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Syntheses, photoluminescene and electroluminescene of two novel platinum(II) complexes

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Two new platinum(II) cyclometallated complexes with (2-(4-trifluoromethyl)phenyl)pyridine (4tfmppy) as main ligand and tetraphenylimidodiphosphinate (tpip) (**Pt-tpip**) and tetra(4fluorophenyl)imidodiphosphinate (ftpip) (**Pt-ftpip**) as ancillary ligands have been developed. All complexes are green phosphors with photoluminescence quantum efficiency yields of 71.5% and 79.2% in CH₂Cl₂ solutions at room temperature, respectively. The organic light-emitting diodes with the double emissive layers structure of ITO / TAPC (1,1-bis(4-(di-ptolylamino)phenyl)cyclohexane, 40 nm / **Pt-tpip** or **Pt-ftpip** : TcTa (4,4',4''-tri(9-carbazoyl)triphenylamine) (5 wt%, 10 nm) / **Pt-tpip** or **Pt-ftpip** : 2,6DCzPPy (2,6-bis(3-(carbazol-9yl)phenyl)pyridine) (5 wt%, 10 nm) / TmPyPB (1,3,5-tri(m-pyrid-3-yl-phenyl)benzene, 40 nm) / LiF (1 nm) / Al (100 nm) showed good performances. Particularly, device based on complex **Ptftpip** with 5 wt% doped concentration showed superior performances with low drive voltage of 3.3 V, a maximum current efficiency of 48.3 cd A⁻¹, a maximum external quantum efficiency of 14.0% and a maximum power efficiency of 35.7 lm W⁻¹, respectively. Even at the brightness of 1000 cd m⁻ , a current efficiency of 47.0 cd A⁻¹ can still be obtained suggesting the ancillary ligands tpip and ftpip can be employed well in Pt(II) complexes, which would have potential applications in OLEDs.

Introduction

Interest in cyclometalated complexes based on iridium(III)¹ and platinum(II)² has soared over the past decade following the demonstration of their potential in the manufacture of high efficient light-emitting devices (OLEDs). The spin-orbit coupling exerted by the heavy metal effect allows the harvest of both singlet and triplet electro-generated excitons in devices, leading to a theoretically achievable 100% internal quantum efficiency.³ Compared with Ir(III) complexes, the square-planar Pt(II) complexes particularly have a great tendency for aggregation through platinum-platinum and $\pi - \pi$ interactions, resulting in detrimental effects on photoluminescence quantum yields and color purity.⁴ It is well understood that the introduction of steric hinderance into the structure can hinder the intermolecular interactions. Photoluminescence quantum efficiencies of the complexes have been significantly improved by the incorporation of bulky substituents. In this work, the bulky ancillary ligands tetraphenylimidodiphosphinate (tpip) and tetra(4-fluorophenyl)imidodiphosphinate (ftpip) were introduced in which the four bulky phenyl groups can lead to a larger spatial separation of the neighboring molecules of the platinum(II) complexes to suppress the self-quenching behaviour.

Additionally, tpip derivatives have stronger polar P=O bonds, which may improve the electron mobility of Pt(II) complexes.

Furthermore, the good electron mobility of the dopants is also important for efficient OLEDs in view of the hole mobility of hole transport material is higher than the electron mobility of electron transport material. Many groups reported efficient devices based complexes with nitrogen, oxygen, phosphor, sulphur and boron-heterocyclic derivatives as ligands to increase the electron mobility.⁵ In our former publications, efficient Ir(III) complexes and devices with tetraphenylimidodiphosphinate (tpip) derivatives have been reported due to the stronger polar P=O bonds, which may improve the electron mobility of the complexes and benefit its OLEDs performances.⁶ Herein, two heteroleptic platinum complexes were synthesized using 2-(4trifluoromethyl)phenylpyridine as main ligand and tpip or ftpip (tetra(4-fluorophenyl)imidodiphosphinate) as ancillary ligands. The synthesis, structural characterization, thermal stability, photophysical properties, electrochemical property and theoretical calculation and OLEDs performances of these two Pt(II) complexes were investigated in details.

