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Highly luminescent platinum(II) complexes based on pyrazolo[1,5-*f*]phenanthridine-containing ligands

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Abstract

A series of highly luminescent [Pt(N^C^C^N)] emitters (ZPt1, ZPt2 and ZPt3) based on pyrazolo[1,5-f]phenanthridine-containing ligands were designed and synthesized. These Pt(II) complexes demonstrated extremely high thermal stabilities with the 5% weight-reduction temperatures over 450°C due to the incorporation of the rigid pyrazolo[1,5-f]phenanthridine motif and the robustness of the tetradentate coordination framework. These Pt(II) complexes have the same coordination set (pyridine^benzene^benzene^pyrazole) but with slightly different linkage between coordination groups. Within ZPt1 and ZPt2, pyridine and the neighboring benzene groups are separated by oxygen and aniline, respectively. In ZPt3, pyridine group is rigidly grafted on the carbazole unit. The effect of the different linkages on the frontier orbital energies, the photophysical and electroluminescent properties of ZPt1-ZPt3 was investigated systematically. Organic light emitting diodes (OLEDs) based on these Pt(II) complexes were fabricated with typical device structure. The Pt(II) complexes displayed intense electroluminescence in the blue to yellowish green spectral region. Among the three Pt(II) complexes, the 3-(pyridin-2-yloxy)phenoxy-based ZPt1 showed highest compound the

electroluminescence performance with the maximum CE, PE, and EQE of 58.0 cd A^{-1} , 51.6 lm W^{-1} , and 16.4%, respectively.

Introduction

Since the report on organic light-emitting diodes (OLEDs) in 1987 [1], there is a continuous interest in developing highly emissive materials. During last decade, a large number of transition metal complexes such as Ir(III), Pt(II), Au(III), Os(II) and Cu(I) have been prepared as dopants in high efficiency OLEDs [2-15]. Among these complexes, Ir(III) complexes have been found to be the most studied case due to their high electroluminescence (EL) performance and high operational stability [16-19]. Recently, cyclometalated platinum(II) complexes have attracted much attention because they exhibited remarkable electroluminescent properties comparable to Ir(III) complexes [20-25]. For example, Fukagawa and coworkers reported red Pt(II) emitter with the maximum PE and EOE of 30 Im W^{-1} and 19%, respectively. Moreover, the half-life of this red OLED is estimated to be about 10000 hr at initial luminance of 1000 cd m⁻² [26]. Che *et al.* reported that high PE of 126 lm W⁻¹ was achieved with green-emitting devices based on [Pt(O^N^C^N)] complex [27]. So far several empirical strategies have been developed for the design of Pt(II) emitters [28]. One practical strategy is to increase the energy level of the non-radiative $5d_x^2 - v^2$ orbital by introducing strong-field ligands [29]. In addition, high thermal stabilities of emissive materials are highly desirable to allow vacuum deposition for OLED fabrication. Che et al. reported a series of [(C^N^N)PtX] complexes with decomposition temperature over 400 °C by using the extended π -conjugated cyclometalated ligands [30].

Typically, Pt(II) ion adopts a four-coordinated square planar geometry, and it can be surrounded by bidentate, tridentate and tetradentate ligands. Although the bidentate ligands are easily achievable as compared with tetradentate ligands, tetradentate coordination pattern is getting more and more popular since it not only decreases the non-radiative vibrational pathways by suppressing the vibration and rotation around metal ion, but also minimizes the excited state distortion and ensures good color purity [31-37]. In this contribution, we reported the design and synthesis of three tetradentated Pt(II) complexes (ZPt1-ZPt3) based on pyrazolo[1,5-f]phenanthridine-containing ligands. Currently Pt(II) complexes based on 1-phenylpyrazole [38-41] and 1,5-diarylpyrazole [42] have been well studied relative pyrazolo[1,5-*f*]phenanthridine-based complexes [43]. to

Pyrazolo[1,5-*f*]phenanthridine and 1-phenylpyrazole are both excellent cyclometalated ligands for the planar platinum(II) complexes. Furthermore, the introduce of this fused-ring system (pyrazolo[1,5-*f*]phenanthridine) could reduce the structural vibration and enhance the thermal stabilities of the resulting complexes. The four coordination groups of each Pt(II) complex are kept the same to investigate the effect of linkages between coordination groups on the electroluminescent properties of ZPt1-ZPt3. OLEDs based on these three complexes were fabricated, and ZPt1 compound showed the high electroluminescence performance with the maximum CE, PE, and EQE of 58.0 cd A^{-1} , 51.6 lm W^{-1} , and 16.4%, respectively, with CIE coordinates of (0.33, 0.57).

