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Highly efficient green OLEDs based on four platinum complexes show a maximum luminance of 39196 cd m⁻², a maximum current efficiency of 40.1 cd A^{-1} and a maximum power efficiency of 31.0 lm W^{-1} , respectively, with low efficiency roll-off.

Photoluminescence and electroluminescence of four platinum complexes with trifluoromethyl-substituted 2-phenylpyridine and tetraphenylimidodiphosphinate ligands

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Abstract: Four cyclometalated platinum complexes with trifluoromethyl-substituted 2-phenylpyridine at different positions on its phenyl group as the main ligands and tetraphenylimidodiphosphinate as the ancillary ligand, Pt1-Pt4 (Pt1 is a trifluoromethyl-free complex), were prepared, and their X-ray crystallography, photoluminescence, thermal stability, electrochemical analyses, theoretical calculation and EL performances were investigated. The positions of trifluoromethyl groups on the phenyl ring affected the emission spectra of platinum complexes greatly, and their corresponding emission peaks at 504/534, 512/545, 495/526 and 510/542 nm were observed at room temperature, respectively. Constructed with complexes Pt1-Pt4 as the emitters, respectively, the organic light-emitting diodes (OLEDs) with double light emitting layers structure of ITO / TAPC (1,1-bis[4-(di-*p*-tolylamino)phenyl]cyclohexane, 40 nm / Pt complexes (5 wt%) : TCTA (4,4',4''-tri(9-carbazoyl)-triphenylamine, 10 nm / Pt complexes (5 wt%): 2,6DCzPPy (2,6-bis(3-(carbazol-9-yl)phenyl)pyridine, 10 nm TmPvPB / (1,3,5-tri(m-pyrid-3-yl-phenyl)benzene, 40 nm) / LiF (1 nm)/ Al (100 nm) showed good performances. Particularly, device G2 based on 2-trifluoromethyl-substituted complex Pt2 obtained a maximum luminance of 39196 cd m^{-2} , a maximum current efficiency of 40.1 cd A^{-1} and a maximum power efficiency of 31.0 lm W^{-1} , respectively, with low efficiency roll-off. The results suggested that these complexes Pt1-Pt4 would have potential applications in efficient OLEDs.

Keywords: Organic light-emitting diode; Platinum(II) complex; Tetraphenylimidodiphosphinate; Trifluoromethyl; High efficiency; Efficiency roll-off

1. Introduction

A breakthrough came with the incorporation of transition metal complexes in 1998 which enabled quantum yields beyond the fluorescence limit of 25% leading to the new class of phosphorescent organic light-emitting devices (PhOLEDs) [1-2]. Therein, the heavy atom is responsible for effective spin–orbit coupling (SOC) and triplet harvesting, leading to exceptional photophysical properties and quantum yields as high as 100% [3]. Although different transition metals were investigated as emitting compounds, neutral iridium(III) [4-24] and platinum(II) [25-31] complexes with cyclometalated ligands showed the most promising results so far. Prominent motifs in such Pt(II) complexes are bidentate cyclometalated aryl pyridine ligands which have been tested together with acetylacetonate ancillary ligands and derivatives thereof [32]. Based on this class of complexes, a lot of variations regarding substituents, size of the π systems and ancillary ligands were investigated to tune their photophysical properties.

As far as we know, Ir(III) complexes carrying trifluoromethyl-substituted 2-phenylpyridine (ppy) ligands have been reported with good performances [33-35], which suggested that the introduction of electron-withdrawing CF₃ groups in Pt(II) complexes may also improve the OLED performances effectively because fluorination can enhance the electron mobility and the bulky CF₃ substituent can affect the molecular packing, providing steric protection around the metal, which can suppress the self-quenching behavior [36-38]. Some groups have studied various heteroleptic fluorinated iridium complexes, which suggested that the fluorine and trifluoromethyl groups in different positions of the ppy ligands showed different effects on the emission properties [39-40]. It may also work in the same way in Pt(II) complexes. However, comprehensive and deeper studies are still needed.