Experimental section

Materials and measurements

All reagents and chemicals were purchased from commercial sources and used without further purification. ¹H NMR spectra were measured on a Bruker AM 500 spectrometer. Mass

spectrometry (MS) spectra were obtained on an electrospray ionization (ESI) mass spectrometer (LCQ fleet, Thermo Fisher Scientific) for ligands and a matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometer (Bruker Daltonic Inc.) for complexes. Elemental analyses for C, H, and N were performed on an Elementar Vario MICRO analyzer. TG-DSC measurements were carried out on a DSC 823e analyzer (METTLER). Absorption and photoluminescence spectra were measured on a UV-3100 spectrophotometer and a F-4600 photoluminescence spectrophotometer, Hitachi respectively. The decay lifetimes were measured with an Edinburgh Instruments FLS-920 fluorescence spectrometer in degassed CH2Cl2 solution at room temperature. Cyclic voltammetry measurements were conducted on a MPI-A multifunctional electrochemical and chemiluminescent system (Xi'an Remex Analytical Instrument Ltd. Co., China) at room temperature, with a polished Pt plate as the working electrode, platinum thread as the counter electrode and Ag-AgNO₃ (0.1 M) in CH₃CN as the reference electrode, tetra-n-butylammonium perchlorate (0.1 M) was used as the supporting electrolyte, using Fc^{+}/Fc as the internal standard, the scan rate was 0.1 V/s. The luminescence quantum efficiencies were calculated comparison of the emission intensities (integrated areas) of a standard sample (*fac*-Ir(ppy)₃) and the unknown sample.⁷

Syntheses

The syntheses routes of the ligands and complexes were listed in Fig. 1. Solvents were carefully dried and distilled from appropriate drying agents prior to use for synthesis of ligands. The 2-(4-trifluoromethyl)phenylpyridine, tpip and ftpip ligands were synthesized with the methods according to our previous publications.⁶ All reactions were performed under nitrogen.

General synthesis of platinum complexes Pt-tpip and Pt-ftpip.

The K₂PtCl₄ (0.415 g, 1 mmol) and 2.5 equivalent of 2-(4trifluoromethyl)phenylpyridine (2.5 mmol, 0.475 g) were mixed in a 3 : 1 mixture of 2-ethoxyethanol and water. The mixture was heated at 80 °C for 16 h and the Pt-dimer was precipitated in water. The resulting yellow-greenish powder was filtered and was subsequently reacted with Ktpip or Kftpip without further purification. A stirred mixture of Pt-dimer (0.33 mmol, 0.30 g) and Ktpip (0.99 mmol, 0.45 g) or Kftpip (0.99 mmol, 0.53 g) in 2-ethoxyethanol (25 mL) was heated at 80 °C for 16 h. After cooling to room temperature, the solution was concentrated under reduced pressure. The resulting residue was subjected to column chromatography (silica gel, CH₂Cl₂/petroleum ether 1 : 2 (v/v)) to give product as yellow powders, which were further purified by sublimation in vacuum.

Pt-tpip. Yield: 40.0%. ¹H NMR (500 MHz, CDCl₃, Fig. S1) δ 9.08 (d, J = 5.13Hz, 1H), 7.92-7.77 (m, 10H), 7.56 (d, J = 8.02 Hz, 1H), 7.38-7.31 (m, 14H), 7.11 (t, J = 6.63 Hz, 1H). MALDI-TOF (Fig. S2), m/z: calcd for C₃₆H₂₇F₃N₂O₂P₂Pt, 833.115 [M];

found 835.015 [M+2]. Anal. Calcd for $C_{36}H_{27}F_3N_2O_2P_2Pt$: C, 51.87; H, 3.26; N, 3.36. Found: C, 51.83; H, 3.73; N, 3.28.

Pt-ftpip. Yield: 25.0%. ¹H NMR (500 MHz, CDCl₃, Fig. S3) δ 9.13-8.99 (m, 1H), 7.91-7.87 (m, 8H), 7.78 (t, J = 7.83 Hz, 1H), 7.37-7.34 (m, 10H), 7.13-7.07 (m, 2H), 6.85 (ddd, J = 2.37, 9.24, 11.84 Hz, 1H). MALDI-TOF (Fig. S4), m/z: calcd for C₃₆H₂₃F₇N₂O₂P₂Pt, 905.080 [M]; found 905.379 [M]. Anal. Calcd for C₃₆H₂₃F₇N₂O₂P₂Pt: C, 47.75; H, 2.56; N, 3.09. Found: C, 46.74; H, 2.59; N, 3.03.