Experiment section

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. ¹H NMR spectra were recorded on a Bruker 400 MHz NMR instrument and ¹³C 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⁻¹ under nitrogen. Matrix-Assisted Laser Desorption/ Ionization Time of Flight Mass Spectrometry (MALDI-TOF-MS) was measured with a BRUKER ultrafleXtreme MALDI-TOF/TOF. HOMO were 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.

Device Fabrication and Measurements

The OLEDs were fabricated through vacuum deposition at ca. 2×10^6 Torr onto commercially ITO-coated glass substrates having a sheet resistance of ca. 30 Ω per square. The ITO substrates were cleaned sequentially with acetone, ethanol, and

deionized water in an ultrasonic bath, then dried in an oven, and finally exposed to UV-ozone for 15 min. During the fabrication of the Pt(II) complexes OLEDs, the Organic layers were deposited at a rate of 2-3 Å s⁻¹. HAT-CN and Liq were deposited at 0.2-0.5 Å s⁻¹, and the Al electrode was deposited (at ca. 5 Å s⁻¹) through a shadow mask without breaking the vacuum. For all the devices, the emitting areas were depended on the overlap of two electrodes as 0.09 cm². The electroluminescence (EL) performance of the devices was measured using a PHOTO RESEARCH Spectra Scan PR 655 PHOTOMETER and a KEITHLEY 2400 Source Meter constant current source at room temperature.

1-(2-bromo-5-methoxyphenyl)-5-(2-bromophenyl)-1H-pyrazole

(2-bromo-5-methoxyphenyl)hydrazine (6.5 mmol) was added to a solution of (*E*)-1-(2-bromophenyl)-3-(dimethylamino)prop-2-en-1-one (5.9 mmol) and Na₂CO₃ (4.0 mmol) in MeOH (40 mL) and H₂O (8 mL) under stirring at room temperature. The resulting mixture was acidified with glacial acetic acid to PH = 4 and heated to 135 °C for 2 hours. After cooling to room temperature, the suspension was diluted with EtOAc (30 mL), the organic layer was washed with H₂O (3×10 mL) and the organic solvent was evaporated under reduce pressure. The residue was purified by flash chromatography on silica gel with petroleum ether/EtOAc (12/1, v/v) as eluent. The target product was obtained as a yellow solid (50%). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.80 (s, 1H), 7.59 (d, *J* = 7.6 Hz, 1H), 7.42 (d, *J* = 8.9 Hz, 1H), 7.24 – 7.12 (m, 3H), 6.94 (d, *J* = 2.6 Hz, 1H), 6.77 (dd, *J* = 8.9, 2.7 Hz, 1H), 6.58 (s, 1H), 3.71 (s, 3H). GC-MS: m/z calcd 408.09, found 407.53.

10-methoxypyrazolo[1,5-f]phenanthridine

Dry 1,4-dioxane (15 mL) was added mixture of to а 1-(2-bromo-5-methoxyphenyl)-5-(2-bromophenyl)-1H-pyrazole (4 g, 9.80 mmol), Pd(PPh₃)₄ (600 mg, 0.52 mmol) and Sn₂(n-Bu)₆ (14.2 g, 24.48 mmol) in a 30 mL microwave tube under glovebox. Then the resulting solution was heated at 140 °C overnight. After the reaction solution cooling to room temperature, the solvent was evaporated under reduce pressure. The crude product was purified by column chromatography using petroleum ether/EtOAc (8/1, v/v) to afford the final product as a white powder (1.6 g, 70%). ¹H NMR (400 MHz, DMSO-*d*6) δ (ppm): 7.81 (s, 1H), 7.68 (d, J = 7.6 Hz, 1H), 7.55 (d, J = 8.9 Hz, 1H), 7.37 – 7.24 (m, 3H), 7.04 (d, J =