Additionally, the emission energy of heteroleptic complexes [(C^N)Pt(LX)] can be fine-tuned by a combination of main ligands (C^N) and LX types of ancillary ligands. Our group has reported highly efficient phosphorescent OLEDs by introducing tetraphenylimidodiphosphinate (tpip) derivatives as ancillary ligands [41-45]. Tpip derivatives have stronger polar P=O bonds, which may improve the electron mobility of the Ir(III) complexes and benefit their OLED performances [41-45]. And the bulky tpip derivatives can also introduce steric hinderance into the structure, which will hinder the intermolecular interactions. So, they may be also a useful ancillary ligand for the phosphorescent Pt(II) complexes. To investigate the effect of the substituted position of the trifluoromethyl group on the photophysical properties of the Pt(II) complexes for their OLED performances and expand the application of tpip ligands, we synthesized a series of Pt(II) complexes with tpip as the ancillary ligand and studied their OLED characteristics.

2. Experimental Section

2.1. General information

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 Hitachi F-4600 photoluminescence spectrophotometer, respectively. The single crystals of complexes were carried out on a Bruker SMART CCD diffractometer using monochromated Mo K α radiation (λ = 0.71073 Å) at room temperature, which are analyzed by direct methods (SHELXS-97) [46-48]. 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 by comparison of the emission intensities (integrated areas) of a standard sample (fac-Ir(ppy)₃) and the unknown sample [49-50].

2.2. OLED fabrication and measurement

All OLEDs were fabricated on the pre-patterned ITO-coated glass substrate with a sheet resistance of 10 Ω /sq. The deposition rate for organic compounds is 1-2 Å/s. The phosphor and the

host TCTA or 2,6DCzPPy were co-evaporated to form emitting layer from two separate sources. The cathode consisting of LiF / Al was deposited by evaporation of LiF with a deposition rate of 0.1 Å/s and then by evaporation of Al metal with a rate of 3 Å/s. 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.

2.3. Syntheses procedure

The synthesis procedures of ligands are listed in Scheme 1.

2.3.1. General synthesis of L2-L4

Tetraphenylimidodiphosphinate acid (Htpip) and potassium tetraphenylimidodiphosphinate (Ktpip) were prepared according to our previous literatures [41-44]. All CF₃-substituted ligands **L2–L4** with a ppy core were synthesized by the reaction of the corresponding 2-bromopyridine (21.1 mmol) and arylboronic acids (25.5 mmol) using tetrakis(triphenylphosphine)-palladium⁽⁰⁾ (0.63 mmol) as the catalyst in 50 mL of THF. After 30 mL of aqueous 2 N Na₂CO₃ was delivered, the reaction mixture was heated at 70 °C for 1 day. The cooled mixture was poured into water and extracted with CH₂Cl₂ (50 mL × 3). Finally, silica column purification (*n*-hexane : EtOAc = 10 : 1 as the eluant) gave white solid products.

2-[2-(Trifluoromethyl)phenyl]pyridine (L2). Yield: 80%. ¹H NMR (CDCl₃, 500 MHz): δ 7.2–7.6 (m, 4H), 7.49 (d, *J* = 7.2 Hz, 1H), 7.55 (d, *J* = 7.3 Hz, 1H), 7.65–7.8 (m, 1H), 8.60 (m, 1H). ESI-MS (m/z): calcd for C₁₂H₈F₃N [M+H]⁺ 224, found 224.

2-[3-(Trifluoromethyl)phenyl]pyridine (**L3**). Yield: 75%. ¹H NMR (CDCl₃, 500 MHz): δ 7.1 (m, 1H), 7.44 (t, *J* = 7.8 Hz, 1H), 7.59–7.71 (m, 3H), 8.06 (d, *J* = 7.8 Hz, 1H), 8.3 (s, 1H), 8.62 (dd, *J* = 4.7, 0.9 Hz, 1H). ESI-MS (m/z): calcd for C₁₂H₈F₃N [M+H]⁺ 224, found 224.

2-[4-(Trifluoromethyl)phenyl]pyridine (**L4**). Yield: 76%. ¹H NMR (CDCl₃, 500 MHz,): δ 7.1 (ddd, *J* = 8.6, 4.7 and 2.1 Hz, 1H), 7.55 (d, *J* = 7.5 Hz, 4H), 7.93 (d, *J* = 8 Hz, 2H), 8.56 (d, *J* = 4.4 Hz, 1H). ESI-MS (m/z): calcd for C₁₂H₈F₃N [M+H]⁺ 224, found 224.