X-ray crystallography

The single crystals of Pt-tpip and Pt-ftpip complexes were carried out on a Bruker SMART CCD diffractometer using monochromated Mo K α radiation ($\lambda = 0.71073$ Å) at room temperature. Cell parameters were retrieved using SMART software and refined using SAINT⁸ on all observed reflections. Data were collected using a narrow-frame method with scan widths of 0.30° in ω and an exposure time of 10 s/frame. The highly redundant data sets were reduced using SAINT and corrected for Lorentz and polarization effects. Absorption corrections were applied using SADABS⁹ supplied by Bruker. The structures were solved by direct methods and refined by fullmatrix least-squares on F2 using the program SHELXS-97.10 The positions of metal atoms and their first coordination spheres were located from direct-methods E-maps; other non-hydrogen atoms were found in alternating difference Fourier syntheses and leastsquares refinement cycles and, during the final cycles, refined anisotropically. Hydrogen atoms were placed in calculated position and refined as riding atoms with a uniform value of Uiso.

OLEDs fabrication and measurement

All OLEDs were fabricated on the pre-patterned ITO-coated glass substrate with a sheet resistance of 15 Ω /sq. The deposition rate for organic compounds (TAPC (1,1-bis(4-(di-ptolylamino)phenyl)cyclohexane, TcTa (4,4',4''-tri(9-carbazoyl)triphenylamine), 2,6DCzPPy (2,6-bis(3-(carbazol-9yl)phenyl)pyridine), TmPyPB (1,3,5-tri(m-pyrid-3-yl-phenyl) benzene)) is 1 Å/s. The phosphors and the host TcTa or 2,6DCzPPy were co-evaporated to form emitting layer from two separate sources. The cathode of LiF and Al were deposited with deposition rates of 0.1 and 3 Å/s, respectively. The characteristic curves of the devices were measured with a computer which controlled KEITHLEY 2400 source meter with a calibrated silicon diode in air without device encapsulation. On the basis of the uncorrected PL and EL spectra, the Commission Internationale de l'Eclairage (CIE) coordinates were calculated using a test program of the Spectra scan PR650 spectrophotometer.

Results and discussion

Preparation and characterization of compounds

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As shown in Fig. 1, the main ligand 2-(4-trifluoromethyl)phenylpyridine was synthesized using a Suzuki coupling reaction from 4-trifluoromethylphenyl boronic acid and 2-bromopyridine. The tpip and ftpip ancillary ligands and their potassium salt were prepared according to our previous publications.⁶ The platinum complexes were prepared by the reaction of corresponding chloride-bridged dimmers [(C^N)Pt(μ -

Cl)]₂ with tpip or ftpip potassium salt to give the products **Pt-tpip** and **Pt-ftpip**. Purification of the mixture by silica gel chromatography provided crude products, which were further purified by vacuum sublimation. All the new compounds were fully characterized by ¹H NMR spectrometry and the crystal structures further confirmed the identity of both complexes.



Fig. 1 The synthetic routes of ligands, Pt-tpip and Pt-ftpip



Fig. 2 Oka Ridge Thermal Ellipsoidal plot (ORTEP) diagrams of **Pt-tpip** (left, CCDC No. 1509840) and **Pt-ftpip** (right, CCDC No. 1509843) complexes with the atom-numbering schemes. Hydrogen atoms are omitted for clarity. Ellipsoids are drawn at 30% probability level.

