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# Journal of Materials Chemistry C

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# Efficient sky-blue emitting Pt(II) complexes based on imidazo[1,2-f]phenanthridine-containing tetradentate ligands

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Three blue-emitting Pt(II) complexes (Pt1, Pt2 and Pt3) supported by imidazo[1,2-f]phenanthridine-containing tetradentate ligands have been designed and prepared. The fused ring system, imidazo[1,2-f]phenanthridine), was introduced into these complexes to minimize the vibration and rotation of the ligand due to its rigidity, and the incorporation of this robust motif led to the high thermal stability of the resulting complexes. In addition, this efficient bidentate possesses high triplet energy  $(E_{\rm T})$  to allow the preparation of blue-emitting complexes. Bulky mesityl group was attached to this rigid unit to reduce the strong intermolecular interaction and suppress the formation of excimer at solid state. Imidazo[1,2-f]phenanthridine was connected with three different pyridine^benzene bidentates to give the corresponding tetradentate ligands (L1, L2 and L3). In L1, the pyridine group was directly bonded to N atom of carbazole group; while in L2 and L3, the pyridine unit was linked to benzene group via oxygen and spiro linkage, respectively. The introduction of heteroatom linkage and spiro linkage into these tetradentate ligands would be effective in breaking the conjugation, leading the wide bandgap and high  $E_{\rm T}$ . Despite

the different linkages applied in the pyridine^benzene bidentates, the complexes **Pt1-Pt3** showed similar photoluminescence spetra with the intense emission peak at 460 nm. Organic light-emitting diodes (OLEDs) based on these complexes were fabricated by vacuum deposition with the typical device configuration. All these complexes showed blue electro-phosphorescence at various doping ratios. Among these Pt(II) complexes, **Pt1** showed the highest OLED performance with the maximum CE, PE, and EQE of 36.5 cd  $A^{-1}$ , 33.1 lm  $W^{-1}$ , and 16.2%, respectively, with the CIE coordinates of (0.18,0.32).

# Introduction

Since Tang and VanSlyke pioneered the electroluminescent device using organic materials as the emitting elements in 1987,<sup>1</sup> the last three decades have witness the tremendous progress in organic optoelectronic field.<sup>2</sup> Organic light-emitting diodes have shown successful commercialization in displays of mobile phones, televisions and panel applications due to the development of material technologies and device architectures. The multi-color emissive materials are considered to be important for the fabrication of full-color OLED display and white lighting. Since phosphorescent metal complexes can harvest 100% of electro-generated singlet and triplet excitons via the strong spin-orbit coupling of metal ions, they have been extensively studied for decades.<sup>3</sup> So far the external quantum efficiency (EQE), lifetime and driving voltage of green and red phosphors have been enhanced greatly to a commercialization level. The blue phosphorescent emitters demonstrated relatively short lifetime although highly efficient blue phosphorescent OLEDs (PhOLEDs) with the maximum EQE over 30% has been achieved.<sup>4</sup> As a result, green and red phosphorescent emitters, and blue fluorescent emitters were typically applied in current OLED products.<sup>5</sup> Traditional fluorescent emitters only exhibited 25% internal quantum efficiency (IOE) and triplet-triplet fusion process can result in 62.5% IOE. Thermally activated delayed fluorescent (TADF)<sup>6</sup> emitters can allow 100% IQE and are considered as an alternative approach to achieve high-efficiency blue OLEDs. Currently, the lifetime of blue TADF devices is short probably due to the synergetic oxidation process.<sup>7</sup>

Although the fluorescent blue emitters have been successfully applied in OLED product, their limited electroluminescence efficiency encouraged the exploration of novel phosphorescent emitters. Ir(III)-based blue emitters have been widely

investigated.<sup>3h,8</sup> The typical strategies to achieve blue-emitting Ir(III) complexes are as follows:1) adding electron-withdrawing group such as F and CF<sub>3</sub> on the aryl group in the arylpyridine series to lower the energy of HOMO; 2) replacing the strong electron-withdrawing group pyridine with azole group or carbene to raise the energy of LUMO and widen the LUMO-HOMO energy gap.<sup>5,9</sup> For example, bis((4,6-difluorophenyl)-pyridine) iridium(III) picolinate (Flrpic), one of most studied blue phosphors with the CIE coordinates of (0.16, 0.37),<sup>10</sup> has two F atoms attached to the benzene ring. However, it has been reported that F substituted emitters would decompose during the evaporation process and the operation of OLEDs.<sup>11</sup> Recently much research has focused on developing Pt(II)-based blue emitters.<sup>12</sup> For example, Li and coworkers reported a new route for the development of stable and efficient blue-emitting Pt(II) complexes by breaking conjugation with 6-membered chelate rings.<sup>9a</sup> In addition, "pure" blue OLEDs based on tetradentated Pt(II) complex has also been realized with a peak EQE of 24.8% and CIE coordinates of (0.148, 0.079).<sup>13</sup> The tetradentate coordination model observed in Pt(II) complexes could suppress the vibration and rotation around metal ion and hence reduce the non-radiative decay.<sup>14</sup> Furthermore, the great degree of rigidity induced by the tetradentate ligand led to a less contribution of intraligand Franck-Condon vibrational modes in the longer wavelength emission, thus ensuring good color purity.<sup>12f, 15</sup>