2.3.2. General synthesis of Pt1-Pt4

The K₂PtCl₄ (0.415 g, 1 mmol) and 1.5 equivalent of C^N ligand (1.5 mmol) were mixed in a 3:1 mixture of 2-ethoxyethanol and water. The mixture was heated at 80 °C for 16 h. The Pt-dimer was precipitated in water. The resulting yellow-greenish powder was filtered and was subsequently reacted with Ktpip without further purification. A stirred mixture of Pt-dimer (0.30 g, 0.33 mmol) and Ktpip (0.99 mmol, 0.45 g) in 2-ethoxyethanol (25 mL) was heated at 80 °C for 16h. After cooling the mixture to room temperature, the solution was concentrated under reduced pressure. The resulting residue was subjected to column chromatography (silica gel, CH_2Cl_2 / petroleum ether 1:2 (v/v)) to give product as a yellow solid, which was further purified by sublimation in vacuum.

Pt1. Yield: 30.0%. ¹H NMR (500 MHz, CDCl₃) (Fig. S7) δ 7.75 (d, J = 5.45 HZ, 1H), 6.64-6.55 (m, 8H), 6.45 (t, J = 8.53 Hz, 1H), 6.34 (d, J = 7.09 Hz, 1H), 6.22 (d, J = 7.45 Hz, 1H), 6.09-6.04 (m, 13H), 5.79 (dd, J = 15.86, 23.24 Hz, 3H). MALDI-TOF (Fig. S2), m/z: calcd for C₃₅H₂₈N₂O₂P₂Pt, 765.127 [M]; found 766.620 [M+1]. Anal. Calcd for C₃₅H₂₈N₂O₂P₂Pt: C, 54.91; H, 3.69; N, 3.66. Found: C, 54.75; H, 3.59; N, 3.65%.

Pt2. Yield: 45.0%. ¹H NMR (500 MHz, CDCl₃) (Fig. S8) δ 9.27 (m, 1H), 8.0 (dd, J = 8.01, 13.74 Hz, 2H), 7.91-7.84 (m, 9H), 7.47 (d, J = 7.41 Hz, 1H), 7.36-7.32 (m, 12H), 7.11-7.18 (m, 2H). MALDI-TOF (Fig. S3), m/z: calcd for C₃₆H₂₇F₃N₂O₂P₂Pt, 833.115 [M]; found 834.189 [M+1]. Anal. Calcd for C₃₆H₂₇F₃N₂O₂P₂Pt: C, 51.87; H, 3.26; N, 3.36. Found: C, 51.68; H, 3.47; N, 3.34%.

Pt3. Yield: 25.0%. ⁴H NMR (500 MHz, CDCl₃) (Fig. S9) δ 9.09 (d, J = 5.13 Hz, 1H), 7.84 (ddd, J = 7.89, 14.19, 23.58 Hz, 13H), 7.61-7.56 (m, 2H), 7.78-7.34 (m, 10H), 7.13 (t, J = 6.08 Hz, 1H). MALDI-TOF (Fig. S4), m/z: calcd for C₃₆H₂₇F₃N₂O₂P₂Pt, 833.115 [M]; found 833.366 [M]. Anal. Calcd for C₃₆H₂₇F₃N₂O₂P₂Pt: C, 51.87; H, 3.26; N, 3.36. Found: C, 51.71; H, 3.40; N, 3.31%.

Pt4. Yield: 50.0% ¹H NMR (500 MHz, CDCl₃) (Fig. S10) δ 9.08 (d, J = 5.13 Hz, 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. S5), m/z: calcd for C₃₆H₂₇F₃N₂O₂P₂Pt, 833.115 [M]; found 835.015 [M+2]. Anal. Calcd for C₃₆H₂₇F₃N₂O₂P₂Pt: C, 51.87; H, 3.26; N, 3.36. Found: C, 51.83; H, 3.53; N, 3.28%.