Single crystals of Pt-tpip and Pt-ftpip were obtained from CH₃OH and CH₂Cl₂ solutions. Fig. 2 shows the Oak Ridge thermal ellipsoidal plot (ORETP) diagrams of Pt-tpip and Ptftpip given by X-ray analysis. Selected parameters of the molecular structures and tables of atomic coordinates were collected in the Table S1 and Table S2. As is shown in Fig. 2, for two complexes, the Pt-C bond lengths are 1.939 and 1.947 Å, respectively. The Pt-O bonds are all over 2Å. The average of the dihedral angles between planes $[C_1-Pt-tpip-N_1]$, $[N_1-Pt-tpip-O_2]$ and $[O_2$ -Pt-tpip- $O_1]$ is 178.58° in **Pt-tpip** and that is 177.60° between planes [C1-Pt-ftpip-N1], [N1-Pt-ftpip-O2] and [O2-Ptftpip-O1] in Pt-ftpip Additionally, when the mean plane is composed of C1, N1, and Pt atoms, the O1 and O2 atoms' displacement values from the mean plane are 0.005 and 0.097 Å in Pt-tpip and those are 0.095 and 0.075 Å in Pt-ftpip, respectively. Correspondingly, referring to the mean plane

constructed with O1, O2, and Pt atoms, the C1 and N1 atoms' displacement values from the mean plane are 0.089 and 0.004 Å in **Pt-tpip** and those are 0.074 and 0.099 Å in **Pt-ftpip**, respectively (Fig. S5 and S6). The discussion above suggests that they maintain a good square-planar coordination geometry with the two O atoms opposite to the C, N atoms of the 4-tfmppy respectively. The bond lengths and angles around the central platinum atom found for these new complexes are in good agreement with the few previously published structures of this type.¹¹

Thermal stability



Fig. 3 The DSC (a) and TG (b) curves of Pt-tpip and Pt-ftpip complexes.

The thermal stability of the emitters is important for the stability of OLEDs. In this case, the thermal properties of the two Pt(II) complexes were characterized by differential scanning calorimetry (DSC) and thermogravimetric (TG) measurements under a nitrogen steam. From the DSC curves in Fig. 3(a) it can be observed the melting points of **Pt-tpip** and **Pt-ftpip** are as high as 260 and 225 °C, respectively. The TG curves give the decomposition temperatures (5% loss of weight) as 328 °C for **Pt-tpip** and 304 °C for **Pt-ftpip**, respectively, indicating that the

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fluorine atoms at the tpip ligand will reduce the melting point effectively and also affect their decomposition temperature obviously. And the high decomposition temperature of the complexes suggested they are suitable for application in OLEDs.

Photophysical property

The absorption spectra of two complexes show broad and intense bands below 300 nm, assigned to the spin-allowed intraligand ¹LC ($\pi \rightarrow \pi^*$) transition of cyclometalated main ligands and tpip ligands. The weak bands last to 450 nm can be assigned to spinallowed metal-ligand charge transfer band (¹MLCT) and spin forbidden ³MLCT transition bands caused by the large spin orbital coupling (SOC) that was introduced by platinum center indicating an efficient spin-orbit coupling that is prerequisite for phosphorescent emission.¹² The complexes **Pt-tpip** and **Pt-ftpip** show green emission at 510/542 nm and 508/540 nm, respectively, suggesting that fluorine atom on ftpip groups has no obvious effect on the emission wavelength of Pt(II) complexes. Both complexes based on tpip or ftpip show high quantum efficiency (Φ) as 79.2% and 71.5% for **Pt-tpip** and **Pt-ftpip**, respectively, indicating that the platinum complexes have potential application in the OLEDs. Furthermore, the lifetimes are in the range of microseconds for two complexes (1.5 μ s for **Pt-tpip** and 1.7 μ s for **Pt-ftpip**, respectively) (Fig. S7). The short lifetimes would improve the spin-state mixing and suppress the excitons annihilation.



Fig. 4 The UV-vis absorption (a) and emission spectra (b) of complexes **Pt-tpip** and **Pt-ftpip** in degassed dichloromethane $(5 \times 10^{-5} \text{ M})$ at room temperature.

