.46, 122.40, 122.29, 122.17, 121.88, 121.29, 106.99, 61.95, 53.48, 35.05, 31.90, 29.76, 22.80, 10.80. MALDI-TOF MS (m/z) for  $C_{204}H_{161}Ir_2N_{11}O_4$ . Calcd: 3214.204; Found: 3215.289.

#### 2.4.6. Synthesis of D-Ir-OXD

Similar synthetic procedures was adopted to afford D-Ir-OXD as an orange red solid (65 mg, 35.5%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.28 (s, 1H), 8.85 (m, 4H), 8.47 (d, *J* = 7.9 Hz, 1H), 8.13 (m, 11H), 7.73 (m, 5H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.43 (m, 2H), 7.29 (s, 2H), 7.24 (s, 3H), 7.08 (m, 23H), 6.85 (s, 1H), 1.52 (s, 18H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  172.71, 167.63, 165.93, 163.81, 151.90, 148.74, 148.43, 147.81, 147.49, 147.23, 147.20, 146.56, 146.24, 139.36, 138.17, 137.83, 135.83, 134.96, 131.62, 130.30, 130.24, 129.49, 129.36, 129.28, 129.06, 128.78, 128.60, 128.32, 127.74, 127.66, 127.24, 127.03, 124.96, 124.93, 124.00, 123.77, 123.59, 123.37, 123.29, 122.11, 35.05, 31.90. MALDI-TOF MS (m/z) for C<sub>199</sub>H<sub>146</sub>Ir<sub>2</sub>N<sub>12</sub>O<sub>5</sub>. Calcd: 3157.084; Found, 3158.101.

#### 3. Results and discussion

#### **3.1.** Thermal properties

The thermogravimetry analysis (TGA) curves of the iridium (III) complexes under nitrogen atmosphere are depicted in Figure 1 and the corresponding data are summarized in Table 1. Three iridium (III) complexes exhibited good thermal stabilities, indicating these iridium (III) complexes are thermally suitable candidates for application in OLEDs. Decomposition temperature ( $T_d$ ) values of 446 °C for D-Ir-Caz, 437 °C for D-Ir-OXD and 414 °C for Mono-Ir were observed at a 5% weight loss, respectively. Obviously, the  $T_d$  values of both dinuclear iridium (III) complexes are higher than that of the corresponding mononuclear iridium (III) complex, which may mainly due to their larger conjugation systems.

### 3.2. Optical properties

The UV-vis absorption spectra of the iridium (III) complexes in dilute DCM solution at RT is shown in Figure 2a, and the detailed photophysical characteristics are summarized in Table 2. The similar absorption spectra of these iridium (III) complexes exhibit quite typical profiles of many other iridium (III) complexes  $^{21-24, 33}$ , and their optical properties can be accordingly interpreted. The high intensity absorption bands in the range of 260 to 360 nm can be normally ascribed to ligand-centered (<sup>1</sup>LC) transitions. The structured bands centered at approximately 417 nm can be ascribed to a mixture of <sup>1</sup>LC and <sup>1</sup>CT (either metal to ligand charge transfer (<sup>1</sup>MLCT) or intraligand charge transfer (<sup>1</sup>ILCT) type) transitions  $^{29}$ . The broad and weak absorptions at wavelengths higher than 470 nm are arise from formally triplet <sup>3</sup>LC and <sup>3</sup>CT transitions that facilitated by the spin-orbit coupling of iridium atom. In terms of the  $\epsilon$  values, the light-harvesting capability of both dinuclear complexes were