3. Results and Discussion

3.1. Crystal structure

Single crystals of Pt2-Pt4 complexes were obtained from the mixture of CH₃OH and CH₂Cl₂ solutions. Fig. 1 shows the Oak Ridge thermal ellipsoidal plot (ORETP) diagrams of Pt2-Pt4 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 shown in Fig. 1, for the complexes Pt2-Pt4, the Pt-C bond lengths are 1.940-1.947 Å, which are slightly shorter than the Pt-N bond lengths (1.967-1.980 Å). The Pt-O bond lengths are all over 2 Å. The average dihedral angles of planes [C1-Pt2-N1], [N1-Pt2-O2] and [O2-Pt2-O1] is 178.00° in Pt2, that is 179.33° of planes [C1-Pt3-N1], [N1-Pt3-O2] and [O2-Pt3-O1] in Pt3 and that is 177.60° of planes [C1-Pt4-N1], [N1-Pt4-O2] and [O2-Pt4-O1] in Pt4, which suggests that they maintain a good square-planar coordination geometry with the two O atoms opposite to the C, N atoms of the -CF₃ substituted ppy respectively. Seen from the crystals of Pt2-Pt4, the bulky CF₃ group will cause distortion to the phenyl pyridine chelate more or less. For complex 2, greater bowing of the cyclometalated ppy chelate was observed. This is revealed by the bowling angle of 10.00° , which is defined as a dihedral angle between the mean planes of the phenyl and pyridine moieties of the ppy chelate. This value was then reduced to 1.60° and 2.00° for complexes 3 and 4, respectively, which suggests that the different positions of CF_3 on the phenyl rings of ppy will cause distortion to the structure of phenyl pyridine in different degrees. 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 [51].

3.2. Thermal property

The thermal stability of the emitters is important for the stable OLEDs. In this cases, the thermal properties of the four platinum complexes were characterized by differential scanning calorimetry (DSC) and thermogravimetric (TG) measurements under a nitrogen steam. From the DSC curves in Fig. S6, it can be observed the melting points of **Pt1-Pt4** are as high as 187, 164, 254 and 262 °C, respectively. The TG curves in Fig. 2 give the decomposition temperatures (5% loss of weight) as 299, 306, 268 and 325 °C for **Pt1-Pt4**, respectively, indicating that the introduction of the unit of trifluoromethyl group and the different positions on the phenyl rings of

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

3.3. Electrochemical property and theoretical calculations

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 Pt1-Pt4, the electrochemical properties were investigated by cyclic voltammetry in deaerated CH₂Cl₂ (Fig. 3). The cyclic voltammograms of the complexes Pt1-Pt4 in the positive range show strong oxidation peaks and only an irreversible oxidation potential (E_{ox}) is observed at 0.734 V for Pt1, 0.928 V for Pt2, 0.832 V for Pt3 and 0.738 V for Pt4 vs Fc/Fc⁺, while the reduction peaks are not obvious, demonstrating that the redox process of the complexes is not reversible completely. According to the equation of $E_{HOMO} = -(E_{ox} + 4.8)$ eV, the HOMO energy levels (E_{HOMO}) of Pt1-Pt4 are calculated to be -5.38 eV, -5.58 eV, -5.44 eV and -5.39 eV, respectively. Based on the E_{HOMO} and optical band gap, the lowest unoccupied molecular orbital (LUMO) energy levels are evaluated to be -2.50 eV and -2.80 eV, -2.56 eV and -2.55 eV for Pt1-Pt4. Additionally, from the Table 1, it is observed that the difference of the HOMO/LUMO values of the four complexes is considerable. This means that the introduction of trifluoromethyl group and the different positions on ppy ligand have obvious effect on electrochemical properties of Pt(II) complexes. Especially, Pt2 has the highest redox voltage (0.928 V) and lowest HOMO/LUMO energy levels (-5.58/-2.80 eV).

The density functional theory (DFT) calculations for Pt(II) complexes are conducted to gain insights into the electronic states and the orbital distribution employing Gaussian09 software with B3LYP functional [52]. The basis set used for C, H, N, O, F and P atoms was 6-31G(d, p) while the LanL2DZ basis set were employed for Pt atoms [53-56]. The solvent effect of CH_2Cl_2 was taken into consideration using conductor like polarizable continuum model (C-PCM) [57]. The optimized HOMO/LUMO structures of both complexes on the ground state are clearly showed in Fig. 4. Concerning the energy levels and compositions, electronic structures of HOMOs/LUMOs are similar with each other in the four complexes. For these complexes, the HOMOs correspond to a mixture of tfmppy (36.34-40.71%) and Pt *d* orbitals (51.22-53.85%) with minor contribution from the tpip ligand (8.07-9.81%), while the LUMOs are mainly localized on the main ligands (91.90-93.11%) with minor contribution from Pt *d* orbitals (5.70-6.46%) and tpip ligand (1.18-1.97%). Therefore, modification of the phenyl ring changes both the HOMO and LUMO energy. The trends of the calculated HOMO and LUMO energies of 1-4 are basically in agreement with the trends of the measured oxidation and reduction potentials: the lower (more negative) E_{HOMO} and E_{LUMO} energies correspond to the higher (more positive) E_{ox} and respectively.