Table 1.	Photop	hyscial	date	ofţ	olatinum	comp	lexes.
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Compound	Absorption ^{a)} λ (nm)	Emission ^{a)} λ _{max} (nm), 298K	$ au_{298 \mathrm{K}}{}^{\mathrm{a})}$ (µs)	Ф ^{b)} (%)	E _{ox} (V)	HOMO/LUMO ^{c)} (eV)
Pt-tpip	278/320/369/445	510/542	1.5	79.2	0.74	-5.39/-2.55
Pt-ftpip	278/301/365/441	508/540	1.7	71.5	0.72	-5.37/-2.53

 T_{m} : Absorption, emission spectra and lifetime were taken in degassed CH₂Cl₂;^b Φ : emission quantum yields were measured relative to Ir(ppy)₃($\Phi = 0.4$) in degassed CH₂Cl₂ solution; ^c From the onset of oxidation potentials of the cyclovoltammety (CV) diagram using ferrocene as the internal standard and the optical band gap from the absorption spectra in degassed CH₂Cl₂. HOMO(eV)=-(E_{ox}-E_{1/2,Fe})-4.8, LUMO(eV)=HOMO+E_{bandgap}.

Electrochemical properties and theoretical calculation

The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of the dopants are important for the design of the OLEDs. In order to determine the HOMO/LUMO values of the Pt-tpip and Ptftpip, the electrochemical properties were investigated by cyclic voltammetry in deaerated CH₂Cl₂ (Fig. 5 (Left)). The cyclic voltammograms of the complexes Pt-tpip and Pt-ftpip in the positive range show strong oxidation peaks, while the reduction peaks are not obvious, demonstrating that the redox process of the complexes is not reversible completely, which is rarely observed in related Ir(III) complexes containing tpip units. From the Table 1, it is observed that the difference of the HOMO/LUMO values of the two complexes is neglectable. This means that the introduction of fluorine atom on tpip groups has no obvious effect on electrochemical properties of Pt(II) complexes, which match the DFT calculation results below very well.



Fig. 5 Cyclic voltammogram curves (Left) and Molecular orbital diagram for the HOMOs/LUMOs and their energy levels of **Pt-tpip** and **Pt-ftpip** calculated in $CH_2Cl_2(Right)$.

In order to gain insights into the electronic states and the orbital distribution, the density functional theory (DFT) calculations¹³ for both Pt(II) complexes were conducted employing Gaussian09 software with B3LYP function.¹⁴ Plots of the HOMO/LUMO and the molecular orbital energy levels are presented in **Fig. 5** (right). The basis set used for C, H, N, O, F and P atoms was 6-31G(d, p) while the LanL2DZ basis set

was employed for Pt atoms.¹⁵ The solvent effect of CH₂Cl₂ was taken into consideration using conductor like polarizable continuum model (C-PCM). All these calculations were performed with Gaussian09. For these complexes, the HOMOs correspond to a mixture of 4-tfmppy (36.36-36.48%) and Pt d orbitals (53.85-52.20%) with minor contribution from the tpip, ftpip ligands (9.81-9.33%), while the LUMOs are mainly localized on the main ligands (93.09-92.89%) with minor contribution from Pt d orbitals (5.70-5.65%) and tpip, ftpip ligands (1.21-1.47%). The calculation results indicate that the orbital distributions of HOMO and LOMO for Pt-tpip and Pt**ftpip** have more contributions from Pt *d* orbitals and 4-tfmppy ligand, less contribution from tpip, ftpip ligands. Therefore, replacing hydrogen atoms with fluorine atoms in tpip ligand almost makes no difference to both the HOMO and the LUMO energy of Pt-tpip and Pt-ftpip.

OLEDs performance



Fig. 6 Energy level diagram of HOMO and LUMO levels (relative to vacuum level) for materials investigated in this work and their molecular structures.

To verify our conjecture, devices **G1** and **G2** using **Pt-tpip** and **Pt-ftpip** as the emitters, respectively, with the structure of ITO / TAPC (40 nm) / **Pt-tpip** or **Pt-ftpip** : TcTa (5 wt%, 10 nm) /

 Table 2. EL performances of the devices G1 and G2.

Pt-tpip or **Pt-ftpip** : 2,6DCzPPy (5 wt%, 10 nm) / TmPyPB (40 nm) / LiF (1 nm) / Al (100 nm) were investigated to evaluate the electroluminescence (EL) performances. The energy diagram of the devices as well as the molecular structure of the materials used are shown in Fig. 6. TAPC was used as hole transport/electron block layer (HTL/EBL) due to its high hole mobility (1×10^{-2} cm² V⁻¹ s⁻¹) and high-lying LUMO level (-1.8 eV), while TmPyPB was used as hole block/electron transport layer (HBL/ETL) due to its lowlying HOMO level (-6.7 eV) and high electron mobility (1×10^{-3} cm² V⁻¹ s⁻¹).¹⁶ p-Type material TcTa and bipolar material 2,6DCzPPy were chosen as host materials of EML1 and EML2, respectively.