2.4 Hz, 1H), 6.98 – 6.90 (m, 1H), 6.64 (s, 1H), 3.71 (s, 3H). GC-MS: m/z calcd 248.29, found 248.10.

pyrazolo[1,5-f]phenanthridin-10-ol

10-methoxypyrazolo[1,5-*f*]phenanthridine (1.5 g, 6.41 mmol) and 47% aqueous hydrobromic acid (25 mL) were mixed in a flask equipped with a magnetic stirrer and heated at 123 °C for 3 days under N₂. After the reaction solution cooling to room temperature, the precipitate was collected by filtration and washed with absolute ethyl alcohol, and dichloromethane, and dried under vacuum to give the corresponding alcohol as a white powder (1.05 g, 74%). ¹H NMR (400 MHz, DMSO-*d*6) δ (ppm): 10.36 (s, 1H), 8.48 (d, *J* = 8.6 Hz, 2H), 8.25 (d, *J* = 7.7 Hz, 1H), 8.06 (s, 1H), 7.87 (d, *J* = 2.2 Hz, 1H), 7.61 (dt, *J* = 26.8, 7.3 Hz, 2H), 7.29 (s, 1H), 7.02 (dd, *J* = 8.8, 2.2 Hz, 1H). GC-MS: m/z calcd 234.26, found 234.18.

10-(3-(pyridin-2-yloxy)phenoxy)pyrazolo[1,5-f]phenanthridine (Z1)

Dry DMF (15 mL) was added to a mixture of pyrazolo[1,5-f]phenanthridin-10-ol (900 mg, 3.85 mmol), 2-(3-bromophenoxy)pyridine (1.44 g, 5.78 mmol), K₃PO₄ (1.63 g, 7.68 mmol), CuI (110 mg, 0.58 mmol) and picolinic acid (142 mg, 0.077 mmol) in a 30 mL microwave tube under glovebox. Then the resulting solution was heated at 100 °C for 40 hours. After the reaction solution cooling to room temperature, the reaction mixture was poured into aqueous EDTA disodium solution (200 mL). The aqueous phase was extracted with dichloromethane (3×100 mL), and the combined organic layer was dried over MgSO₄. The crude product was purified by column chromatography using petroleum ether/EtOAc (4/1, v/v) to afford the final product as a white powder (1.0 g, 65%). ¹H NMR (400 MHz, DMSO-*d*6) δ (ppm): 8.71 (d, J = 8.9 Hz, 1H), 8.59 (d, J = 7.9 Hz, 1H), 8.30 (d, J = 7.9 Hz, 1H), 8.19 (d, J = 4.5 Hz, 1H), 8.07 (s, 1H), 7.98 (d, J = 2.4 Hz, 1H), 7.86 (t, J = 6.9 Hz, 1H), 7.73 – 7.63 (m, 2H), 7.52 (t, J = 8.3 Hz, 1H), 7.35 – 7.28 (m, 2H), 7.17 – 7.11 (m, 1H), 7.05 (dd, J =16.1, 7.4 Hz, 4H). ¹³C NMR (151 MHz, CDCl₃) δ (ppm): 163.26, 158.05, 157.54, 155.51, 147.78, 141.21, 139.52, 137.68, 135.16, 130.55, 128.33, 127.62, 126.68, 125.20, 124.41, 123.30, 122.41, 118.78, 116.86, 116.47 (d, J = 6.0 Hz), 115.36, 112.47, 111.75, 105.58, 99.31. GC-MS: m/z calcd 403.44, found 403.15.

Preparation of ZPt1

Z1 (900 mg, 2.23 mmol), K₂PtCl₄ (973 mg, 2.34 mmol), CHCl₃ (2 mL) and HOAc (18 mL) were added to a 100 mL flask under N₂. Then the mixture was heated at 140 °C for 5 days. After the reaction solution cooling to room temperature, the reaction mixture was poured into aqueous sodium carbonate solution (200 mL). The aqueous phase was extracted with dichloromethane (3×100 mL), and the combined organic layer was dried over MgSO₄. The crude product was purified by column chromatography using petroleum ether/EtOAc (5/1, v/v) to afford the final product as a greenish yellow powder (585 mg, 40%). ¹H NMR (400 MHz, DMSO-*d*6) δ (ppm): 9.08 (d, *J* = 5.4 Hz, 1H), 8.72 (d, *J* = 8.1 Hz, 1H), 8.55 (d, *J* = 7.1 Hz, 2H), 8.40 (d, *J* = 8.7 Hz, 1H), 8.26 (t, *J* = 7.4 Hz, 1H), 7.84 (t, *J* = 7.5 Hz, 1H), 7.75 (t, *J* = 7.4 Hz, 1H), 7.70 (d, *J* = 2.0 Hz, 1H), 7.57 (d, *J* = 8.2 Hz, 1H), 7.47 (t, *J* = 6.3 Hz, 1H), 7.37 (d, *J* = 8.7 Hz, 1H), 7.22 (t, *J* = 7.8 Hz, 1H), 7.15 (d, *J* = 7.6 Hz, 1H), 6.99 (d, *J* = 7.3 Hz, 1H). MALDI-TOF (m/z): calculated for: 596.081, found: 596.104. Anal. Calcd. For C₂₆H₁₅N₃O₂Pt: C, 52.35; H, 2.53; N, 7.04; found: C, 52.46; H, 2.66; N, 7.16.

