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# New platinum(II) one-armed Schiff base complexes for blue and orange PHOLEDs applications





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# ABSTRACT

The condensation of different groups substituted salicylaldehydes with aniline and 2,4,5-trifluoroaniline, afforded five one-armed Schiff base ligands  $HL^1$ ,  $HL^2$ ,  $HL^3$ ,  $HL^4$  and  $HL^5$ . And their platinum(II) complexes  $Pt(L^1)_2$ ,  $Pt(L^2)_2$ ,  $Pt(L^3)_2$ ,  $Pt(L^4)_2$ ,  $Pt(L^5)_2$  and  $PtL^5$ . DMSO were prepared through the metallation of ligands with  $K_2PtCl_4$ . All ligands and complexes were characterized by <sup>1</sup>H NMR, infrared spectroscopy, mass spectrometry and single crystal X-ray diffraction. And their thermal stability, photophysical properties, and electrochemical behaviors were investigated in detail. Using these complexes as phosphorescent emitting materials, blue to orange light-emitting devices were fabricated with moderate efficiencies. The maximum current efficiency, power efficiency, and brightness for the 3.0 wt %  $Pt(L^3)_2$  doped OLED are 1.12 cd  $A^{-1}$ , 0.62 1 m  $W^{-1}$  and 1521 cd  $m^{-2}$ , respectively. Given the synthetic simplicity and ease of structural variation, the results here indicate that these platinum(II) Schiff base complexes are good candidates for phosphorescent OLEDs.

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Schiff bases condensed from salicylaldehydes and amines had attracted remarkable attention as a class of preparative accessibility and thermal stability luminescent materials [1–5]. Generally, the metal complexes of Schiff base display the planar structure, which always gave a higher emission quantum yield than that of free ligands. Among the transition metal complexes of Schiff base, zinc Schiff base complexes were in the most investigated queue [6–9]. In 2012, we reported some donor- $\pi$ -acceptor zinc(II) and nickel(II) Schiff base complexes with good two-photon induced fluorescence (TPIF) [10,11]. However, zinc complexes only can emit in the singlet state with low quantum yield efficiency. On the other hand, the

heavy metal (Pt, Ir, Ru and so on) complexes have attracted considerable interest as they can harvest both the singlet and triplet excitons due to the efficient spin—orbit coupling (consequence of the heavy atom effect), leading to the excellent quantum yields (can reach around 100%) [12–29]. Thus, the metal complexes with triplet state emission have been known as an important type of materials in OLEDs nowadays.

Recently, phosphorescent platinum(II) metal complexes were reported by Che [30,31], Thompson [32], and so on. Among them, Che have developed a serial of salen and salophen platinum(II) Schiff base complexes with strong triplet state emission and high quantum efficiency since 2004 [33–35]. However, it was found that the formation of aggregate/excimer would reduce the emission efficiency and color purity of the platinum(II) Schiff base complexes when they were at high concentration. This phenomenon can be attributed to the triplet-triplet annihilation, Pt…Pt and  $\pi$ - $\pi$  interactions at the high concentration in solid state. Later, we developed a series of new symmetric and asymmetric salen and

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salophen platinum(II) Schiff base complexes with bulky substituents such as *tert*-butyl and triphenylamino groups, yielding a high efficiency in OLED devices due to effectively suppressing of the aggregation or excimer formation [36]. More recently, another series of donor– $\pi$ –acceptor salophen platinum(II) Schiff base complexes have been developed by our group [37]. The emission of complexes can be tuned from yellow to red with the variation of substituent group. Moreover, the diamine linker in the platinum(II) or other transition metal salen and salophen Schiff base complexes can partly control the emission wavelength according to the previous research.

Those platinum(II) Schiff base complexes reported previously mainly focus on the yellow (salen complexes) and red (salophen complexes) emissions due to the large conjugated systems of salen and salophen complexes. To the best of our knowledge, there is few report of *trans*-bis(salicylaldiminato) platinum(II) complexes (onearmed Schiff base complexes). One-armed Schiff bases can be easily synthesized through 1:1 condensation of salicylaldehyde and monoamine, and they show better flexibility and lower conjugation than salen and salophen Schiff bases, which may lead to a blueshifted emissive complexes. Hence, in this contribution, five onearmed Schiff base ligands were developed by the condensation of different groups substituted salicylaldehydes with aniline or 2,4,5trifluoroaniline. And their platinum(II) complexes were prepared and characterized.

Based our previous research. The HOMOs mainly locate on the phenolate fragments and LUMOs mainly locate on the imino part of Schiff bases. Different substituents on the Schiff bases can change the HOMO-LUMO energy gaps, emission wavelengths and somewhat improve the emission efficiency. In this work, the strong electron withdrawing units in the complexes such as fluorine and bromine. and electron donating units such as 4diethylaminophenyl and 3.5-di-tert-butyl-phenyl were introduced into the new one-armed Schiff base complexes to tune their emission wavelengths. Then the blue to orange phosphorescent organic light emitting devices (PHOLEDs) were fabricated using a single EML composed of the Schiff base complexes and blue emitting materials. Though the efficiencies of PHOLEDs based on these platinum(II) Schiff base complexes cannot compete with Ir(III) systems, they are still attractive because of their preparative accessibility and thermal stability, and would provide access to new classes of phosphorescent materials for practical interest.

#### 1. Results and discussion

#### 1.1. Synthesis

The one-armed Schiff base ligands (**HL<sup>1</sup>**, **HL<sup>2</sup>**, **HL<sup>3</sup>**, **HL<sup>4</sup>** and **HL<sup>5</sup>**) were prepared via the condensation of the substituted 2-hydroxybenzaldehydes with monoamines according to the



Scheme 1. The synthetic routes for the Schiff base ligands and their platinum(II) complexes.

traditional method (Scheme 1) [38,39]. Then the ligands were reacted with potassium tetrachloroplatinate(II) and KOH in DMF at 70 °C to give the corresponding *trans*-bis(salicylaldiminato) platinum(II) complexes  $Pt(L^1)_2$ ,  $Pt(L^2)_2$ ,  $Pt(L^3)_2$ ,  $Pt(L^4)_2$  and  $Pt(L^5)_2$ [36,37]. In addition, we also separated the complexes of  $Pt(L^5)_2$ ·DMSO containing only single ligand and one molecule of dimethyl sulphoxide (DMSO). These complexes  $Pt(L^1)_2$ ,  $Pt(L^2)_2$ ,  $Pt(L^3)_2$ ,  $Pt(L^4)_2$ ,  $Pt(L^5)_2$  and  $PtL^5$ ·DMSO show good solubility in common organic solvents. The new Schiff base ligands and platinum(II) complexes were characterized by <sup>1</sup>H NMR, infrared spectroscopy (IR), mass spectrometry (MS), UV–visible spectrum and elemental analysis. Furthermore, the structure of  $Pt(L^1)_2$ ,  $Pt(L^3)_2$ and  $PtL^5$ ·DMSO were confirmed by the single crystal X-ray diffraction.