Theoretically speaking, the stepwise HOMO levels of TAPC (-5.5 eV), TcTa (-5.7 eV), and 2,6DCzPPy (-6.1 eV) are beneficial for the injection and transport of holes, while the stepwise LUMO levels of TmPyPB (-2.7 eV), 2,6DCzPPy (-2.6 eV) and TcTa (-2.4 eV) are beneficial for the injection and transport of electrons. Therefore, balanced distribution of carriers (holes and electrons) and wide recombination zone could be expected. More importantly, the LUMO level of TAPC is 0.6 eV higher than that of TcTa while the HOMO level of TmPyPB is 0.6 eV lower than that of 2,6DCzPPy; thus, holes and electrons are well confined within EMLs and and the triplet excitons quenching of will be effectively avoided. Since the HOMO and LUMO levels of Pt-tpip or Pt-ftpip (-5.39/-5.37 eV and -2.55/-2.53 eV, respectively) are within those of TcTa and 2,6DCzPPy, carrier trapping is conceived to be the dominant EL mechanism of these devices. In addition, the triplet energies of TcTa (2.83 eV) and 2,6DCzPPy (2.71 eV) are higher than that of Pt-tpip or Pt-ftpip (2.43 eV), which effectively avoids the reverse energy transfer from dopant to host molecules. In this device, the optimized Pt(II) complexes with 5 wt% doped concentration in TcTa and 2,6DCzPPy, respectively, were used as the two emitting layers. In most cases, double emitting layers will broad the hole-electron recombination zone which can increase the unilization ratio of the hole-electron causing the improved efficiency and impressed efficiency roll-off.

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Table 2. EE performances of the devices of and 02.								
Device	Emitter	V _{turn-on} ^{a)}	L _{max} (Voltage) ^{b)}	$\eta_c(voltage)^{c}$	$\eta_{c, L1000}^{d}$	EQE _{max} ^{e)}	$\eta_p(voltage)^{f}$	CIE
-		(V)	$(cd m^{-2}(V))$	$(cd A^{-1}(V))$	$(cd A^{-1})$	(%)	(lm W ⁻¹⁽ V))	(x,y)
G1	Pt-tpip	3.3	25544(7.7)	40.6(4.1)	38.0	12.0	30.1(4.0)	(0.27,0.62)
G2	Pt-ftpip	3.3	17014(11.2)	48.3(5.4)	47.0	14.0	35.7(4.4)	(0.31,0.60)

^{a)} V_{tum-on}: Turn-on voltage recorded at a luminance of 1 cd m⁻²; ^{b)} L_{max}: maximum luminance; ^{c)} η_c : maximum current efficiency; ^{d)} $\eta_{c, L1000}$: current efficiency at 1000 cd m⁻²; ^{e)} EQE_{max}: maximum external quantum efficiency; ^{f)} η_p : maximum power efficiency.

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Fig. 7 Characteristics of devices with configuration ITO / TAPC (40 nm) / **Pt-tpip** or **Pt-ftpip**: TcTa (10 nm, 5 wt%) / **Pt-tpip** or **Pt-ftpip**: 2,6DCzPPy (10 nm, 5 wt%) / TmPyPB (40 nm) / LiF (1 nm) / Al (100 nm): (a) EL spectra , (b) luminance(L) versus voltage (V), (c) current efficiency (η_c) as a function of luminance (L) and (d) power efficiency (η_p) as a function of luminance (L) for **G1** and **G2**.