Preparation of N-(4-(tert-butyl)phenyl)-N-(3-(pyrazolo[1,5-f]phenanthridin-10yloxy)phenyl)pyridin-2-amine (Z2), ZPt2, 10-((9-(pyridin-2-yl)-9H-carbazol-2yl)oxy)pyrazolo[1,5-f]phenanthridine (Z3) and ZPt3

Z2, Z3, ZPt2, and ZPt3 were prepared by the procedures similar to those used for Z1 and ZPt1, respectively. The final product Z2 was obtained as a white powder (800 mg, 52%). ¹H NMR (400 MHz, DMSO-*d*6) δ (ppm): 8.67 (d, *J* = 9.0 Hz, 1H), 8.57 (d, *J* = 8.0 Hz, 1H), 8.30 (d, *J* = 7.4 Hz, 1H), 8.14 (d, *J* = 4.0 Hz, 1H), 8.10 (s, 1H), 7.94 (d, *J* = 2.3 Hz, 1H), 7.72 – 7.62 (m, 2H), 7.55 (t, *J* = 7.8 Hz, 1H), 7.42 (t, *J* = 8.1 Hz, 1H), 7.34 (d, *J* = 8.5 Hz, 3H), 7.29 – 7.24 (m, 1H), 7.10 (d, *J* = 8.4 Hz, 2H), 6.97 (t, *J* = 7.6 Hz, 2H), 6.89 – 6.83 (m, 2H), 6.72 (d, *J* = 8.4 Hz, 1H), 1.20 (s, 9H). ¹³C NMR (151 MHz, CDCl₃) δ (ppm): 158.75, 158.47, 156.91, 148.17, 147.80 (d, *J* = 3.4 Hz), 142.88, 141.15, 137.67, 137.42, 135.09, 130.31, 128.29, 127.50, 126.72, 126.45, 126.10, 125.08, 124.38, 123.22, 122.35, 121.03, 116.86, 116.49, 116.37, 116.17, 114.83, 114.33, 104.94, 99.28, 34.39, 31.34. GC-MS: m/z calcd 534.66, found 534.26.

ZPt2 was obtained as a greenish yellow powder (600 mg, 61%). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 9.09 (d, J = 5.2 Hz, 1H), 8.54 (d, J = 8.2 Hz, 1H), 8.26 (d, J = 7.9 Hz, 1H), 8.20 (d, J = 8.8 Hz, 1H), 8.08 (s, 1H), 7.75 (t, J = 7.5 Hz, 1H), 7.67 – 7.53 (m, 4H), 7.46 (d, J = 8.6 Hz, 1H), 7.37 (d, J = 8.3 Hz, 2H), 7.20 – 7.12 (m, 2H), 7.00 (t, J = 8.0 Hz, 1H), 6.85 (t, J = 8.0 Hz, 2H), 6.56 (d, J = 7.6 Hz, 1H), 1.39 (s, 9H).

MALDI-TOF (m/z): calculated for: 727.191, found: 727.240. Anal. Calcd. For C₃₆H₂₈N₄OPt: C, 59.42; H, 3.88; N, 7.70; found: C, 59.39; H, 3.98; N, 7.74.