#### 1.2. Characterization of the ligands and complexes

The <sup>1</sup>H NMR spectrum of the Schiff base ligands **HL**<sup>1</sup>, **HL**<sup>2</sup>, **HL**<sup>3</sup>,  $HL^4$  and  $HL^5$  in CDCl<sub>3</sub> exhibit board singlet at  $\delta$  13.31, 13.69, 13.81, 12.69 and 13.36 ppm for the O-H protons, respectively. The chemical shift is typical for resonance-assisted hydrogen bonded (RAHB) proton of  $O-H \cdots N=C$ . The other characteristic imino protons of the ligands HL<sup>1</sup>, HL<sup>2</sup>, HL<sup>3</sup>, HL<sup>4</sup> and HL<sup>5</sup> appear as sharp singlet at  $\delta$  8.58, 8.64, 8.41, 8.59 and 8.64 ppm, respectively. The <sup>1</sup>H NMR spectrum of Schiff base complexes Pt(L<sup>1</sup>)<sub>2</sub>, Pt(L<sup>2</sup>)<sub>2</sub>, Pt(L<sup>3</sup>)<sub>2</sub>,  $Pt(L^4)_2$ ,  $Pt(L^5)_2$  and  $PtL^5$  DMSO in CDCl<sub>3</sub> exhibit singlet at  $\delta$  8.42, 8.20, 7.72, 8.50, 7.98 and 8.10 ppm for the imino protons, respectively. In addition, the peak of O-H protons disappeared, indicating the coordination of platinum. The spectrum of PtL<sup>5</sup> DMSO showed some difference with the other complexes. The chemical shift of  $\delta$  3.49 ppm can be attributed to the protons of dimethyl sulphoxide (DMSO), which is consistent with the crystal structure of PtL<sup>5</sup> DMSO.

The Schiff base ligands and their platinum(II) complexes were further characterized by IR and MS. The IR absorption peak between 1598 and 1655 cm<sup>-1</sup> can be assigned to the C=N stretching vibration. The MALDI-TOF-MS spectrums of platinum(II) complexes exhibit the  $[M]^+$  or  $[M+H]^+$  peaks values less than 9 ppm from the theoretical values.

# 1.3. Crystal structure of platinum(II) complexes

Complex **Pt(L<sup>1</sup>)**<sub>2</sub> and **Pt(L<sup>3</sup>)**<sub>2</sub> were characterized by X-ray crystallography (Figs. 1 and 2). The Pt(II) ion coordinates two N atoms and two O atoms in a square planar geometry. The average Pt–N and Pt–O distances are 2.01 and 1.99 Å, respectively. The closest Pt(II)/Pt(II) distance of **Pt(L<sup>3</sup>)**<sub>2</sub> is 8.78 Å due to the bulky 4-diethylaminophenyl substituents, which is outside the range of 2.7–3.5 Å for any metallophilic interaction [36]. Moreover, the presence of the bulky groups effectively inhibits intermolecular  $\pi$ – $\pi$  stacking interactions of the aryl rings.

Complex **PtL<sup>5</sup>**•**DMSO** was also characterized by single crystal Xray diffraction (Fig. 3). It can be clearly seen that the Pt(II) ion in **PtL<sup>5</sup>**•**DMSO** coordinated a molecule of dimethyl sulphoxide (DMSO). The Pt(II) ion was coordinated with N, S, O and Cl atoms in a square planar geometry. The average Pt–N, Pt–O, Pt–S, Pt–Cl, distances are 2.03, 1.99, 2.23 and 2.28 Å, respectively.

#### 1.4. UV-visible absorption of the ligand and complexes

The UV-visible absorption spectra of the Schiff base ligands **HL**<sup>1</sup>, **HL**<sup>2</sup>, **HL**<sup>3</sup>, **HL**<sup>4</sup> and **HL**<sup>5</sup> exhibit bands between 200 and 450 nm (Fig. 4), which can be assigned to the intra-ligand  $\pi$ - $\pi$ \* and n- $\pi$ \* transitions. Specifically, the ligand **HL**<sup>3</sup> shows a much stronger absorption peak at 374 nm compared with the other ligands, due to



**Fig. 1.** A perspective view of  $Pt(L^1)_2$ . Selected bond lengths (Å): Pt(1)-N(1) 2.013(11), Pt(1)-N(1A) 2.013(11), Pt(1)-O(1) 1.985(10), Pt(1)-O(1A) 1.985(10). Selected bond angles (°): N(1)-Pt(1)-N(1A) 180.0 (5), O(1)-Pt(1)-O(1A) 180.0(5), N(1)-Pt(1)-O(1) 91.9(4).

the intra-ligand  $n-\pi^*$  transitions of 4-diethylaminophenyl fragments.

Apart from the multiple bands within 200-400 nm, the six platinum(II) complexes show intense absorption bands in the range of 400–600 nm, which can be assigned to the  $\pi$ - $\pi$ <sup>\*</sup> transitions of LLCT mixed with metal-to-ligand charge-transfer (MLCT) (Fig. 4) [33,34,40]. This assignment is also supported by the DFT calculation data, in which the lowest absorption energy bands of the platinum complexes are ranged in 400-600 nm, arising from MLCT and LLCT. The maximum absorption peak of  $Pt(L^4)_2$  and  $Pt(L^5)_2$  is also redshifted compared with  $Pt(L^1)_2$  and  $Pt(L^2)_2$ , due to the withdrawing property of fluorine involved in the complexes. In our DFT study of the Schiff base complexes, it was found that the HOMO mainly located on the phenolate fragments and metal ion while the LUMO located on the imino part [10,37]. And the electron donating groups of the phenolate fragments and the electron withdrawing groups at the imino can effectively adjust the HOMO and LUMO energy levels.

# 1.5. Emission of the ligand and complexes

At room temperature, the emission spectra of the Schiff base ligands appear in the visible range (400-700 nm) in CH<sub>2</sub>Cl<sub>2</sub>, which



**Fig. 2.** A perspective view of  $Pt(L^3)_2$ . Selected bond lengths (Å): Pt(1)–N(1) 2.009(3), Pt(1)–N(1A) 2.009(3), Pt(1)–O(1) 1.992(2), Pt(1)–O(1A) 1.992(2). Selected bond angles (°): N(1)–Pt(1)–N(1) 180.0, O(1)–Pt –O(1A) 180.0, N(1)–Pt(1)–O(1) 91.49(10), N(2) –Pt(1)–O(2) 91.50(10).