In this paper, three tetradentated platinum(II) complexes (Pt1, Pt2, and Pt3) have been successfully prepared based on imidazo[1,2-f]phenanthridine motif, which has been widely used in the construction of fluorine-free blue Ir(III)-based emitter.<sup>16</sup> On the contrary, the incorporation of this rigid unit into tetradentate ligands for the preparation of blue Pt(II)-based emitters has been rarely reported.<sup>17</sup> Herein, three tetradentate ligands (L1-L3) were prepared by linking imidazo[1,2-f]phenanthridine with three different pyridine^benzene bidentates, namely 9-(pyridin-2-yl)-9H-carbazole, 2-phenoxy-pyridine and 2-(9-phenyl-9H-fluoren-9-yl)-pyridine. Bulky mesityl group was attached to the reactive 3-position of imidazo[1,2-f]phenanthridine to reduce the side reaction under electric-excitation condition and increase the solubility of resulting complexes. OLEDs based on Pt1-Pt3 were fabricated to investigate the effect of different linkages applied in pyridine<sup>^</sup>benzene bidentates on the electroluminescence properties of the three Pt(II) complexes. Among these three Pt(II) complexes, Pt1 showed the highest OLED performance with the maximum CE, PE, and EQE of 36.5 cd A<sup>-1</sup>, 33.1

Im  $W^{-1}$ , and 16.2%, respectively, which was comparable to the best sky-blue Pt(II)-based emitters.

#### Experimental

Published on 25 August 2017. Downloaded by Fudan University on 25/08/2017 14:35:18.

#### **General Information**

All chemicals were used as received from J&K Scientific, Alfa Aesar, Acros, and Strem chemicals. Anhydrous solvents were obtained from an Innovative Technology solvent purification system. <sup>1</sup>H NMR spectra were recorded on a Bruker 400 MHz NMR instrument and <sup>13</sup>C NMR spectra were recorded on Agilent DD2-600 MHz NMR instrument. Thermogravimetric analysis (TGA) was recorded on a TA SDT 2960 instrument at a heating rate of 10 °C min<sup>-1</sup> under nitrogen. Matrix-Assisted Laser Desorption/ Ionization Time of Flight Mass Spectrometry (MALDI-TOF-MS) was measured with a BRUKER ultrafleXtreme MALDI-TOF spectrometer. The HOMO was determined from Ultraviolet Photoemission Spectroscopy (Kratos Analytical Shimadzu Group Company). UV-vis absorption spectra were measured on Cary 60 spectrometer (Agilent Technologies). PL spectra and phosphorescent spectra were recorded on a Hitachi F-4600 fluorescence spectrophotometer. Different parameters were used in the DFT simulations for structure optimizations and vibration analyses. Both the ground states and triplet states of molecules were optimized in vacuum by the restricted and unrestricted formalism of three-parameter hybrid exchange functional and correlation functional (B3LYP)/6-31G(d) with no assistance of experimental data.

#### Synthesis of 2-bromo-5-methoxybenzonitrile

2-Bromo-5-methoxybenzaldehyde (9 g, 41.85 mmol), hydroxylamine hydrochloride (7.42 g, 106.7 mmol) were added into a mixture of ethanol (50 mL) and pyridine (50 mL) under N<sub>2</sub>. The reaction system was heated to reflux overnight. After cooling down to the room temperature, the mixture was extracted with DCM. After the removal of organic solvent, the residue was dissolved in acetic anhydride (100 mL) with trace amount of sodium acetate (0.236 g, 2.88 mmol), and this mixture was refluxed at 140 °C for 6 h. After cooling down to the room temperature, the solvent

was removed under reduced pressure. The crude product was purified by column chromatography (SiO<sub>2</sub>, DCM:PE, 2:3) to afford a white solid (7.8 g, 87.9%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.54 (d, J = 8.9 Hz, 1H), 7.15 (d, J = 2.8 Hz, 1H), 7.00 (dd, J = 8.9, 2.9 Hz, 1H), 3.82 (s, 3H). GC-MS: m/z calcd 210.96, found 210.94.

*Synthesis of 8-methoxyphenanthridin-6-amine* 

An aqueous solution of Na<sub>2</sub>CO<sub>3</sub> (2M, 20 mL) was added into a solution of 2-bromo-5-methoxybenzonitrile (5.81)27.40 mmol), g, 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (6 g, 27.40 mmol), and (Ph<sub>3</sub>P)<sub>2</sub>PdCl<sub>2</sub> (0.8 g, 1.14 mmol) in DMF (100 mL) under N<sub>2</sub>. The reaction mixture was heated to 80 °C overnight before cooling down to the room temperature. After the removal of solvent, the residue was extracted with DCM (3×100 mL) and washed with water. The combined organic phase was dried over MgSO<sub>4</sub>. The crude product was purified by column chromatography (SiO<sub>2</sub>, DCM:triethylamine, 50:1) to afford a light yellow solid (5.1 g, 82.3%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.43 (d, J = 9.0 Hz, 1H), 8.26 (d, J = 8.0 Hz, 1H), 7.77 (d, J = 8.0 Hz, 1H), 7.54 (t, J = 7.6 Hz, 1H), 7.48 (d, J = 8.9 Hz, 1H), 7.40 (t, J = 7.5 Hz, 1H), 7.35 (s, 1H), 3.99 (s, 3H). GC-MS: m/z calcd 224.10, found 224.12.