Z3 was obtained as a white powder (700 mg, 62%). ¹H NMR (400 MHz, DMSO-*d*6) δ (ppm): 8.69 (d, *J* = 9.0 Hz, 2H), 8.58 (d, *J* = 8.0 Hz, 1H), 8.37 (d, *J* = 8.4 Hz, 1H), 8.29 (d, *J* = 4.4 Hz, 2H), 8.08 (t, *J* = 7.2 Hz, 1H), 7.97 (s, 1H), 7.89 (d, *J* = 2.4 Hz, 1H), 7.82 (d, *J* = 8.7 Hz, 2H), 7.72 – 7.62 (m, 3H), 7.52 – 7.42 (m, 2H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.31 (dd, *J* = 8.8, 2.1 Hz, 2H), 7.23 (d, *J* = 8.5 Hz, 1H). ¹³C NMR (151 MHz, CDCl₃) δ (ppm): 159.58, 154.85, 151.52, 149.64, 141.15, 140.61, 140.03, 138.55, 137.69, 135.16, 128.30, 127.43, 126.81, 125.82, 125.11, 124.40, 124.05, 123.18, 122.35, 121.26 (dd, *J* = 23.6, 7.5 Hz), 119.90, 118.94, 116.20, 115.67, 113.83, 111.10, 104.38, 103.40, 99.23. GC-MS: m/z calcd 476.54, found 476.15.

ZPt3 was obtained as a yellow powder (500 mg, 55%). ¹H NMR (400 MHz, DMSO-*d*6) δ (ppm): 9.53 (d, *J* = 5.2 Hz, 1H), 8.72 (dd, *J* = 14.2, 5.1 Hz, 2H), 8.57 (d, *J* = 7.8 Hz, 1H), 8.43 (d, *J* = 8.8 Hz, 1H), 8.33 (d, *J* = 8.4 Hz, 1H), 8.28 – 8.17 (m, 2H), 8.12 (d, *J* = 8.1 Hz, 1H), 7.99 (d, *J* = 8.3 Hz, 1H), 7.84 (t, *J* = 7.6 Hz, 1H), 7.76 (dd, *J* = 8.6, 5.0 Hz, 2H), 7.52 – 7.37 (m, 5H). MALDI-TOF (m/z): calculated for: 669.113, found: 669.142. Anal. Calcd. For C₃₂H₁₈N₄OPt: C, 57.40; H, 2.71; N, 8.37; found: C, 57.57; H, 2.86; N, 8.39.

Results and discussion

The synthetic routes for ZPt1, ZPt2 and ZPt3 were illustrated in Scheme 1. 1,5-Diarylpyrazole was prepared by the tandem amine-exchange/heterocyclization of (E)-1-(2-bromophenyl)-3-(dimethylamino)prop-2-en-1-one [45]. Catalytic stannylation [46] of the dibromide followed by intramolecular Stille coupling reaction finished the synthesis of pyrazolo[1,5-*f*]phenanthridine. Cleavage of 10-methoxypyrazolo[1,5-f]phenanthridine by HBr afforded the free phenol derivative, which was further connected with N^C bidentates via CuI/picolinic acid catalyzed coupling reaction to give the corresponding tetradentate ligands Z1, Z2 and Z3. The Pt(II) complexes were prepared by the reaction of the respective ligands and K₂PtCl₄ in the mixture of chloroform and acetic acid. ZPt1, ZPt2 and ZPt3 contain fused 6-6-5 membered metallacycle rings. Che and coworkers reported several different types of Pt(II) complexes with 5-5-5 [47], 6-5-6 [48] and 6-5-5 [49] membered metallacycle rings. Recently, Li et al. reported a new strategy for the development of deep blue phosphorescent emitter by replacing the typical 5-membered metal chelation rings

with 6-membered chelation [50].

ZPt1, ZPt2 and ZPt3 demonstrated extremely high thermal stability with the 5% weight-reduction temperatures ($\Delta T_{5\%}$) of 450 °C, 446 °C and 492 °C, respectively (Figure 1). The highest occupied molecular orbital (HOMO) values of Pt(II) complexes were determined by Ultra-Violet Photoemission Spectroscopy (UPS) measurement (Figure S10). The HOMOs for these complexes are -5.21 eV, -5.39 eV and -5.43 eV, respectively. The lowest unoccupied molecular orbital (LUMO) values were estimated from the difference between the HOMO and the corresponding optical band gap. ZPt1, ZPt2 and ZPt3 were fully characterized by ¹H NMR, elemental analysis and MALDI-TOF. Due to the poor solubility, their ¹³C NMR spectra were not acquired. The ¹H and ¹³C NMR spectra of ligands were given in the supporting information (Figure S1-S9).