**Fig. 3.** A perspective view of **PtL**<sup>5</sup>·**DMSO**. Selected bond lengths (Å): Pt(1)–N(1) 2.031(4), Pt(1)–O(1) 1.993(3), Pt(1)–S(1) 2.2328(13), Pt(1)–Cl(1) 2.2889(15). Selected bond angles (°): O(1)–Pt(1)–Cl(1) 175.09(9), S(1)–Pt(1)–N(1) 175.19(12), O(1)–Pt(1)–N(1) 91.61(14), S(1)–Pt(1)–Cl(1) 87.35(5).

are attributable to the singlet state. However, we couldn't record any emission data of the Schiff base platinum(II) complexes in organic solvent as the phosphorescent emission can be easily quenched by solvent. Thus, the phosphorescence of complexes was determined in the solid powder. As shown in Table 1 and Fig. 5, the emission spectra of the platinum(II) Schiff base complexes display the shoulder peaks in the visible range (526–629 nm) with the highest quantum yield of 7.92% for PtL<sup>5</sup> DMSO. These complexes emitted green to orange light with the decay times in microsecond scale  $(1.16-1.88 \mu s)$ , indicating the emission arise from the triplet state. The platinum(II) complexes of  $Pt(L^3)_2$ ,  $Pt(L^4)_2$  and  $Pt(L^5)_2$ electron-donating modified with strong group (4diethylaminophenyl) or electron-withdrawing groups (fluorine) show a much red-shifted emission comparing with  $Pt(L^2)_2$ . Based on our DFT study, the emission arise from the triplet state, which can be attributed to intraligand charge transfer and metal-to-ligand charge-transfer (MLCT).

# 1.6. Electrochemical properties and thermal stability

The cyclic voltammetry of platinum(II) Schiff base complexes have been examined. Cyclic voltammetry study can give fundamental information on the number of oxidation/reduction processes and the redox potentials of the compounds. Furthermore, the HOMO-LUMO energy gap can be estimated from its redox potentials. Cyclic voltammetry behaviors of the platinum(II) Schiff base complexes were recorded in degassed acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte at a scan rate of 50 mV s<sup>-1</sup>. A glassy carbon electrode was used as working electrode, and a platinum(II) wire was used as the auxiliary electrode with an Ag/Ag<sup>+</sup> as the reference electrode [41]. The cyclic voltammogram of  $Pt(L^1)_2$ ,  $Pt(L^2)_2$ ,  $Pt(L^3)_2$ ,  $Pt(L^4)_2$ ,  $Pt(L^5)_2$ and  $PtL^5$ ·DMSO is shown in Fig. 6, and the electrochemical data of the three complexes are listed in Table 2. The irreversible anodic waves are attributed to the oxidation of Schiff base ligands. The



Fig. 4. UV-visible absorption spectra of the Schiff base ligands and their corresponding platinum(II) complexes in DCM ( $1.0 \times 10^{-5}$  M).

Table	1
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Summary of UV-visible absorption and luminescent data at room temperature in DCM ( $1.0 \times 10^{-5}$  M) and solid.

Absorption $\lambda_{max}$ (nm) <sup>a</sup>	Luminescence $\lambda_{max} (nm)^{b}$	$\Phi_{em}{}^{c}$ (%)	τ (μs)
270, 306, 322, 353	545	_	_
279, 309, 325, 354	572	_	-
270, 374	526	_	-
272, 314, 329, 359	560	_	-
280, 320, 359	595	_	-
341, 472	d		
343, 487	527, 618	0.01	1.45
267, 313, 386, 446	613	3.22	1.26
337, 450, 511	593, 629	0.13	1.16
337, 451, 497	565, 609	0.02	1.52
299, 442	566, 606	7.92	1.88
	Absorption $\lambda_{max} (nm)^a$ 270, 306, 322, 353           279, 309, 325, 354           270, 374           272, 314, 329, 359           280, 320, 359           341, 472           343, 487           267, 313, 386, 446           337, 450, 511           337, 451, 497           299, 442	Absorption $\lambda_{max}$ (nm) <sup>a</sup> Luminescence $\lambda_{max}$ (nm) <sup>b</sup> 270, 306, 322, 353         545           279, 309, 325, 354         572           270, 374         526           272, 314, 329, 359         560           280, 320, 359         595           341, 472         -d           343, 487         527, 618           267, 313, 386, 446         613           337, 450, 511         593, 629           337, 451, 497         565, 609           299, 442         566, 606	Absorption $\lambda_{max}$ (nm) <sup>a</sup> Luminescence $\lambda_{max}$ (nm) <sup>b</sup> $\Phi_{em}^{c}$ (%)           270, 306, 322, 353         545         -           279, 309, 325, 354         572         -           270, 374         526         -           270, 320, 359         560         -           280, 320, 359         595         -           343, 487         527, 618         0.01           267, 313, 386, 446         613         3.22           337, 450, 511         593, 629         0.13           337, 451, 497         566, 609         0.02           299, 442         566, 606         7.92

<sup>a</sup> Photophysical measurements were made with a concentration of  $1 \times 10^{-5}$  M in CH<sub>2</sub>Cl<sub>2</sub>.

<sup>b</sup> Photophysical measurements were made with a concentration of  $1 \times 10^{-5}$  M in CH<sub>2</sub>Cl<sub>2</sub> (ligands) and solid powder (complexes) at room temperature.

<sup>c</sup> Quantum yields ( $\Phi$ ) were measured by absolute method using an integrating sphere.

<sup>d</sup> Due to the limitation of sample and instrument, we were unable to determine the emission for **Pt(L<sup>1</sup>)**<sub>2</sub>.



Fig. 5. Emission spectrum of Schiff base ligands in DCM ( $1.0 \times 10^{-5}$  M) (left) and Schiff base platinum(II) complexes in solid (right).

onset of the first oxidation process of  $Pt(L^1)_2$ ,  $Pt(L^2)_2$ ,  $Pt(L^3)_2$ ,  $Pt(L^4)_2$  and  $Pt(L^5)_2$  occurs at about 0.63–0.78 V, while  $PtL^5 \cdot DMSO$ shows a less anodic potential with the onset of the first oxidation at about 0.57 V. Apparently, the electron releasing molecule of DMSO accelerates the oxidation of PtL<sup>5</sup> · DMSO. The LUMO- HOMO energy gap can be calculated by UV-vis absorption spectra. The energy gaps of these complexes are ranged 2.05-2.61 eV. Furthermore, the HOMO and LUMO energy levels of these complexes are estimated from the oxidation and energy gap [calculated according to the following equations: HOMO =  $-(E_{ox} + 4.71)$  eV and LUMO =  $(E_{gap}+HOMO) eV]$  to be -5.49 to -5.28 eV and -3.37 to -2.67 eV, respectively. The complexes  $Pt(L^4)_2$  and  $Pt(L^5)_2$  shows a comparable HOMO level as  $Pt(L^1)_2$ ,  $Pt(L^2)_2$ , and  $Pt(L^3)_2$ , but a much lower LUMO than  $Pt(L^1)_2$ ,  $Pt(L^2)_2$ , and  $Pt(L^3)_2$  due to the electron deficient property of 2,4,5-trifluorobenzen substituents at imino part. In addition, PtL<sup>5</sup> DMSO exhibits a higher HOMO than the other complexes due to the electron donating property of DMSO.