### Synthesis of 11-methoxyimidazo-[1,2-f]-phenanthridine

An aqueous solution of Na<sub>2</sub>CO<sub>3</sub> (6.13 g, 57.87 mmol) was added into a solution of 8-methoxyphenanthridin-6-amine (4.32 g, 19.29 mmol), chloroacetaldehyde (14.1 g, 57.87 mmol) in isopropanol (100 mL) under N<sub>2</sub>. The reaction mixture was heated to 80 °C overnight before cooling down to the room temperature. After the removal of solvent, the residue was extracted with DCM (3×100 mL) and washed with water. The combined organic phase was dried over MgSO<sub>4</sub>. The crude product was purified by column chromatography (SiO<sub>2</sub>, DCM:EA, 2:1) to afford a light yellow solid (4.0 g, 83.7%). <sup>1</sup>H NMR (400 MHz, DMSO)  $\delta$  8.62 (dd, J = 19.7, 6.8 Hz, 3H), 8.31 (d, J = 8.2 Hz, 1H), 7.93 (d, J = 2.1 Hz, 1H), 7.66 (t, J = 7.6 Hz, 1H), 7.60 – 7.50 (m, 2H), 7.31 (dd, J = 8.9, 2.2 Hz, 1H), 3.96 (s, 3H). GC-MS: m/z calcd 248.10, found 248.19. *Synthesis of 3-bromo-11-methoxyimidazo-[1,2-f]-phenanthridine* 

11-Methoxyimidazo-[1,2-*f*]-phenanthridine (3.77 g, 15.20 mmol) and NBS (2.71 g, 15.20 mmol) were dissolved in DMF (100 mL) under N<sub>2</sub>. The reaction mixture was stirred at the room temperature overnight. After the removal of solvent, the residue was extracted with DCM ( $3 \times 100$  mL) and washed with water. The combined organic phase was dried over MgSO<sub>4</sub>. The crude product was purified by column

chromatography (SiO<sub>2</sub>, DCM:EA, 4:1) to afford a yellow solid (4.5 g, 90.7%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.25 (d, *J* = 8.0 Hz, 1H), 8.33 (d, *J* = 7.4 Hz, 1H), 8.20 (d, *J* = 9.0 Hz, 1H), 7.98 (s, 1H), 7.57 - 7.46 (m, 3H), 7.21 (d, *J* = 8.8 Hz, 1H), 3.99 (s, 3H). GC-MS: m/z calcd 326.00, found 326.15.

Synthesis of 3-mesityl-11-methoxyimidazo-[1,2-f]-phenanthridine

An aqueous solution of K<sub>3</sub>PO<sub>4</sub> (3 g, 10 mL) was added into a solution of 3-bromo-11-methoxyimidazo-[1,2-*f*]-phenanthridine (3.8 g, 11.66 mmol), mesitylboronic acid (3.82 g, 23.32 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (0.214 g, 0.233 mmol) and P(*t*-Bu)<sub>3</sub>HBF<sub>4</sub> (0.272 g, 0.936 mmol) in toluene (100 mL) under N<sub>2</sub>. The reaction mixture was heated to 85 °C overnight before cooling down to the room temperature. The crude product was purified by column chromatography (SiO<sub>2</sub>, DCM:EA, 8:1) to afford a white solid (2.2 g, 51.3%). <sup>1</sup>H NMR (400 MHz, DMSO)  $\delta$  8.61 (d, *J* = 8.1 Hz, 1H), 8.56 (d, *J* = 9.0 Hz, 1H), 8.02 (d, *J* = 2.3 Hz, 1H), 7.45 (t, *J* = 7.2 Hz, 1H), 7.35 – 7.20 (m, 4H), 7.11 (s, 2H), 3.98 (s, 3H), 2.38 (s, 3H), 1.95 (s, 6H). GC-MS: m/z calcd 366.17, found 366.18.

Synthesis of 3-mesitylimidazo-[1,2-f]-phenanthridin-11-ol

The solution of 3-mesityl-11-methoxyimidazo-[1,2-*f*]-phenanthridine (2 g, 5.46 mmol) in HBr (50 mL, 48%) was heated to 125 °C under N<sub>2</sub> for 3 days before cooling down to the room temperature. After the removal of solvent, the residue was extracted by DCM (3×100 mL) and washed with water. The combined organic phase was dried over MgSO<sub>4</sub>. The product was purified by column chromatography (SiO<sub>2</sub>, DCM:EA, 3:1) to afford a white solid (1.2 g, 62.1%). <sup>1</sup>H NMR (400 MHz, DMSO)  $\delta$  8.64 (d, J = 9.2 Hz, 2H), 8.37 (s, 1H), 7.52 (d, J = 7.1 Hz, 1H), 7.47 (t, J = 7.5 Hz, 1H), 7.37 (s, 1H), 7.30 (t, J = 7.8 Hz, 1H), 7.23 (d, J = 8.6 Hz, 1H), 7.12 (s, 2H), 6.30 (s, 1H), 2.38 (s, 3H), 1.95 (s, 6H). GC-MS: m/z calcd 352.16, found 352.21.