Photophysical properties

The UV-vis absorption and photoluminescence (PL) spectra at room temperature in CH_2Cl_2 solution with a concentration of 10^{-5} M were depicted in Figure 2, and the photophysical parameters are summarized in Table 1. The three Pt(II) complexes ZPt1, ZPt2 and ZPt3 showed similar absorption properties with the absorption cutoff wavelength around 400 nm. The intense absorption with wavelength below 300 nm could be assigned to the intraligand π - π^* transition and the weak absorption beyond 350 nm could be assigned to metal-to-ligand charge transfer (MLCT). Upon photo-excitation at 370 nm in degassed dichloromethane (10^{-5} M) at room temperature, ZPt1, ZPt2 and ZPt3 showed highly-structured emission spectra with vibronic splitting of 1342 cm⁻¹, 1307 cm⁻¹ and 1425 cm⁻¹, respectively, indicating that PL could mainly arise from the ligand-centered (LC) excited states [51]. The Natural Transition Orbital (NTO) analyses also supported the ligand-centered emission since the NTO are mainly localized on the tetradentate ligands (Figure S11). The PL quantum yields of the complexes are in the range of 0.24-0.70. The luminescent properties of the neat films for ZPt1-ZPt3 have been studied, and the related PL spectra were showed in Figure S12. The PL quantum yields of neat film for ZPt1, ZPt2, and ZPt3 were 10.34%, 4.27% and 2.38%, respectively, much lower than those measured in the solution, which could be due to strong intermolecular interaction in the neat film. The luminescent properties of ZPt1, ZPt2, and ZPt3 in poly(methyl

methacrylate) film (PMMA 15 wt%) have been studied (Figure S13), and the emission peaks of ZPt1-ZPt3 doped in the PMMA film are obviously blue-shifted in comparison with their emission peaks of the neat films, which is attributed to the reduced intermolecular interaction in PMMA. Among these Pt(II) complexes, ZPt2 demonstrated the narrowest emission spectrum, which could be attributed to the high energy level of LC states of the phenyl-pyridin-2-yl-amine unit. Li *et al.* reported the significant spectral narrowing in the room temperature emission spectrum for one tetradentated Pt(II) complex by introducing an electron-donating group (*tert*-butyl) to the coordination backbone [41].

DFT Calculations

Density functional theory (DFT) calculations were carried out for these complexes with Gaussian 09 to investigate the photophysical properties of these emitters. 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 HOMOs and LUMO distributions are shown in Figure 3.

For these three complexes, the HOMO distributions are mainly localized on phenyl-oxygen-phenyl motifs. For ZPt3, the HOMO distributions also extend to the whole carbazole unit. The phenylamine based complex (ZPt2) exhibited higher HOMO energy levels than the carbazole substituted complex (ZPt3), which is consistent with the better electron-donating ability of phenylamine [52]. The LUMO distributions for ZPt1, ZPt2 and ZPt3 are largely confined to pyridine unit. Due to the strong electron-donating effect of phenylamine, the electron-withdrawing ability of pyridine in ZPt2 decrease and ZPt2 showed the highest LUMO among the three Pt(II) complexes. For ZPt1- ZPt3, the HOMOs are in the range from -4.81 eV to -5.00 eV and the LUMOs are in the range from -1.12 eV to -1.40 eV. ZPt2 exhibited the largest bandgap (3.68 eV) than other two complexes (3.62 for ZPt1 and 3.49 for ZPt3). The optimized structures of ZPt1, ZPt2 and ZPt3 indicated that the molecular frameworks slightly deviated from square planar geometries (Figure S14). The dihedral angles between pyridine and pyrazolo[1,5-f]phenanthridine in ZPt1-ZPt3 are 24.1°, 37.8° and 32.7°, respectively. The pending 4-(tert-butyl)phenyl group in ZPt2 was pointing away from the coordination plane around Pt(II) ion, and the dihedral angle between this benzene ring and pyrazolo[1,5-f]phenanthridine was 77.8°.

Electroluminescent Properties

The OLEDs based on the three Pt(II) complexes were fabricated with the following device configuration: ITO/HAT-CN (10 nm)/TAPC (45 nm)/TCTA (10 nm)/ CBP (or 26mCPy):Pt(II) complexes (x wt%, 20 nm)/TmPyPB (50 nm)/Liq (2 nm)/Al (110 nm). HAT-CN (1, 4, 5, 8, 9, 11-hexaazatriphenylene-hexacarbonitrile) was used as hole injection layer, and Liq (8-hydroxyquinolinolato lithium) as electron injection layer. TAPC (1,1-bis[4-[N,N-di(p-tolyl)-amino]phenyl]cyclohexane) was used as hole transport layer, and TmPyPB (1,3,5-tri[(3-pyridyl)-phen-3-yl]benzene) as electron transport layer. CBP (4,4'-bis(9-carbazolyl)biphenyl) was used as host material for ZPt1 and ZPt3, and 26mCPy (2,6-bis(N-carbazolyl)pyridine) was used as host material for ZPt2.