found to be enhanced in comparison with their parent complex, resulting from the expanded conjugation bridging and as each metal-based unit possesses its own absorption properties in a polynuclear specie <sup>34</sup>. The photoluminescence (PL) spectra of three iridium (III) complexes in DCM solution at 298 k and 77 k under opto-excitation are presented in Figure 2b, and the corresponding data are summarized in Table 2. At 298 k, complexes Mono-Ir, D-Ir-Caz and D-Ir-OXD exhibited a remarkable NIR emission peak at 698, 699 and 700 nm with a shoulder around 792 nm, respectively. It indicates that these iridium (III) complexes possess the same  ${}^{3}LC/{}^{3}ILCT$  transition on the phosphor ligand  ${}^{27}$ . Furthermore, the luminescence quantum yields  $(\Phi_L)$  and lifetime  $(\tau)$  of the mononuclear and dinuclear iridium (III) complexes were investigated (Figure S1, and the resulting data are summarized in Table 1). As results, a  $\Phi_L$  of 2.25% and a  $\tau$  of 1.04 µs were observed in the mononuclear complex Mono-Ir, whereas a large decrease in  $\Phi_{\rm L}$  is detected of 0.7% for D-Ir-Caz and 1.22% for D-Ir-OXD, respectively. Meanwhile, the large extended  $\tau$ value of 1.41 µs for D-Ir-Caz and 1.42 µs for D-Ir-OXD were observed, respectively. Obviously, these nonradiative rate constants  $(k_{nr})$  are essentially identical for the three iridium (III) complexes, and indicating that the same nonradiative deactivation pathway occurred in the iridium (III) complexes. Furthermore, a more than two-fold decreased radiative rate constants (k<sub>r</sub>) was found in dinuclear iridium (III) complexes due to the relatively decreased <sup>3</sup>CT character <sup>35</sup>. As compared to the observed increased k<sub>r</sub> value in the dimetallic complexes (with centrosymmetric environment at the phosphor ligand) <sup>36</sup>, apparently, centrosymmetric environment at the ancillary

ligand may provide less metal component in the excited states and give rise to a lower degree of spin-orbit coupling (SOC), in spite of an additional metal center. When cooled to 77 K in DCM matrix, the monomer complex Mono-Ir shows much more structured emission spectra with a small rigid chromic blue-shift of 5 nm in comparison to its emission spectra in DCM at 298 k, while D-Ir-Caz and D-Ir-OXD exhibit a little rigidochromic red-shift of 3 and 4 nm, respectively. This indicates that these dimetallic iridium (III) complexes have stronger <sup>3</sup>LC character on the emissive excited states than that of the monomer complex <sup>35,37</sup>.

#### **3.3. Electrochemical Properties**

The electrochemical properties of the iridium (III) complexes were investigated through cyclic voltammetry (CV). Figure 3 shows the recorded CV curves of the complexes using an Ag/AgCl electrode as a reference and the redox potential of ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) as a calibrated standard, and the resulting electrochemical data are summarized in Table 1. The oxidation potentials of these complexes are similar to those of many other TPA-based complexes <sup>38-40</sup>, shows a similar HOMO localization on the TPA portion. The onset of oxidation potentials ( $E_{ox}$ ) of Mono-Ir, D-Ir-Caz, and D-Ir-OXD are observed at 0.41 V, 0.47 V and 0.56 V vs Fc/Fc<sup>+</sup>, respectively. As the energy level of ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) is approximately -4.8 eV below the vacuum level, the HOMO energy levels ( $E_{HOMO}$ ) of three complexes can be calculated according to the following equation:  $E_{HOMO} = -(E_{ox}^{\text{on}} + 4.80)$  eV, where  $E_{ox}^{\text{on}}$  is the recorded onset oxidation potentials of these complexes. As a calculate result, the  $E_{HOMO}$  values are -5.21, -5.27 and -5.34 eV for

the Mono-Ir, D-Ir-Caz, and D-Ir-OXD, respectively. Meanwhile, the LUMO energy levels of these complexes can be estimated based on their optical energy gap <sup>18</sup>, calculated to be -2.96, -3.02 and -3.09 eV for Mono-Ir, D-Ir-Caz, and D-Ir-OXD, respectively, trapped well in PBD-CBP matrix. It indicates that the grafted different  $\pi$ -conjugated bridges into monomer iridium (III) complex presents a little influence on electrochemical properties in the dinuclear iridium (III) complexes.

#### 3.4. Electroluminescent properties

To investigate these complexes' application in electroluminescence (EL) devices, the single-emissive-layer OLED was prepared as shown in Figure 4. We choose TFB act as an interfacial layer in these devices since its HOMO level is aligned with those of these complexes at around 5.2-5.3 eV <sup>41</sup>. TmPyPB is a suitable candidate for charge transporting with high electron mobility and high triplet energy level <sup>42</sup>, and act as an electron transporting layer here. CBP/PBD are efficient hole/electron-transporting host, the carrier mobility could be balanced by tuning the blend ratio of the two host materials, and achieve high efficiency device performance <sup>43</sup>. The optmized doping concentration for the three complexes is 10 wt % in the emitting layer.