Synthesis of ligand L1

6.04 K<sub>3</sub>PO<sub>4</sub> (1.28)g, mmol) was added into а solution of 2-bromo-9-pyridin-2-yl-9H-carbazole (0.65)g, 2.01mmol), 3-mesitylimidazo-[1,2-f]-phenanthridin-11-ol (0.89 g, 2.52 mmol), CuI (72 mg, 0.38 mmol) and picolinic acid (93 mg, 0.76 mmol) in DMSO (100 mL) under N<sub>2</sub>. The reaction mixture was heated to 120 °C under microwave for 18 hours. Then the DMSO was removed by distillation under reduced pressure. The residue was extracted with DCM (3×100 mL) and washed with water. The combined organic phase was dried over MgSO<sub>4</sub>. The crude product was purified by column

chromatography (SiO<sub>2</sub>, DCM:EA, 6:1) to afford a white solid (1.0 g, 66.6%). <sup>1</sup>H NMR (600 MHz, DMSO)  $\delta$  8.63 (d, J = 3.8 Hz, 1H), 8.56 (t, J = 8.9 Hz, 2H), 8.29 (d, J = 8.4 Hz, 1H), 8.22 (d, J = 7.7 Hz, 1H), 8.04 – 7.98 (m, 1H), 7.95 (d, J = 2.1 Hz, 1H), 7.76 (d, J = 8.0 Hz, 2H), 7.65 (d, J = 1.5 Hz, 1H), 7.46 – 7.35 (m, 4H), 7.32 (t, J = 7.5 Hz, 1H), 7.25 – 7.20 (m, 1H), 7.16 (ddd, J = 20.4, 12.0, 6.8 Hz, 3H), 7.02 (s, 2H), 2.29 (s, 3H), 1.86 (s, 6H). <sup>13</sup>C NMR (151 MHz, DMSO)  $\delta$  158.90, 154.75, 150.89, 149.93, 139.90, 139.84, 138.59,131.66, 128.96, 126.53, 122.50, 122.31, 121.72, 120.70, 119.45, 114.29, 111.59, 109.86, 103.76, 21.28, 20.42. GC-MS: m/z calcd 594.24, found 594.34.

# Synthesis of Pt1

L1 (0.8 g, 1.35 mmol) and K<sub>2</sub>PtCl<sub>4</sub> (0.62 g, 1.48 mmol) were added into a mixture of CHCl<sub>3</sub>/AcOH (40 mL, v/v= 1:9) under N<sub>2</sub>. The reaction solution was heated to 140 °C for 5 days. After cooling down to the room temperature, the precipitate was collected by filtration. The crude product was purified by column chromatography (SiO<sub>2</sub>, DCM:PE, 6:1) to afford a yellow solid (0.9 g, 84.5%). <sup>1</sup>H NMR (400 MHz, DMSO)  $\delta$  9.61 (d, *J* = 5.3 Hz, 1H), 8.73 (d, *J* = 8.1 Hz, 1H), 8.32 (d, *J* = 8.8 Hz, 2H), 8.26 (t, *J* = 7.5 Hz, 1H), 8.20 (d, *J* = 7.5 Hz, 1H), 8.12 (d, *J* = 8.1 Hz, 1H), 7.99 (t, *J* = 3.8 Hz, 2H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.45 (dt, *J* = 14.9, 7.9 Hz, 5H), 7.34 (d, *J* = 5.0 Hz, 2H), 7.21 (s, 2H), 2.43 (s, 3H), 2.12 (s, 6H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  153.27, 151.86, 148.56, 142.55, 139.44, 132.37, 128.61, 127.21, 126.74, 124.89, 122.74, 119.68, 118.06, 115.90, 115.19, 114.44, 113.66, 93.98, 21.38, 20.51. MALDI-TOF (m/z): calculated for: 787.191, found: 787.292. Anal. calcd for: C<sub>41</sub>H<sub>28</sub>N<sub>4</sub>OPt :C, 62.51; H, 3.58; N, 7.11; found: C, 62.35; H, 3.82; N, 7.01%.

Synthesis of L2, Pt2, L3 and Pt3

L2, Pt2, L3 and Pt3 were prepared by the procedures similar to those used for L1 and Pt1, respectively. L2 was obtained as a white solid (1.0 g, 56.2%). <sup>1</sup>H NMR (600 MHz, DMSO)  $\delta$  8.67 (d, J = 16.3 Hz, 2H), 8.20 (dd, J = 4.7, 1.2 Hz, 1H), 8.05 (d, J = 2.4 Hz, 1H), 7.86 (s, 1H), 7.50 (dd, J = 18.1, 9.9 Hz, 3H), 7.31 (d, J = 8.7 Hz, 2H), 7.23 (d, J = 8.4 Hz, 1H), 7.14 (s, 1H), 7.11 (s, 2H), 7.08 – 7.04 (m, 2H), 7.01 (d, J = 13.6 Hz, 2H), 2.37 (s, 3H), 1.94 (s, 6H). <sup>13</sup>C NMR (151 MHz, DMSO)  $\delta$  163.03, 157.55, 157.24, 155.74, 147.95, 142.17, 140.73, 139.31, 138.64, 132.95, 131.77, 131.38, 129.01, 128.93, 128.48, 127.51, 126.22, 125.76, 125.37, 125.01, 123.14, 121.82, 120.56, 119.81, 117.33, 115.78, 115.00, 112.96, 112.21, 110.80, 21.33, 20.47. GC-MS: m/z calcd 521.21, found 521.36.