All the complexes are thermally stable with onset decomposition temperatures ( $T_d$ ) within the range from 248 to 295 °C (Table 2). The thermalgrams of differential scanning calorimetry and thermal gravimetric analysis (DSC-TGA) of **Pt(L<sup>3</sup>)**<sub>2</sub> is shown in Fig. 7.

#### 1.7. Theoretical calculation

All density functional theory (DFT) and time dependent density functional theory (TD–DFT) calculations were performed with Gaussian 09 [42]. The DFT geometry optimisations as well as TD–DFT calculations [43–48] were carried out using the B3LYP method. A 6–31g(d) basis set was used for C, H, N, F, O and S atoms, and landl2dz was used for heavy atoms (Pt and Br) for accuracy



Fig. 6. Cyclic voltammogram of the complexes.

Table 2	
Summary of cyclic voltammetry and TGA data	

Compound	Eox	HOMO <sup>a</sup>	LUMO <sup>b</sup>	Egap <sup>c</sup>	$T_{\rm d}/^{\circ}{\rm C}$
$Pt(L^1)_2$	0.63	-5.34	-2.95	2.39	260
$Pt(L^2)_2$	0.78	-5.49	-3.12	2.37	295
$Pt(L^3)_2$	0.76	-5.47	-2.93	2.54	272
$Pt(L^4)_2$	0.65	-5.36	-3.31	2.05	281
Pt(L <sup>5</sup> ) <sub>2</sub>	0.72	-5.43	-3.37	2.06	284
PtL <sup>5</sup> DMSO	0.57	-5.28	-2.67	2.61	248

<sup>a</sup> Estimated from the oxidation potentials HOMO =  $-(E_{ox} + 4.71)$  eV.

 $^{\rm b}\,$  Deduced from the HOMO and  $E_{gap}$ 

<sup>c</sup> Estimated from the UV-vis absorption spectra.

[49–52]. The optimized geometries of the complex are shown in Fig. 8. It is clear that the platinum center and the Schiff bases are coplanar in all these three compounds.

The HOMOs mainly locate on the phenolate fragments and middle metal atom in the complexes. The HOMO ( $\pi$  orbital) was formed by p orbital of C, N and O and *d* orbital of platinum, which contain a few proportion *s* orbital (Fig. 9). The LUMOs mainly locate on the imino part, which is composed by  $p-\pi^*$  orbital of C, N and O. The electrons transfer from phenolate fragments and middle metal to imino part when they are excited from the ground states to the excited states according to molecular orbital analysis. Fig. 9 shows the electron cloud distributions and composition characteristics of the frontier molecular orbitals.

The electronic transitions of complexes were calculated by Time-Dependent B3LYP methods, and their wavelength, transition energies and oscillator strengths are listed in Table 3. Take  $Pt(L^3)_2$  as an example, the S1 transition originates from the transition of



Fig. 7. Thermal gravimetric analysis (DSC-TGA) of Pt(L<sup>3</sup>)<sub>2</sub>.



Fig. 8. Optimized geometry of platinum(II) Schiff base complexes.

HOMO  $\rightarrow$  LUMO ( $\pi \rightarrow \pi^*$ , LLCT and MLCT). The maximum UV–visible absorption wavelength of **Pt(L<sup>3</sup>)**<sub>2</sub> was determined as 446 nm in experiment, which is consistent with the calculated value of 460 nm. And the S1 transition of **Pt(L<sup>4</sup>)**<sub>2</sub> and **Pt(L<sup>5</sup>)**<sub>2</sub> (508 and

515 nm), originated from the HOMO $\rightarrow$ LUMO ( $\pi \rightarrow \pi^*$ , LLCT and MLCT) transition, is obviously red shifted induced by the electron acceptor F group.



Fig. 9. The frontier molecular orbitals of platinum(II) Schiff base complexes.

Table 3
Theoretical results of major transition (percentage), transition energies (E), oscillato
strengths (f) of complexes.

Pt(L <sup>1</sup> ) <sub>2</sub>	
S1 HOMO $\rightarrow$ LUMO (70.051%) 502.40 0.0	465
S2 HOMO $\rightarrow$ LUMO+2 (69.754%) 453.17 0.0	010
S3 HOMO $\rightarrow$ LUMO+3 (65.584%) 388.56 0.0	010
S4 HOMO-1→LUMO (69.773%) 370.91 0.0	010
S5 HOMO-3→ LUMO (69.706%) 358.91 0.0	010
S6 HOMO-1→ LUMO+1 (68.745%) 340.53 0.1	125
$Pt(L^2)_2$	
S1 HOMO $\rightarrow$ LUMO (68.987%) 511.91 0.0	418
S2 HOMO→ LUMO+1 (70.000%) 480.22 0.0	044
S3 HOMO $\rightarrow$ LUMO+2 (63.749%) 411.82 0.0	120
S4 HOMO-1→ LUMO (69.596%) 402.37 0.0	043
S5 HOMO-1→ LUMO+1 (67.950%) 382.69 0.0	887
S6 HOMO-3→LUMO (65.679%) 356.84 0.0	001
$Pt(L^3)_2$	
S1 HOMO $\rightarrow$ LUMO (69.187%) 460.24 0.0	521
S2 HOMO → LUMO+1 (69.207%) 426.63 0.0	000
S3 HOMO → LUMO+2 (63.602%) 391.08 0.0	000
S4 HOMO-1→LUMO (68.797%) 382.03 0.6	198
S5 HOMO-1→LUMO+1 (56.187%) 355.54 0.0	019
S6 HOMO-2→LUMO (53.632%) 341.98 0.0	001
Pt(L <sup>4</sup> ) <sub>2</sub>	
S1 HOMO $\rightarrow$ LUMO (70.026%) 508.51 0.0	445
S2 HOMO $\rightarrow$ LUMO+1 (69.719%) 463.59 0.0	010
S3 HOMO $\rightarrow$ LUMO+2 (62.342%) 402.11 0.0	010
S4 HOMO-1→ LUMO (69.894%) 382.05 0.0	010
S5 HOMO-3→ LUMO (70.408%) 361.80 0.0	008
S6 HOMO-1→ LUMO+1 (69.465%) 352.86 0.0	953
$Pt(L^5)_2$	
S1 HOMO→LUMO (70.134%) 515.96 0.0	488
S2 HOMO→LUMO+1 (69.866%) 467.37 0.0	010
S3 HOMO $\rightarrow$ LUMO+2 (62.590%) 408.33 0.0	010
S4 HOMO-1→LUMO (69.751%) 396.86 0.0	010
S5 HOMO-1→ LUMO+1 (69.753%) 364.18 0.0	751
S6 HOMO-3→LUMO (66.066%) 361.75 0.0	330
PtL <sup>5</sup> . DMSO	
S1 HOMO→ LUMO (66.670%) 497.78 0.0	001
S2 HOMO→LUMO+1 (66.095%) 447.70 0.0	273
S3 HOMO $\rightarrow$ LUMO+2 (44.045%) 439.91 0.0	198
S4 HOMO-1→LUMO+1 (52.863%) 408.19 0.0	302
S5 HOMO-1→ LUMO (46.934%) 398.62 0.0	246
S6 HOMO-2→LUMO+1 (54.741%) 389.64 0.0	029