The current density-voltage-luminance (J-V-L) characteristics and electroluminescent (EL) spectra of ZPt1 at various doping ratios are depicted in Figure 4. The shape and the position of EL spectra are kept essentially constant at different doping levels, indicating the negligible intermolecular interaction between dopants. Although there is no bulky group attached to the coordination sphere of ZPt1, the considerable distortion from planarity induced by the oxygen linking atoms as indicated by DFT calculation could be responsible for the suppression of strong intermolecular interaction even at high doping levels. Highly electroluminescent OLEDs based on ZPt1 have been achieved with a maximum efficiency of 58.0 cd A⁻¹, 51.6 lm W⁻¹ and 16.4% at doping level of 30% with CIE coordinates of (0.33, 0.57), and the turn-on voltages for these devices were found to be below 3.8 V (Table 2). OLEDs based on ZPt2 exhibited blue electro-phosphorescence (Figure S15), and the peak PE, CE and EQE were 16.5 cd A^{-1} , 9.2 lm W^{-1} and 7.7%, respectively, with CIE coordinates of (0.18,0.30). **OLEDs** based ZPt3 exhibited yellowish on green electro-phosphorescence as observed for ZPt1. As shown in Figure 5c, the emission band of the host CBP was observed at 400 nm [53] at the doping ratio of 5%, indicating the insufficient energy transfer from host to dopant, which accounted in part for the low efficiency. As the doping ratio goes up to 20%, a maximum efficiency of 52.5 cd A^{-1} , 47.1 lm W^{-1} and 15.7% with CIE coordinates of (0.35, 0.55) was achieved, and the CBP emission band disappeared in the EL spectrum.

Conclusion

Three Pt(II) complexes (ZPt1, ZPt2 and ZPt3) based on pyrazolo[1,5-*f*]phenanthridine have been successfully prepared. Pyrazolo[1,5-*f*]phenanthridine showed strong coordination capability with Pt(II) ion, and the resulting complexes demonstrated extremely high thermal stabilities. These complexes have the same coordination groups, which are linked in the same sequence. The different linkages didn't affect the absorption properties of these complexes significantly, but changed their PL and EL properties remarkably. OLED based on the Pt(II) complexes displayed intense electro-phosphorescence in the blue to yellowish green spectral region. The red shift observed in the EL spectra of ZPt1 and ZPt3 relative to their PL spectra in solution could be due to the strong intermolecular interaction at the solid state. For ZPt2, the similarity observed in its EL spectra and PL spectra in solution indicated that the pending 4-(tert-butyl)phenyl group could weaken the intermolecular interaction. ZPt1 showed high OLED performance ($\Pi_{c.max} = 58.0$ cd A⁻¹, $\Pi_{p.max} = 51.6$ lm W⁻¹, and $\Pi_{EQE.max} = 16.4\%$), indicating its potential utility as an OLED phosphor.

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REAL



Scheme 1. The synthetic routes of ZPt1, ZPt2 and ZPt3.



Figure 1. TGA curves of ZPt1, ZPt2 and ZPt3.



Figure 2. UV-vis absorption and PL spectra at room temperature in CH₂Cl₂ solution.

Compound	$\lambda_{abs}[nm]^a$	$\lambda_{em} \left[nm ight]^a$	$\Phi_p{}^b$	LUMO [eV] ^c	HOMO [eV] ^d	$E_{\rm g} \left[{ m eV} ight]^{ m e}$	
7Pt1	266, 282,	443, 471sh	0.70	-2.05	-5.43	3.16	
ZPt2	273, 309	449, 477sh	0.24	-2.37	-5.39	3.02	
ZPt3	270, 330	444, 474sh	0.34	-2.40	-5.21	3.03	

Table 1. Photophysical and electrochemical data of platinum(11) comple

^a Measured in CH₂Cl₂ at room temperature with a concentration of 10⁻⁵ M, sh = shoulder. ^b Measured in degassed CH₂Cl₂ relative to *fac*-[Ir(ppy)₃] (Φ_p = 0.4). ^c LUMO = HOMO + *E*_g. ^d HOMO were calculated from UPS. ^e The optical band gap estimated from the absorption spectra.