**Pt2** was obtained as a yellow solid (0.71g, 68.9%). <sup>1</sup>H NMR (600 MHz, DMSO)  $\delta$  9.14 – 9.08 (m, 1H), 8.69 (d, *J* = 8.0 Hz, 1H), 8.27 (d, *J* = 8.7 Hz, 1H), 8.24 – 8.18 (m, 1H), 7.86 (s, 1H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.52 (d, *J* = 8.3 Hz, 1H), 7.46 – 7.35 (m, 3H), 7.30 (d, *J* = 8.3 Hz, 1H), 7.19 (dd, *J* = 10.1, 5.3 Hz, 3H), 7.08 (dd, *J* = 7.9, 1.1 Hz, 1H), 6.95 (dd, *J* = 7.8, 1.1 Hz, 1H), 2.41 (s, 3H), 2.08 (s, 6H). <sup>13</sup>C NMR (151 MHz, DMSO) δ 157.73, 154.61, 153.87, 151.12, 150.35, 141.65, 140.06, 139.42, 129.07, 128.27, 126.84, 126.39, 125.24, 124.41, 121.16, 119.43, 116.00, 115.62, 110.71, 97.96, 21.38, 20.63. MALDI-TOF (m/z), calculated for: 714.160, found: 714.232 . Anal. calcd for: C<sub>35</sub>H<sub>25</sub>N<sub>3</sub>O<sub>2</sub>Pt :C, 58.82; H, 3.53; N, 5.88; found: C, 58.81; H, 3.73; N, 5.92%.

L3 was obtained as a white solid (0.95 g, 75.2%). <sup>1</sup>H NMR (600 MHz, DMSO)  $\delta$  8.62 – 8.53 (m, 3H), 7.95 (d, J = 2.6 Hz, 1H), 7.88 (d, J = 7.5 Hz, 2H), 7.61 – 7.53 (m, 3H), 7.43 (t, J = 7.5 Hz, 1H), 7.36 (t, J = 7.4 Hz, 2H), 7.33 – 7.30 (m, 2H), 7.27 (dd, J = 14.7, 7.3 Hz, 4H), 7.21 (d, J = 8.3 Hz, 1H), 7.17 (dd, J = 7.0, 5.2 Hz, 1H), 7.08 (s, 2H), 7.04 – 6.99 (m, 2H), 6.78 (dd, J = 8.8, 5.0 Hz, 2H), 2.34 (s, 3H), 1.92 (s, 6H). <sup>13</sup>C NMR (151 MHz, DMSO)  $\delta$  163.16, 157.56, 155.79, 149.93, 149.38, 148.79, 140.35, 139.31, 138.64, 137.22, 131.78, 130.48, 129.03, 128.51, 128.39, 128.33, 126.98, 126.09, 125.74, 124.95, 123.83, 122.53, 121.82, 121.49, 120.93, 120.27, 119.32, 117.78, 114.99, 110.24, 67.01, 21.33, 20.47. GC-MS: m/z calcd 669.28, found 669.45.

**Pt3** was obtained as a yellow solid (0.22g, 17.1%). <sup>1</sup>H NMR (600 MHz, DMSO) δ 9.50 (d, J = 5.4 Hz, 1H), 8.72 (d, J = 8.1 Hz, 1H), 8.62 (d, J = 7.8 Hz, 2H), 8.29 (d, J = 8.6 Hz, 1H), 7.97 (d, J = 7.6 Hz, 2H), 7.86 (t, J = 7.8 Hz, 1H), 7.66 – 7.53 (m, 3H), 7.42 (dt, J = 12.9, 7.9 Hz, 4H), 7.31 (d, J = 8.4 Hz, 1H), 7.28 (t, J = 7.6 Hz, 2H), 7.18 (s, 2H), 7.07 (d, J = 7.8 Hz, 1H), 6.85 (d, J = 8.3 Hz, 1H), 6.76 (t, J = 7.8 Hz, 1H), 6.38 (d, J = 7.8 Hz, 1H), 2.41 (s, 3H), 2.11 (s, 6H). <sup>13</sup>C NMR (151 MHz, DMSO) δ 160.28, 153.91, 153.12, 151.58, 140.10, 139.39, 139.07, 129.07, 132.83, 132.26, 129.07, 128.61, 128.36, 128.16, 127.55, 126.91, 126.39, 125.84, 125.24, 125.10, 124.63, 123.29, 121.15, 119.24, 118.10, 116.87, 115.68, 71.55, 21.38, 20.71. MALDI-TOF (m/z): calculated for: 862.227, found: 862.201. Anal. calcd for: C<sub>48</sub>H<sub>33</sub>N<sub>3</sub>OPt: C, 66.81; H, 3.85; N, 4.87; found: C, 66.67; H, 4.27; N, 4.83%.

#### **Device Fabrication and Measurements**

The OLED devices were fabricated through vacuum deposition on commercial

ITO-coated glass substrates having a sheet resistance of 15  $\Omega$  per square. The ITO surface was ultrasonically cleaned with acetone, ethanol, and deionized water, then dried in an oven at 120 °C and treated by UV ozone for 15 min.

All layers were deposited under a base pressure of  $2 \times 10^{-6}$  Torr. The deposition rates and doping concentration of the films were monitored in situ by the calibrated thickness monitors. The typical evaporation rate for HAT-CN, organic layers and Liq were 0.4-0.8, 2-3 and 0.2-0.5 Å s<sup>-1</sup>, respectively. Finally, the Al electrode was evaporated (5 Å s<sup>-1</sup>) through a shadow mask without breaking the vacuum.

The emitting area of each device was  $3 \times 3 \text{ mm}^2$ . Electroluminescence (EL) spectra, CIE coordinates and current-voltage (*I-V*) characteristics were measured by a constant current source (Keithley 2400s Source Meter) combined with a photometer (Photo Research PR 655 spectrophotometer).