#### 1.8. Electrophosphorescent OLEDs characterization

All of the new platinum(II) Schiff base complexes can be readily sublimed under vacuum which should be amenable to thermally evaporated OLED device fabrication. Using  $Pt(L^2)_2$ ,  $Pt(L^3)_2$ ,  $Pt(L^5)_2$ and PtL<sup>5</sup> DMSO as phosphorescent emitters, devices with the structure ITO/MoO<sub>3</sub> (8 nm)/1,4-bis(1-naphthylphenylamino)biphenyl (NPB) (80 and 60 nm)/1,3-Bis(N-carbazolyl)benzene (mCP) (10 nm)/mCP: 3 wt % Pt(II) complex (25 nm)/1,3,5-tri(1phenyl-1H-benzo[d]imidazol-2-yl)phenyl (TPBI) (40 nm)/LiF (1 nm)/Al, were fabricated as shown in Fig. 10. In the devices, the layers of NPB and TPBI were used as the hole- and electrontransporting layer, respectively. And mCP is chosen as the host material because its emission spectrum overlaps with the absorption spectra of the platinum(II) complexes in this work. The selected platinum(II) Schiff base complexes with 3 wt % doping concentration in the host material mCP served as the emissive layer. Another thin layer of mCP was inserted between emissive layer and hole transporting layer, with LUMO of at least 0.3 eV above that of the dopant and host, thus preventing electron leakage from the emissive layer. MoO<sub>3</sub> and LiF function as the hole- and electron-injecting layers, respectively. The indium tin oxide (ITO) coated glass substrate with 20  $\Omega$  per square sheet resistivity was used as transparent anode.



Fig. 10. The device structure and energy level diagram of a OLEDs using  $Pt(L^2)_2$  as the emitting material.

The performances of the devices using  $Pt(L^2)_2$ ,  $Pt(L^3)_2$ ,  $Pt(L^5)_2$ and PtL<sup>5</sup> DMSO as electrophosphorescent dopant materials are summarized in Table 4. The EL spectra of all the devices match the photoluminescence (PL) spectra of the corresponding complexes, revealing that all EL emissions come directly from the triplet excited state of the phosphorescent emitters. The devices fabricated with complexes  $Pt(L^3)_2$  and  $Pt(L^5)_2$  showed blue emission with CIE coordinates at around (0.29, 0.29) (Fig. 11). In addition, the OLEDs of PtL<sup>5</sup> DMSO emit the green light, while the devices of complex  $Pt(L^2)_2$  showed orange emission. To optimize the device efficiency, NPB layer thickness (80 nm and 60 nm) dependence experiments were carried out. In the device containing 80 nm thickness of NPB layer, the Schiff base platinum(II) complexes showed a little better current efficiency, power efficiency and external quantum efficiency than the 60 nm thickness device. As a hole transport material, NPB can accelerate the holes transport in the OLEDs, which may lead to much better charge balance. As mCP has a relatively higher triplet energy level, an efficient exothermic energy transfer from the triplet state of mCP to the triplet state of platinum(II) Schiff base complexes, which would give the perfect alignment of triplet state energy, leading to excellent triplet exciton confinement within the emissive layer. However, it is worth noting that incomplete electron trapping by the platinum(II) Schiff base complexes is evident due to the observation of a strong EL band at 415 nm, which primarily comes from the fluorescence of the host material mCP.

The blue OLED doped with 3 wt % Pt(L<sup>3</sup>)<sub>2</sub>(80 nm) shows a moderate performance with a turn-on voltage  $(V_{on})$  of 6.3 V, a maximum brightness ( $L_{max}$ ) of 1521 cd m<sup>-2</sup> at 17.4 V, a peak external quantum efficiency  $(\eta_{ext,\ max})$  of 0.54%, a peak luminance efficiency  $(\eta_{L,\ max})$  of 1.12 cd  $A^{-1}$  and a peak power efficiency  $(\eta_{P}$  $_{max}$ ) of 0.62 l m W<sup>-1</sup> (Table 4). Another blue light-emitting device with 3 wt % Pt(L<sup>3</sup>)<sub>2</sub> (60 nm) is also showing a moderate EL efficiency of 0.51%, 0.99 cd  $A^{-1}$  and 0.55 l m  $W^{-1}$ . This device turns on at 6.1 V and its light output can reach 528 cd  $m^{-2}$  at 16.5 V (Fig. 11, Table 4). The EL spectra using  $Pt(L^3)_2$ ,  $Pt(L^5)_2$  or  $PtL^5$  DMSO with 3 wt % dopant were found to show significant spectral blue shifts compared with the emission of pure solid (Figs. 5 and 11). This phenomenon was attributed to the 3 wt % dopant emission layer lower the tendency of complex to form aggregates through Pt…Pt and/or  $\pi$ - $\pi$  stacking interactions in the thin films. To the best of our knowledge, using  $Pt(L^2)_2$ ,  $Pt(L^3)_2$ ,  $Pt(L^5)_2$  or  $PtL^5 \cdot DMSO$  as the single EML, the device performance is moderate and comparable to

#### Table 4

Summary of device performances at best dopant concentrations.

Dopant	Doping concentration/wt%	NPB/nm	$V_{\rm on}^{\rm a}/{\rm V}$	$L_{\rm max}^{\rm b}/{\rm cd}~{\rm m}^{-2}$	$\eta_{\rm L,max}^{\rm c}/{\rm cd}~{\rm A}^{-1}$	$\eta_{\rm P,max}^{\rm d}/{ m lm}~{ m W}^{-1}$	$\eta_{\rm ext,max}^{\rm e}$ /%	EL <sub>max</sub> <sup>f</sup> /nm	CIE x, y
Pt(L <sup>2</sup> ) <sub>2</sub>	3	80	8.4	475	0.16	0.06	0.11	608	0.51, 0.35
$Pt(L^2)_2$	3	60	8.2	266	0.14	0.05	0.11	616	0.52, 0.34
$Pt(L^3)_2$	3	80	6.3	1521	1.12	0.62	0.54	564	0.29, 0.29
$Pt(L^3)_2$	3	60	6.1	1870	0.99	0.55	0.51	528	0.27, 0.30
$Pt(L^5)_2$	3	80	7.3	97	0.29	0.14	0.15	564	0.30, 0.33
$Pt(L^5)_2$	3	60	6.4	84	0.22	0.08	0.13	564	0.29, 0.29
PtL <sup>5</sup> DMSO	3	80	6.9	150	0.35	0.17	0.18	560	0.31, 0.38
PtL <sup>5</sup> DMSO gggMSO	3	60	7.1	156	0.35	0.14	0.18	560	0.30, 0.39

<sup>a</sup> Turn-on voltage.