Figure 5 shows the EL properties of the iridium (III) complexes with 10 wt % doping concentration in CBP/PBD hosts. Obviously, NIR emissions peak at 698 nm along with a shoulder at 762 nm are observed in the given complexes. All complexes exhibit similar EL spectra and are almost identical to those of their PL counterparts, negligible fluorescence from the CBP/PBD hosts could be observed, indicating the

efficient energy transfer from hosts to dopants.

The current densities-voltage-radiant emittance (J-V-R) characteristics and external quantum efficiency-current density curves (EQE-J) of the iridium (III) complexes- doped devices at 10 wt % dopant concentration are shown in Figure 6 and Figure 7, respectively. For comparison, the device performances are summarized in Table 3. As results, the almost same turn-on voltage of these devices is observed to be around 7.0 V. A maximum EQE of 1.29% at 3.4 mA cm<sup>-2</sup> with a radiant emittance of 0.59  $\mu$ W sr<sup>-1</sup> cm<sup>-2</sup> was achieved in the Mono-Ir-based device. Unfortunately, the D-Ir-Caz-based device exhibited a relatively lower EQE of 0.27% at 11.6 mA cm<sup>-2</sup>, as well as the D-Ir-OXD-based devices provided a EQE of 0.41% at 5.0 mA cm<sup>-2</sup>, respectively, correspond well with their poorer  $\Phi_{\rm L}$  values in solution. Furthermore, a radiant emittance of 0.54  $\mu$ W sr<sup>-1</sup> cm<sup>-2</sup> for the D-Ir-Caz-based device and 0.62  $\mu$ W sr<sup>-1</sup> cm<sup>-2</sup> for the D-Ir-OXD-based device were obtained, respectively. Distinctly, with increasing the current density, the Mono-Ir-based device show apparent efficiency-roll off at high currents and the EQE value was dropped down comparable to that in D-Ir-Caz- and D-Ir-OXD-based device at 100 mA cm<sup>-2</sup>. The relative small values of efficiency roll-off of the D-Ir-Caz- and D-Ir-OXD-based devices should be attributed to their bulky structure that efficiently inhibite molecular aggregation. Besides, the better device performance should be achieved when coupled with electron transporting bridging at high currents.

#### 4. Conclusions

In summary, two novel dinuclear iridium (III) complexes with carbazole-hole or

oxadiazole-electron transporting bridging, and their analogue iridium (III) complex were synthesized and characterized. All the iridium (III) complexes show similar emission spectra peaked at around 700 nm in DCM solution. Furthermore, the dinuclear iridium (III) complexes present lower  $\Phi_L$  which may be caused by the centrosymmetric environment at the ancillary ligand. As expected, the NIR EL emission peaked at 698 nm with a shoulder at 762 nm was observed in the iridium (III) complexes-doped SEL OLEDs. A maximum EQE of 1.29% at 3.4 mA cm<sup>-2</sup> with a radiant emittance of 0.59  $\mu$ W sr<sup>-1</sup> cm<sup>-2</sup> was achieved in the Mono-Ir-based device. However, a relatively lower EQE of 0.27% at 11.6 mA cm<sup>-2</sup> for the D-Ir-Caz-doped device and a EQE of 0.41% at 5.0 mA cm<sup>-2</sup> for the D-Ir-OXD-based device were observed, respectively, accompanied with negligible efficiency roll-off values. This also demonstrate that the structure of bulky ancillary ligand can efficiently inhibite molecular aggregation.

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#### Appendix A. Supplementary data

The following is the supplementary data related to this article:

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### **Figures and Tables**

Scheme 1. Synthetic routes of the iridium (III) complexes.

Figure 1. TGA curves of the iridium (III) complexes..

**Figure 2.** UV-vis absorption spectra (a) and PL spectra (b) of the iridium (III) complexes in  $CH_2Cl_2$  solution (10<sup>-5</sup> M) at 298 K (solid line) and 77 K (dash line).

Figure 3. Cyclic voltammograms of the iridium (III)complexes coated on a platinum

electrode in acetonitrile solution containing 0.1 mol L<sup>-1</sup> Bu<sub>4</sub>NPF<sub>6</sub> at a scan rate of 100

mV s<sup>-1</sup> using ferrocene as an internal standard

Figure 4. EL device structure and energy level diagram of the devices.

Figure 5. The EL spectra of the complexes-doped devices.