#### **Results and Discussion**

# **Preparation and Characterization**

The synthetic route of complexes Pt1-Pt3 was illustrated in Scheme 1. 8-methoxyphenanthridin-6-amine was prepared by Suzuki Miyaura coupling of aminoboronic ester and 2-halobenzonitrile followed by intramolecular nucleophilic addition. Amine-aldehyde condensation and nucleophilic substitution afforded the precursor imidazo-[1,2-f]-phenanthridine. Subsequent selective bromination using NBS, followed by Suzuki Miyaura coupling with mesitylboronic acid and hydrolysis in the presence of HBr completed the synthesis of the intermediate 3-mesitylimidazo-[1,2-f]-phenanthridin-11-ol. CuI/2-picolinic acid catalyzed coupling reactions of phenol derivative and aryl bromides provided the target ligands L1-L3. Within L1 and L2, the O and N linkage applied in the pyridine<sup>b</sup>enzene bidentates were both electron-donating, which could enhance the energy level of HOMO of corresponding Pt(II) complexes; while in L3 a spiro-linkage was used, which could sufficiently suppress the strong intermolecular interaction and reduce the formation of excimer.<sup>14c</sup> Pt(II) complexes Pt1-Pt3 were prepared via one-pot reaction of K<sub>2</sub>PtCl<sub>4</sub> and the respective ligands in the mixture of chloroform and acetic acid. All Pt(II) complexes were purified by column chromatography and sublimation, and their structures were confirmed by <sup>1</sup>H and <sup>13</sup>C NMR, MALDI-TOF and elemental analysis. The thermal stability of these complexes was investigated by thermal gravimetric analysis under nitrogen. Pt1-Pt3 showed high thermal stability with the 5%

weight-reduction temperatures ( $\Delta T_{5\%}$ ) over 430 °C, which could be attributed in part to the introduce of extending  $\pi$ -conjugation system into the tetradentate ligands.<sup>18</sup> The HOMOs of Pt(II) complexes were determined by Ultra-Violet Photoemission Spectroscopy (UPS) measurement. As expected, the HOMOs of **Pt1** and **Pt2** were slightly highly than that of **Pt3**. The LUMOs were calculated from the difference between the HOMO and the corresponding optical band gap. The <sup>1</sup>H, <sup>13</sup>C NMR spectra (Figure S1-Figure S18), thermal gravimetric analysis (TGA) curves (Figure S19) and UPS spectra (Figure S20) of **Pt1-Pt3** are given in the supporting information.

# **Photophysical Properties**

The absorption and emission spectra of complexes **Pt1-Pt3** are depicted in Figure 1, and the photophysical data are summarized in Table 1. All the complexes showed strong absorption below 350 nm, which could mainly be assigned to phenyl-O-phenyl  $\rightarrow$  pyridine intraligand (IL)  $\pi$ - $\pi$ \* transition. There is a red-shift of about 15 nm in the absorption spectrum of Pt2 relative to that of Pt3, which could be attributed to the oxygen lone pair delocalization onto the aryl ring. A 7 nm red-shift has been observed in the absorption spectrum of **Pt1** in comparison with that of **Pt2**, which could be due to the presence of large conjugation system (carbazole) in **Pt1**. The absorption bands with the wavelength over 350 nm of **Pt1-Pt3** could be assigned to the metal-to-ligand charge-transfer (MLCT). Upon photoexcitation at 340 nm, Pt1-Pt3 exhibited intense emission bands at 460 nm with well-resolved vibronic features, indicating the photoluminescence could mainly arise from the LC excited states, which was also supported by the analyses of Natural Transition Orbital (NTO). The NTO was mostly localized on the tetradentate ligands (Figure S21). The triplet lifetimes of Pt(II) complexes in both solution and solid state at room temperature have been determined in the range of  $8.33-10.0 \ \mu s$  (Table 1).

#### **DFT Calculations**

Density functional theory (DFT) calculations were carried out for complexes **Pt1-Pt3** with Gaussian 09. The calculations were performed using a B3LYP method with a basis set of 6-31G(d) for C, H, O and N atoms and a LANL2DZ basis set for Pt atom. The orbital densities of HOMOs and LUMOs were shown in Figure 2, and the calculation result was listed in Table S1.

Since pyridine unit is the most electron-withdrawing group used in these ligands, the LUMOs of Pt1-Pt3 mainly resided on pyridine part. As estimated from the composition of the frontier orbitals, the pyridine group made about 83.83% contribution to the LUMO of Pt1, 87.07% for Pt2 and 84.98% for Pt3. Due to the weak electron-donating capability of spiro linkage, the LUMO of Pt3 (-1.30 eV) was slightly lower than those of Pt1 (-1.28 eV) and Pt2 (-1.02 eV). The HOMOs are primarily localized on the phenyl-O-phenyl motif, and platinum atom made about 18.65%, 20.78% and 22.06% contribution to the HOMOs of these complexes. The optimized structures of **Pt1-Pt3** showed that the mesityl group is essentially perpendicular to the imidazo-[1,2-f]-phenanthridine with the dihedral angle of 89.97°. The molecular structures of Pt1-Pt3 significantly deviated from square planar geometries due to the steric hindrance between imidazo-[1,2-f]-phenanthridine and pyridine The dihedral angles between pyridine group. and imidazo-[1,2-f]-phenanthridine are 41.89°, 20.46° and 31.69° for Pt1, Pt2 and Pt3, respectively.