<sup>b</sup> Maximum luminance.

<sup>c</sup> Maximum current efficiency.

<sup>d</sup> Maximum power efficiency.

<sup>e</sup> Maximum external quantum efficiency.

<sup>f</sup> Peak emission wavelength.

the ever reported with analogous platinum(II) complexes as single EML. Our primary results indicate that these platinum(II) Schiff bases are competitive candidates as phosphorescent dopant as blue to orange OLEDs.

# 2. Conclusions

In this work, a series one-armed platinum(II) Schiff base complexes have been developed and fully characterized by <sup>1</sup>H NMR, IR, MS, UV–visible absorption, elemental analysis and single crystal Xray diffraction. These complexes with different electron withdrawing and donating substituents show green to orange phosphorescent emissions in solid state. Using these complexes as phosphorescent emitting materials, blue to orange light-emitting devices were fabricated with moderate efficiency. The maximum current efficiency, power efficiency and brightness for the 3.0 wt %  $Pt(L^3)_2$  doped OLEDs are 1.12 cd A<sup>-1</sup>, 0.62 l m W<sup>-1</sup> and 1521 cd m<sup>-2</sup>, respectively. Given the synthetic simplicity and ease of structural variation, the preliminary results indicate that these platinum(II) Schiff base complexes are good candidates for phosphorescent OLEDs, and further investigation of the lifetime of the devices based on the these platinum(II) Schiff base is currently underway.

# 3. Experimental section

# 3.1. Materials and methods

The chemicals were purchased from Aladdin Reagent Company and used as received. Silica gel 60 (0.04–0.063 mm) for column chromatography was purchased from Qingdao Haiyang Chemical





Fig. 11. Performance of OLEDs using a single EML doped with Schiff base platinum(II) complexes and mCP: (a) EL spectrum characteristics of devices; (b) current–voltage and brightness–voltage characteristics of devices; (c) external quantum efficiency-current characteristics of devices; (d) current efficiency-current.

Co., Ltd. NMR spectra were recorded on a Bruker Ultrashield 400 Plus NMR spectrometer. High-resolution matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were recorded with a Bruker Autoflex MALDI-TOF mass spectrometer. The C, H and N microanalyses were performed with a Carlo Erba 1106 elemental analyzer. The IR spectra were recorded with a Shimadzu IRAffinity-1 FTIR spectrometer as KBr disc. Thermogravimetrical studies were performed from 30 °C to 1000 °C at 10 °C/min under nitrogen on a TA Instruments SDTQ600 (TA instruments). Electronic absorption spectra in the UV–visible region were recorded on a Shimadzu UV-2450 UV/Vis spectrophotometer. Steady-state visible fluorescence, lifetime and quantum yields were recorded on a FLS980 Photoluminescence Spectrometer (Edinburgh Instruments).

**HL**<sup>1</sup> To a stirred solution of aniline (307 mg, 2.59 mmol) in absolute ethanol (15 mL), 5-bromo-2-hydroxybenzaldehyde (521 mg, 3.23 mmol) was added. The resulting mixture was refluxed 6 h. After cooling to room temperature, the orange product precipitated was washed with cold ethanol and petroleum ether. Yield: 0.622 g (87.0%). <sup>1</sup>HMMR(CDCl<sub>3</sub>, 400 MHZ)  $\delta$  13.31 (s, 1H, OH), 8.58 (s, 1H, HC=N), 7.54 (d, 1H, *J* = 2.0Hz, Ar–H), 7.45–7.49 (m, 3H, Ar–H), 7.30–7.36 (m, 3H, Ar–H), 6.96 (d, 1H, *J* = 8.0Hz, Ar–H). IR: 3346, 2887, 1655, 1560, 1474, 1346, 1279, 1113, 1063, 961, 845, 808, 679. C<sub>13</sub>H<sub>10</sub>BrNO (276.1286): calcd. C 56.55, H 3.65, N 5.07; found C 56.43, H 3.61, N 5.11.

**HL<sup>2</sup>** To a stirred solution of aniline (307 mg, 3.27 mmol) in absolute ethanol (15 mL), 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (756 mg, 3.23 mmol) was added. The resulting mixture was refluxed 6 h. After cooling to room temperature, the orange product precipitated was washed with cold ethanol and petroleum ether. Yield: 0.504 g (50.3%). <sup>1</sup>HMMR(CDCl<sub>3</sub>, 400 MHZ)  $\delta$  13.69 (s, 1H, OH), 8.64 (s, 1H, HC=N), 7.47–7.38 (m, 4H, Ar–H), 7.28 (d, J = 7.5 Hz, 2H, Ar–H), 7.22 (d, J = 2.4 Hz, 1H, Ar–H), 1.48 (s, 9H, CH<sub>3</sub>), 1.33 (s, 9H, CH<sub>3</sub>). IR: 3427, 3180, 2860, 2555, 2483, 2328, 1614, 1575, 1361, 1247, 1170, 972, 866, 759. C<sub>21</sub>H<sub>27</sub>NO (309.4452): calcd. C 81.51, H 8.79, N 4.53; found C 81.66, H 8.64, N 4.54.

**HL<sup>3</sup>** To a stirred solution of aniline (347 mg, 3.73 mmol) in absolute ethanol (15 mL), 4-(diethylamino)-2-hydroxybenzaldehyde (720 mg, 3.73 mmol) was added. The resulting mixture was refluxed 6 h. After cooling to room temperature, the deep orange product precipitated was washed with cold ethanol and petroleum ether. Yield: 0.66 g (66.4%). <sup>1</sup>HNMR(400 MHz,CDCl<sub>3</sub>): $\delta$  13.81 (s, 1H,O–H), 8.41 (s, 1H,N=CH), 7.37 (t, *J* = 7.7 Hz, 2H,Ar-H), 7.23 (d, *J* = 7.6 Hz, 2H,Ar-H), 7.20–7.14 (m, 2H,Ar-H), 6.25 (dd, *J* = 8.7, 2.1 Hz, 1H,Ar-H), 6.19 (s, 1H,Ar-H), 3.40 (q, *J* = 7.0 Hz, 4H, CH<sub>2</sub>), 1.21 (t, *J* = 7.0 Hz, 6H, CH<sub>3</sub>). IR (cm<sup>-1</sup>, KBr): 3419, 2972, 1631, 1583, 1519, 1485, 1423, 1342, 1197, 1136, 823, 694. C<sub>17</sub>H<sub>20</sub>N<sub>2</sub>O (268.3535): calcd. C 76.09, H 7.51, N 10.44; found C 76.05, H 7.62, N 10.37.