Figure 6. The current density-voltage-radiance (*J-V-R*) curves of devices.

Figure 7. The EQE versus current density characteristics of the devices.

**Table 1.** Physical properties of the iridium (III) complexes in degassed CH<sub>2</sub>Cl<sub>2</sub> at 298 K except where stated otherwise.

 Table 2. Electrochemical properties and thermal parameters of the iridium (III)

 complexes.

Table 3. EL characteristics of the iridium (III) complexes.

# Scheme 1.



# Figure 1.



# Figure 3.



Figure 5.



# Figure 7.



Complexes	$E_{\mathrm{ox}}^{a}(\mathrm{V})$	$E_{g}^{b}(eV)$	$E_{\rm HOMOcal}^{c}(\rm eV)$	$E_{\text{LUMOcal}}^{c}$ (eV)	$T_{\rm d}$ (°C)
Mono-Ir	0.41	2.25	-5.21	-2.96	414
D-Ir-Caz	0.47	2.25	-5.27	-3.02	446
D-Ir-OXD	0.54	2.25	-5.34	-3.09	437

#### Table 1.

<sup>a</sup> The potential of Fc/Fc<sup>+</sup> vs Ag/AgCl electrode was measured to be 0.67 V; <sup>b</sup> Calculated from the absorption band edge,  $E_{g}^{opt} = 1240/\lambda_{abs}$ , onset; <sup>c</sup> Calculated from empirical equation:  $E_{HOMO} = -4.8-E_{ox}$ ,  $E_{LUMO} = E_{ox} + E_{g}^{opt}$ .

### Table 2.

Compound	$\lambda_{abs,max}$	$\lambda_{abs,max}$ $\lambda_{em,max}$		τ	$k_{\rm r}  (\times 10^5 {\rm s}^{-1})/$	Emission at 77 $K^b$	
	(nm)	(nm)	(%)	(µs)	$k_{\rm nr}  (\times 10^5 {\rm s}^{-1})^a$	$\lambda_{max}$ (nm)	τ (μs)
Mono-Ir	240,307,416,	698	2.25	1.04	0.24/0.4	693	4.82
	441,511	792 <sub>sh</sub>	2.25	1.04	0.24/9.4	$760_{sh}$	
D-Ir-Caz	237,307,417,	699	0.70	1 /1	0.05/7.0	702	5.05
	441,511	792 <sub>sh</sub>	0.70	1.41	0.03/7.0	773 <sub>sh</sub>	
D-Ir-OXD	237,307,417,	700	1.22	1.42	0.09/6.1	704	4.67
	441,511	792 <sub>sh</sub>	1.22	1.42	0.00/0.1	$778_{\rm sh}$	

<sup>*a*</sup>  $k_r$  and  $k_{nr}$  are rate constants calculated by using the equations  $k_r = \Phi_L/\tau$  and  $k_{nr} = (1 - \Phi_L)/\tau$ , assuming that  $\Phi_{ISC} = 1$  (ISC = intersystem crossing). <sup>*b*</sup> Measured in DCM glass at 77 K.

# Table 3.

Dopant	$V_{ m on}{}^a$	$\lambda_{ m EL}$	$J^{b}$	$EQE_{\max}^{c}$	$\mathbf{R}^{d}$
(10 wt%)	(V)	(nm)	$(mA cm^{-2})$	(%)	$(\mu W \ sr^{-1} \ cm^{-2})$
Mono-Ir	9.0	698, 762	3.4	1.29	0.59
D-Ir-Caz	9.0	698, 762	11.6	0.27	0.54
D-Ir-OXD	9.0	698, 762	5.0	0.41	0.62

<sup>*a*</sup> Turn-on voltage. <sup>*b*</sup> Current density at maximum *EQE*. <sup>*c*</sup> The maximum external quantum efficiency. <sup>*d*</sup> The maximum radiant intensity.

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# **Research Highlights**

- Two dinuclear iridium (III) complexes containing functionalized  $\pi$ -conjugated bridge and their monomer complex were successfully synthesized.
- Compared with their monomer complex, much lower  $\Phi_{\rm L}$  of the dinuclear iridium complexes were observed.
- Similar NIR emission peaked at 698 nm with a shoulder at 792 nm were observed in their doped single-emissive-layer OLEDs.
- A maximum EQE of 1.29% at 3.5 mA/cm<sup>2</sup> was achieved in the monomer complex-based device.