# **Electroluminescent Properties**

In order to study the electroluminescent properties of **Pt1-Pt3**, OLEDs based on these dopants were fabricated with a normal sandwiched structure: ITO/HAT-CN (10 nm)/TAPC (40 nm)/TCTA(10 nm)/26mCPy:dopant (x wt%, 20 nm)/TmPyPB (45 nm)/Liq (2 nm)/Al (120 nm) (dopant = **Pt1**, **Pt2**, **Pt3**; x = 2.5, 5, 7.5, 10). 1, 4, 5, 8, 9, 11-hexaazatriphenylene-hexacarbonitrile (HAT-CN) and 8-hydroxyquinolinolato lithium (Liq) were used as hole and electron injection layers, respectively. 1,1-bis[4-[N,N-di(p-tolyl)-amino]phenyl]cyclohexane (TAPC) and 1,3,5-tri[(3-pyridyl)-phen-3-yl]benzene (TmPyPB) were utilized as hole and electron transport layers, respectively. 2,6-bis(N-carbazolyl)pyridine (26mCPy) with high  $E_T$  of 2.8 eV was used as bipolar host material.<sup>19</sup>

To optimize the device efficiency, OLEDs were fabricated with **Pt1-Pt3** at different doping ratios. The EL spectra of **Pt1-Pt3** were depicted in Figure 3, 5 and 7, respectively. All the complexes showed intense EL emission band at around 460 nm with the shoulder at around 490 nm, matching well with their PL spectra, which could be due to the efficient triplet confinement of the excitons blocking layers.<sup>20</sup> The CIE coordinates (Table 2) for Pt(II) complexes were in the sky-blue region, and they were shifted slightly as the doping level was increased from 2.5% to 10%, suggesting that

the bulky mesityl group could make the molecule less prone to excimer formation. The EQE-luminance-current efficiency curves of **Pt1-Pt3** were showed in Figure 4, 6 and 8, respectively. The best performance was achieved for **Pt1** with the doping ratio at 10%, which reached maximum EQE, current efficiency, and power efficiency of 16.2%, 36.5 cd A<sup>-1</sup>, and 33.1 lm W<sup>-1</sup>, respectively. For **Pt1**, the EQE of 14.1% and 12.7% were achieved at the brightness of 100 cd m<sup>-2</sup> and 1000 cd m<sup>-2</sup>, respectively. Although the maximum EQE (16.2%) for **Pt1** is not very high, compared to the state-of-the-art Ir(III)-based blue OLEDs,<sup>4,8g</sup> **Pt1** showed comparable device performance with the best sky-blue Pt(II)-based emitters. For example, Li *et al.* demonstrated efficient sky-blue OLEDs employing a tetradentate platinum complex with EQE of 14.6% at 1000 cd m<sup>-2</sup>,<sup>12c</sup> and blue OLEDs based on PtNON with EQE of 11.5% at 1000 cd m<sup>-2</sup> and CIE coordinates of (0.18, 0.39).<sup>9a</sup>

Among **Pt1-Pt3**, **Pt1** demonstrated the best electro-luminescence properties. The device based on **Pt2** at the doping level of 10 wt% achieved a maximum efficiency of 18.5 cd  $A^{-1}$ , 15.7 lm  $W^{-1}$  and 7.9%, and 12.0 cd  $A^{-1}$ , 11.3 lm  $W^{-1}$  and 5.9% for **Pt3**. Considering that these complexes showed similar PL and EL spectra, the relatively poor EL properties of **Pt2** and **Pt3** could be attributed to the unbalanced charge transport in the emitting layer, which could arise from the different linkage applied in the pyridine^benzene bidentates.

#### Conclusions

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In summary, three blue-emitting tetradentated Pt(II) complexes **Pt1-Pt3** have been successfully prepared, where the rigid imidazo[1,2-*f*]phenanthridine motif with high  $E_{\rm T}$  was used as efficient bidentate. In addition, breaking the conjugation via the introduce of heteroatoms and spiro linkage accounted in part for the high  $E_{\rm T}$  of Pt(II) complexes. The pending mesityl group was used to block the active site and to suppress the formation of excimer, which led to the small variation in CIE coordinates at different doping levels. The emission lifetime of **Pt1** is slightly shorter than those of **Pt2** and **Pt3**, which could account in part for the higher efficiency observed in **Pt1**-based device. Although different linkages were applied in the pyridine^benzene bidentates, these Pt(II) complexes showed similar PL and EL spectra. However, they demonstrated different EL properties, which could be due to different charge-transporting properties of these pyridine^benzene bidentates. Notably, OLEDs based on **Pt1** showed high device performance with the maximum  $\Pi_{\rm c}$  of 36.5 cd A<sup>-1</sup>,

#### Acknowledgements

We thank Mr. Yun Hu for the UPS measurement. We acknowledge financial support from the National Key R&D Program of China (2016YFB0400703), the National Natural Science Foundation of China (21472135, 61307036) and Natural Science Foundation of Jiangsu Province of China (BK20151216). This project is also funded by the 111 Project, Collaborative Innovation Center of Suzhou Nano Science and Technology (CIC-Nano), Soochow University and by the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD).

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Scheme 1 The synthetic routes of Pt(II) complexes Pt1-Pt3

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Figure 1 Optical absorption and photoluminescence spectra of complexes **Pt1-Pt3** in dilute dichloromethane solution at room temperature.

Compour	nd $\lambda_{abs}[nm]^a$	$\lambda_{em}\left[nm\right]^{a}$	$\Phi_p{}^b$	$\Phi_{\mathrm{film}}{}^{\mathrm{b}}$	$\tau[\mu s]_{so}$ <sup>c</sup>	$\tau[\mu s]_{\rm film}{}^c$	LUMO [eV] <sup>d</sup>	HOMO [eV] <sup>e</sup>	$E_{g} \left[ eV \right]^{f}$
Pt1	272, 295, 326, 372	460, 487sh	0.36	0.63	8.33	8.71	-2.29	-5.27	2.98
Pt2	256, 286, 316, 352	460, 489sh	0.29	0.43	8.98	10.0	-2.28	-5.31	3.03
Pt3	243, 267, 289, 330	460, 490sh	0.33	0.34	8.76	9.22	-2.17	-5.32	3.15

Table 1 Photophysical and electrochemical data obtained experimentally for the platinum(II) complexes.