**HL<sup>4</sup>** To a stirred solution of 2,4,5-trifluoroaniline (448 mg, 3.05 mmol) in absolute ethanol (10 mL), 5-bromo-2-hydroxybenzaldehyde (604 mg, 3.00 mmol) was added. The resulting mixture was refluxed 6 h. After cooling to room temperature, the orange product precipitated was washed with cold ethanol and petroleum ether. Yield: 0.798 g (80.9%). <sup>1</sup>HMMR (CDCl<sub>3</sub> 400 MHZ)  $\delta$  12.69 (s, 1H, OH), 8.59 (s, 1H, HC=N), 7.54–7.44 (m, 2H, Ar–H), 7.17–7.04 (m, 2H, Ar–H), 6.95 (d, *J* = 8.7 Hz, 1H, Ar–H). IR: 3417, 3066, 1627, 1517, 1477, 1429, 1330, 1278, 1155, 869, 767, 719, 626. C<sub>13</sub>H<sub>7</sub>BrF<sub>3</sub>NO (330.1000): calcd. C 47.30, H 2.14, N 4.24; found C 47.36, H 2.07, N 4.29.

**HL<sup>5</sup>** To a stirred solution of 2,4,5-trifluoroaniline (397 mg, 2.70 mmol) in absolute ethanol (15 mL), 3-bromo-5-(*tert*-butyl)-2-hydroxybenzaldehyde (653 mg, 2.54 mmol) was added. The resulting mixture was refluxed 6 h. After cooling to room temperature, the orange product precipitated was washed with cold ethanol and petroleum ether. Yield: 0.735 g (74.9%). <sup>1</sup>HMMR(CDCl<sub>3</sub>

400 MHZ)  $\delta$  13.36 (s, 1H, OH), 8.64 (s, 1H, HC=N), 7.71 (d, 1H, J = 4.0Hz, Ar-H), 7.35 (d, 1H, J = 4.0Hz, Ar-H), 7.15–7.26 (m, 1H, Ar-H), 7.05–7.11 (m, 1H, Ar-H),1.33 (s, 9H, -CH<sub>3</sub>). IR: 3390, 3076, 2960, 1629, 1514, 1454, 1371, 1267, 1197, 1155, 881, 773. C<sub>17</sub>H<sub>15</sub>BrF<sub>3</sub>NO (386.2063): calcd. C 52.87, H 3.91, N 3.63; found C 52.99, H 3.96, N 3.68.

 $Pt(L^1)_2$  A solution of  $HL^1$  (250 mg, 0.91 mmol), 1 equivalent of potassium hydroxide (51 mg, 0.91 mmol) were stirred about half an hour in 5 mL DMF under nitrogen at 70 °C. Then, potassium tetrachloroplatinate (II) (188 mg, 0.45 mmol) in DMSO (3 mL) were added to the solution for 24 h under nitrogen at 70 °C. D. I. water was then added, the mixture was filtered extracted with CHCl<sub>3</sub> and dry in the vacuum. The crude product was purified by silica-gel column chromatography using a solvent mixture of hexane and CHCl<sub>3</sub> as eluent to give red solid of  $Pt(L^1)_2$  Yield: 129 mg (38.1%). <sup>1</sup>HNMR(400 MHz,CDCl<sub>3</sub>+pyridine-d5): δ 8.42 (s, 1H,N=CH), 7.95 s, (1H,N=CH), 7.79 (q, J = 4.0 Hz, 2H,Ar-H), 7.53 (q, J = 4.0 Hz, 1H,Ar-H), 7.36-7.50 (m, 6H,Ar-H), 7.05-7.12 (m, 5H, Ar-H), 6.97 (d, J = 8.0 Hz, 1H, Ar–H), 5.89 (d, J = 8.0 Hz, 1H, Ar–H). IR (cm<sup>-1</sup>, KBr): 3404, 1601, 1518, 1456, 1366, 1302, 1242, 1163, 1109, 961, 843, 756, 692. HRMS (MALDI-TOF, positive mode, DCTB): m/z = 745.9331 $[M]^+$  (C<sub>26</sub>H<sub>18</sub>Br<sub>2</sub>N<sub>2</sub>O<sub>2</sub>Pt: calcd.745.9357,  $\Delta_m = -3.47$  ppm). C<sub>26</sub>H<sub>18</sub>Br<sub>2</sub>N<sub>2</sub>O<sub>2</sub>Pt (745.3253): calcd. C 41.90, H 2.43, N 3.76; found C 41.95, H 2.42, N 3.66.

Pt(L<sup>2</sup>)<sub>2</sub> A solution of HL<sup>2</sup> (209 mg, 0.67 mmol), 1 equivalent of potassium hydroxide (28 mg, 0.70 mmol) were stirred about half an hour in 5 mL DMF under nitrogen at 70 °C. Then, potassium tetrachloroplatinate (II) (148 mg, 0.36 mmol) in DMSO (3 mL) were added to the solution for 24 h under nitrogen at 70 °C. D. I. water was then added, the mixture was filtered extracted with CHCl<sub>3</sub> and dry in the vacuum. The crude product was purified by silica-gel column chromatography using a solvent mixture of hexane and CHCl<sub>3</sub> as eluent to give red solid of  $Pt(L^2)_2$  Yield: 105 mg (38.6%). <sup>1</sup>HMMR(CDCl<sub>3</sub> 400 MHZ)  $\delta$ 8.20 (s, 2H, HC=N), 7.63 (d, J = 2.5 Hz, 4H, Ar-H), 7.56 (d, J = 2.4 Hz, 8H, Ar-H), 7.10 (d, J = 2.5 Hz, 1H, Ar-H), 7.01 (d, J = 2.5 Hz, 1H, Ar-H), 1.26 (d, J = 18.1 Hz, 36H, CH<sub>3</sub>). IR: 2956, 2904, 2868, 2079, 1614, 1577, 1523, 1458, 1431, 1359, 1255, 1172, 803, 701. HRMS (MALDI-TOF, positive mode, DCTB): m/  $z = 811.3695 \text{ [M]}^+ (C_{42}H_{52}N_2O_2Pt: calcd. 811.3675, \Delta_m = 2.49 \text{ ppm}).$ C42H52N2O2Pt (811.9585): calcd. C 62.13, H 6.46, N 3.45; found C 62.20, H 6.41, N 3.40.