Figure 3. Density functional theory calculation of orbit density for the HOMOs and LUMOs of ZPt1, ZPt2 and ZPt3.



Figure 4. (a) Current density-voltage-luminance (*J*-V-*L*) characteristics, (b) current efficiency (CE)-, power efficiency (PE)- and external quantum efficiency (EQE)-luminance, and (c) electroluminescent (EL) spectra curves of ZPt1 at different doping ratios at 5 mA cm⁻².



Figure 5. (a) Current density-voltage-luminance (*J*-V-*L*) characteristics, (b) current efficiency (CE)-, power efficiency (PE)- and external quantum efficiency (EQE)-luminance, and (c) electroluminescent (EL) spectra curves of ZPt3 at different doping ratios at 5 mA cm⁻².

Dopont	Dopant ratio	$\eta_{c.max.}/\eta_{c.500}/\eta_{c.1000}$		$\eta_{p.max.}/\eta_{p.500}/\eta_{p.1000}$		η _{EQE.max.} / η ₅₀₀ /η ₁₀₀₀		λ _{em}	λ_{sh}	$CIE(\mathbf{x},\mathbf{y})^{(d)}$	V _{turn-on}			
Dopant	[wt %]	$[cd A^{-1}]^{(a)}$ [lm W ⁻¹]		b)	[%] ^(c)			[nm]	[nm]	CIL (x,y)	[V]			
ZPt1	15	45.4	34.1	25.9	40.4	25.3	17.0	12.9	9.6	7.3	542	-	(0.34, 0.57)	3.80
	20	49.9	40.2	32.4	44.0	30.0	21.6	14.1	11.3	9.1	540	-	(0.34, 0.57)	3.77
	25	56.4	49.2	42.4	49.8	37.1	28.8	16.0	14.0	12.0	540	-	(0.33, 0.57)	3.71
	30	58.0	54.7	50.1	51.6	42.7	35.8	16.4	15.5	14.1	540	-	(0.33, 0.57)	3.65
ZPt2	3	2.5	1.5	-	2.1	0.6	-	1.3	0.8	-	456	486	(0.25, 0.27)	5.06
	10	7.1	4.3	3.4	6.2	2.4	1.6	3.7	2.3	1.8	456	486	(0.19, 0.27)	4.14
	15	10	6.0	4.4	9.0	3.6	2.0	4.9	2.9	2.2	456	486	(0.19, 0.27)	3.90
	20	16.5	12.9	9.8	15.4	9.2	5.7	7.7	6.0	4.6	456	487	(0.18, 0.30)	3.57
ZPt3	5	8.5	-	-	7.3	-		3.1	-	-	533	497	(0.38, 0.44)	5.03
	10	28.0	12.6	7.7	24.6	8.4	4.5	8.7	4.0	2.5	534	503	(0.31, 0.53)	4.05
	15	45.5	29.8	21.3	39.9	21.9	13.9	13.8	10.3	6.5	538	503	(0.33, 0.55)	3.80
	20	52.5	47.5	40.6	47.1	37.1	29.0	15.7	14.2	12.1	541	-	(0.35, 0.55)	3.64

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

^{a)} Maximum current efficiency ($\Pi_{c.max}$), and current efficiency ($\Pi_{c.500}$, $\Pi_{c.1000}$) measured at a brightness of 500 cd m⁻² and 1000 cd m⁻², respectively; ^{b)} Maximum power efficiency ($\Pi_{p.max}$), and power efficiency ($\Pi_{p.500}$, $\Pi_{p.1000}$) measured at a brightness of 500 cd m⁻² and 1000 cd m⁻², respectively; ^{c)} Maximum external quantum efficiency ($\Pi_{EQE.max.}$), and EQE ($\Pi_{EQE.500}$, $\Pi_{EQE.1000}$) measured at 500 cd m⁻² and 1000 cd m⁻², respectively; ^{d)} Commission Internationale de L'Eclairage coordinates measured at 5 mA cm⁻².

Table of Contents



A series of platinum(II) complexes based on pyrazolo[1,5-*f*]phenanthridine-containing ligands have been prepared for highly efficient phosphorescent OLEDs.

Highlights

Three highly luminescent Pt(II) emitters based on pyrazolo[1,5-*f*]phenanthridine-containing ligands were designed and synthesized.

The rigid and conjugated motif led to the extremely high thermal stabilities of Pt(II) complexes.

ZPt1 showed high OLED performance, indicating its potential utility as an OLED phosphor.