<sup>a</sup> Measured in CH<sub>2</sub>Cl<sub>2</sub> at 293 K with a concentration of  $10^{-5}$  M, sh = shoulder.

<sup>b</sup> Measured in degassed CH<sub>2</sub>Cl<sub>2</sub> relative to *fac*-[Ir(ppy)<sub>3</sub>] ( $\Phi_p = 0.4$ ) and film doped in PMMA.

c The extracting triplet lifetimes ( $\tau$ ) in degassed CH<sub>2</sub>Cl<sub>2</sub> and doped in PMMA at room temperature.

<sup>d</sup> LUMO= HOMO + Eg.

<sup>e</sup>HOMO were calculated from UPS.

<sup>f</sup>The optical band gap estimated from the absorption spectra.

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Figure 2 Density functional theory calculation of orbit density for the HOMOs (bottom) and LUMOs (top) of **Pt1-Pt3**.



Figure 3. The EL spectra of complex Pt1 with different doping ratios at  $5 \text{ mA/cm}^2$ .



Figure 4. The EQE-luminance-current efficiency curves for **Pt1** at different doping ratios.

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Dopant	Dopant level [wt %]	$\frac{\eta_{c.max.}}{\left[ cd \ A^{-1} \right]^{(a)}}$		$\begin{array}{c} \eta_{p.max.} / \; \eta_{p.500} / \eta_{p.1000} \\ [ lm \; W^{\text{-1}} ] \; ^{(b)} \end{array}$		$\frac{\eta_{\text{EQE.max}}}{[\%]} \frac{\eta_{500}}{\eta_{1000}}$			λ <sub>em</sub> [nm]	λ <sub>sh</sub> [nm]	CIE $(x,y)^{(d)}$	V <sub>turn-on</sub> <sup>(e)</sup> [V]		
Pt1	2.5	14.0	10.3	8.6	12.1	6.8	5.1	7.1	5.3	4.4	460	492	(0.17,0.28)	4.2
	5	23.5	18.6	16.1	20.5	13.2	10.2	11.7	9.6	8.0	460	492	(0.17,0.28)	4.0
	7.5	30.5	26.5	23.0	27.3	19.6	15.6	14.2	12.6	11.1	460	492	(0.17,0.30)	3.8
	10	36.5	30.6	27.5	33.1	23.9	19.8	16.2	14.1	12.7	460	492	(0.18,0.32)	3.7
Pt2	2.5	6.0	4.6	3.8	4.9	2.6	1.9	3.2	2.4	2.0	460	492	(0.18,0.27)	4.8
	5	13.0	7.7	6.2	11.8	5.4	3.8	5.5	3.6	2.9	460	492	(0.21,0.32)	4.0
	7.5	16.0	11.8	9.9	13.5	7.6	5.7	7.3	5.7	4.8	460	492	(0.19,0.30)	4.3
	10	18.5	14.3	12.5	15.7	9.3	7.4	7.9	6.5	5.8	460	492	(0.20,0.31)	4.3
Pt3	2.5	4.0	2.8	-	3.6	1.8	-	1.8	1.5	-	464	494	(0.23,0.30)	4.3
	5	7.0	4.9	4.0	6.3	3.4	2.5	3.5	2.5	2.1	464	494	(0.19,0.29)	4.0
	7.5	11.0	7.7	6.3	10.1	5.7	4.2	5.5	3.9	3.1	464	494	(0.18,0.29)	3.9
	10	12.0	8.7	7.4	11.3	6.6	5.1	5.9	4.3	3.7	464	494	(0.17,0.29)	3.7

Table 2. EL performance of the Pt(II) complexes-doped OLEDs.

<sup>a)</sup> Maximum current efficiency ( $\Pi_{c.max}$ ), and current efficiency ( $\Pi_{c.500}$ ,  $\Pi_{c.1000}$ ) measured at a brightness of 500 cd m<sup>-2</sup> and 1000 cd m<sup>-2</sup>, respectively; <sup>b)</sup> Maximum power efficiency ( $\Pi_{p.max}$ ), and power efficiency ( $\Pi_{p.500}$ ,  $\Pi_{p.1000}$ ) measured at a brightness of 500 cd m<sup>-2</sup> and 1000 cd m<sup>-2</sup>, respectively; <sup>c)</sup> Maximum external quantum efficiency ( $\Pi_{EQE.max.}$ ), and EQE ( $\Pi_{EQE.500}$ ,  $\Pi_{EQE.1000}$ ) measured at 500 cd m<sup>-2</sup> and 1000 cd m<sup>-2</sup>, respectively; <sup>d)</sup> Commission Internationale de L'Eclairage coordinates measured at 5 mA cm<sup>-2</sup>; <sup>e)</sup>Turn-on voltage at 200 cd m<sup>-2</sup> for **Pt1-Pt3**.

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# **Table of Contents**



Three blue-emitting platinum(II) complexes based on imidazo[1,2-*f*]phenanthridinecontaining tetradentate ligands have been prepared as efficient dopants for phosphorescent OLEDs.