Pt(L<sup>3</sup>)<sub>2</sub> A solution of HL<sup>3</sup> (200 mg, 0.74 mmol), 1 equivalent of potassium hydroxide (30 mg, 0.75 mmol) were stirred about half an hour in 5 mL DMF under nitrogen at 70 °C. Then, potassium tetrachloroplatinate (II) (170 mg, 0.41 mmol) in DMSO (3 mL) were added to the solution for 24 h under nitrogen at 70 °C. D. I. water was then added, the mixture was filtered extracted with CHCl<sub>3</sub> and dry in the vacuum. The crude product was purified by silica-gel column chromatography using a solvent mixture of hexane and CHCl<sub>3</sub> as eluent to give orange solid of  $Pt(L^3)_2$  Yield: 107 mg (39.6%). <sup>1</sup>HNMR(400 MHz, CDCl<sub>3</sub>):δ 7.72 (s, 2H,N=CH), 7.41-7.38 (m, 6H,Ar-H), 7.28 (s, 4H, Ar-H), 7.02 (d, J = 9.0 Hz, 2H, Ar-H), 6.03 (d, J = 2.5 Hz, 1H, Ar–H), 6.00 (d, J = 2.5 Hz, 1H, Ar–H), 5.29 (d, J = 2.4 Hz, 2H, Ar–H), 3.24 (q, J = 7.1 Hz, 8H,CH<sub>2</sub>), 1.13 (t, J = 7.1 Hz, 12H,CH<sub>3</sub>). IR (cm<sup>-1</sup>, KBr):2962, 2920, 1608, 1571, 1496, 1352, 1317, 1186, 1139, 825, 759, 687. HRMS (MALDI-TOF, positive mode, DCTB): m/z 729.2654 [M]<sup>+</sup> (C<sub>34</sub>H<sub>38</sub>N<sub>4</sub>O<sub>2</sub>Pt: calcd.729.2640, =  $\Delta_{\rm m} = -3.47$  ppm). C<sub>34</sub>H<sub>38</sub>N<sub>4</sub>O<sub>2</sub>Pt (729.7751): calcd. C 55.96, H 5.25, N 7.68; found C 55.87, H 5.23, N 7.73.

**Pt(L<sup>4</sup>)**<sub>2</sub> A solution of **HL<sup>4</sup>** (253 mg, 0.76 mmol), 1 equivalent of potassium hydroxide (43 mg, 0.76 mmol) were stirred about half an hour in 5 mL DMF under nitrogen at 70 °C. Then, potassium tetrachloroplatinate (II) (158 mg, 0.38 mmol) in DMSO (3 mL) were added to the solution for 24 h under nitrogen at 70 °C. D. I. water was then added, the mixture was filtered extracted with CHCl<sub>3</sub> and

dry in the vacuum. The crude product was purified by silica-gel column chromatography using a solvent mixture of hexane and CHCl<sub>3</sub> as eluent to wine red solid of **Pt(L<sup>4</sup>)**<sub>2</sub> Yield: 149 mg (46.0%). <sup>1</sup>HMMR(CDCl<sub>3</sub> 400 MHZ)  $\delta$  8.50 (s, 2H, *HC*=N), 7.97 (s, 2H, Ph-*H*), 7.84 (d, *J* = 2.3 Hz, 2H, Ph-*H*), 7.55 (ddd, *J* = 11.4, 9.1, 2.4 Hz, 2H, Ph-*H*), 7.47 (d, *J* = 2.5 Hz, 2H, Ph-*H*), 7.43–7.34 (m, 2H, Ph-*H*). IR: 3396, 3269, 2360, 1620, 1598, 1516, 1456, 1381, 1305, 1157, 1024, 815, 723, 652. C<sub>26</sub>H<sub>12</sub>Br<sub>2</sub>F<sub>6</sub>N<sub>2</sub>O<sub>2</sub>Pt (853.2681): calcd. C 36.60, H 1.42, N 3.28; found C 36.56, H 1.49, N 3.33.

**Pt(L<sup>5</sup>)<sub>2</sub>** and **PtL<sup>5</sup>** · **DMSO** A solution of **HL<sup>5</sup>** (252 mg, 0.65 mmol), 1 equivalent of potassium hydroxide (37 mg, 0.65 mmol) were stirred about half an hour in 5 mL DMF under nitrogen at 70 °C. Then, potassium tetrachloroplatinate (II) (149 mg, 0.36 mmol) in DMSO (3 mL) were added to the solution for 24 h under nitrogen at 70 °C. D. I. water was then added, the mixture was filtered extracted with CHCl<sub>3</sub> and dry in the vacuum. The crude product was purified by silica-gel column chromatography using a solvent mixture of hexane and CHCl<sub>3</sub> as eluent to give red solid of **Pt(L<sup>5</sup>)<sub>2</sub>** Yield: 40.7 mg (12.9%) and yellow solid of **PtL<sup>5</sup> · DMSO** Yield: 63 mg (19.0%).

**Pt(L<sup>5</sup>)**<sub>2</sub>: <sup>1</sup>HNMR (400 MHz, CDCl<sub>3</sub>) δ7.98 (s, 2H, *HC*=N), 7.74 (d, J = 2.5 Hz, 2H, Ar–*H*), 7.40–7.31 (m, 2H, Ar–*H*), 7.18 (d, J = 2.5Hz, 2H, Ar–*H*), 7.14–7.09 (m, 2H, Ar–*H*), 1.24 (s, 18H,CH<sub>3</sub>). IR: 3435, 2956, 2868, 1598, 1517, 1442, 1311, 1257, 1205, 1155, 904, 871, 751. HRMS (MALDI-TOF, positive mode, DCTB): m/z = 965.9961 [M]<sup>+</sup> (C<sub>34</sub>H<sub>28</sub>Br<sub>2</sub>F<sub>6</sub>N<sub>2</sub>O<sub>2</sub>Pt: calcd.966.0047,  $\Delta_m$  = -8.86 ppm). C<sub>34</sub>H<sub>28</sub>Br<sub>2</sub>F<sub>6</sub>N<sub>2</sub>O<sub>2</sub>Pt (965.4807): calcd. C 42.30, H 2.92, N 2.90; found C 42.25, H 2.89, N 2.94.

**PtL<sup>5</sup>**·**DMSO**: <sup>1</sup>HNMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.10 (s, 1H, *HC*=N), 7.94 (d, *J* = 2.4 Hz, 1H, Ar–*H*), 7.29 (s, 1H, Ar–*H*), 7.17–7.00 (m, 2H, Ph-*H*), 3.49 (s, 6H, S–CH<sub>3</sub>), 1.30 (s, 9H, CH<sub>3</sub>). IR: 3446, 2358, 1606, 1589, 1519, 1444, 1300, 1255, 1155, 1110, 1026, 869, 742. C<sub>19</sub>H<sub>20</sub>BrClF<sub>3</sub>NO<sub>2</sub>PtS (693.8688): calcd. C 32.89, H 2.91, N 2.02; found C 32.78, H 2.94, N 2.06.

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#### Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.orgel.2016.12.024.

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