The EL spectra, luminance (L) versus voltage (V), current efficiency (η_c) versus luminance (L) and power efficiency (η_n) versus luminance (L) characteristics of each device are shown in Fig. 7. The key EL data are summarized in Table 2. Devices G1 and G2 all emit green light with the EL emission peaks at 505/540 and 507/540 nm and the Commission Internationale de l'Eclairage (CIE) coordinate for G1 and G2 is (0.27, 0.62) and (0.31, 0.60), respectively. Additionally, the emission spectra are almost invariant of the current density and also do not show any concentration dependent. As is shown in Fig. 7(a), the EL spectra are very close to the PL spectra of the complexes in CH₂Cl₂ solution indicating that the EL emission of the device originates from the triplet excited states of the phosphors. Furthermore, the residual emission from the host 2,6DCzPPv for each device is not obvious suggesting that the energy and/or charge transfer from the host exciton to the phosphor is nearly complete upon electrical excitation.

The OLEDs based on complexes **Pt-tpip** or **Pt-ftpip** exhibit encouraging EL performances. Both devices **G1** and **G2** display low turn-on voltages ($V_{turn-on}$) (3.3 V). Moreover, the device **G1** shows a maximum current efficiency ($\eta_{c,max}$) of 40.6 cd A⁻¹, a maximum external quantum efficiency (EQE_{max}) of 12.0% with a maximum power efficiency ($\eta_{p,max}$) of 30.1 lm W⁻¹. Device **G2** exhibits a little higher efficiency with a $\eta_{c,max}$ of 48.3 cd A⁻¹, an EQE_{max} of 14.0% and a $\eta_{p,max}$ of 35.7 lm W⁻¹, respectively. Furthermore, both devices show low efficiency roll-off. For example, even at the brightness of 1000 cd m⁻², the current efficiencies can still be kept at 38.0 and 47.0 cd A⁻¹ for devices **G1** and **G2**, respectively.

The good EL properties should be firstly due to the application of tpip and ftpip as the ancillary ligand, which can improve the electron mobility of the complexes. Secondly, the LUMO levels of the dopants are low and they are just in the range of the ones of two host materials, which will benefit electron transport properties. Thirdly, we have designed and fabricated the high performances green EL devices by doping Pt-tpip or Pt-ftpip into host materials with stepwise energy levels, which is beneficial for the injection and transport of both holes and electrons. Finally, double light-emitting layers are adopted in this device, which displayed higher EL efficiency, slower roll-off of efficiency, and higher brightness attributed to better balance of holes and electrons, broadening recombination zone and improved trapping of holes and electrons.¹⁷ Furthermore, compared with Pt-tpip, four fluorine atoms are introduced in the four phenyl of tpip ligand in Pt-ftpip, which can result in more superior electron mobility of Pt-ftpip than

that of **Pt-tpip**. Therefore, it can be observed that the current efficiency of **Pt-ftpip** is higher than that of **Pt-tpip**.

Conclusions

In conclusion, two cyclometalated platinum complexes **Pt-tpip** and **Pt-ftpip** with tetraphenylimidodiphosphinate and tetra(4-fluorophenyl)imidodiphosphinate as the ancillary ligands have been successfully prepared and applied in the OLEDs. EL devices with the double emissive layers configuration of ITO / TAPC (40 nm) / **Pt-tpip** or **Pt-ftpip** (5 wt%) : TcTa (10 nm) / **Pt-tpip** or **Pt-ftpip** (5 wt%) : 2,6DCzPPy (10 nm) / TmPyPB (40 nm) / LiF (1 nm) / Al (100 nm) showed good performances (a η_{cmax} of 48.3 cd A⁻¹, a peak *EQE* of 14.0% and a peak η_p of 35.7 lm W⁻¹) with low efficiency roll-off. Even at the brightness of 1000 cd m⁻², a current efficiency of 47.0 cd A⁻¹ can still be obtained. This study suggested the ancillary ligands tpip and ftpip can be employed well in Pt(II) complexes, which would have potential applications in OLEDs.

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Notes and references

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[†]Electronic Supplementary Information (ESI) available: the photoluminescence lifetime curve, the crystallographic data, selected bonds and angles, ¹H NMR spectra, the MALDI-TOF spectra, atoms' displacement values spectra and current density (J) versus voltage (V) spetra of complexes **Pt-tpip** and **Pt-ftpip**.

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Graphical abstract



Highly efficient green OLEDs based on two platinum complexes show a peak current efficiency of 48.3 cd A^{-1} with low efficiency roll-off, and even at the brightness of 1000 cd m⁻², a current efficiency of 47.0 cd A^{-1} can still be obtained.