3.4. Photophysical property

The UV-vis absorption spectra and emission spectra of complexes Pt1-Pt4 in degassed CH₂Cl₂ at 5×10^{-5} M are shown in Fig. 5, and the related data are listed in Table 1. The absorption spectra of these complexes shows intense bands below 320 nm, which were assigned to the spin-allowed intraligand ¹LC ($\pi \rightarrow \pi^*$) transition of cyclometalated ppy derivatives and tpip ligands. The bands around 370 nm can be assigned to spin allowed metal-ligand charge-transfer (¹MLCT) bands. The spin-forbidden ³MLCT transition bands around 440 nm indicate an efficient spin-orbit coupling that is prerequisite for phosphorescent emission [58]. Compared with the complex Pt1 in CH₂Cl₂ with a emission band at 504/534 nm, complexes Pt2 and Pt4 show obvious red-shifted emissions at 512/545 and 510/542 nm, respectively, whereas Pt3 is blue-shifted to 495/526 nm (Fig. 5b). These results suggest that the position of the trifluoromethyl group on the phenyl ring affects the emitting properties of Pt(II) complexes. The trifluoromethyl group on position 3 (Scheme 1) leads to a hypsochromic shift of the emission of the complex Pt3, while the trifluoromethyl group on positions 2 and 4 (Scheme 1) causes a bathochromic shift of the emission of the complexes Pt2 and Pt4, respectively. To better understand the emission properties of four complexes, the radiative (K_r) and non-radiative (K_{nr}) constants were also computed and summed up in Table 1. Both the K_r and K_{nr} values are all around 10^5 s⁻¹. And the K_r value for **Pt1**, **Pt3** of 1.92×10^5 s⁻¹, 1.77×10^5 s⁻¹, respectively, is smaller than that of **Pt2** and **Pt4** of 3.94×10^5 s⁻¹ and 5.28×10^5 s⁻¹. On the contrary, The $K_{\rm nr}$ value for Pt2, Pt4 of $1.06 \times 10^5 \, {\rm s}^{-1}$, $1.38 \times 10^5 \, {\rm s}^{-1}$, respectively, is smaller than that of Pt1 and Pt3 of 3.34×10^5 s⁻¹ and 4.48×10^5 s⁻¹. Furthermore, among the four complexes, Pt3 exhibits the weakest PL intensity and lowest quantum yield (28.4%), but Pt2 and Pt4 have almost the same quantum yield as high as 78.9% and 79.2%, respectively, indicating that they are potential emitters for efficient OLEDs. Perhaps there are two reasons for the higher emission quantum yields of Pt2 and Pt4 than that of Pt1 and Pt3. Firstly, it may be attributed to

the enhanced metal-ligand interaction of **Pt2** and **Pt4**, which hence suppress the nonradiative decay rate constant, giving rise to the intense phosphorescence. Secondly, compared to **Pt2** and **Pt4**, **Pt1** and **Pt3** may have enhanced solvent affinity and thus increase the efficiency quenching in the solvents. In addition, the lifetimes for complexes **Pt1-Pt4** are all in the range of microseconds $(1.5 - 2.0 \ \mu s)$ (Table 1, Fig. S1) and indicative of the phosphorescent origin from the excited states. The short lifetimes would improve the spin-state mixing and suppress the excitons annihilation.

3.5. OLEDs Performance

As schematically shown in Scheme 2, the optimized OLEDs (named G1-G4, respectively) of ITO / TAPC (1,1-bis-(di-4-tolylaminophenyl)cyclohexane, 40 nm) / Pt1-Pt4: TCTA (4,4',4"-tris(carbazol-9-yl)triphenylamine, 10 5 wt%) Pt1-Pt4: 2,6DCzPPy nm, (2,6-bis(3-(9H-carbazol-9-yl)phenyl)pyridine, 10 5 wt%) nm. 1,3,5-tri[(3-pyridyl)-phen-3-yl]benzene (TmPyPB, 40 nm) / LiF (1 nm) / Al (100 nm) were used to test the device performances of these complexes. To obtain good device performances, double gradient emitting layers were introduced with hole transport material TCTA and bipolar material 2,6DCzPPy as the hosts. The device structure may balance charge transporting for several reasons. Effective electron charging could be realized because of little LUMO energy barrier between TmPyPB, 2,6DCzPPy and TCTA. And TAPC possesses an effectively electron blocking properties with LUMO level 0.6 eV higher than that of TCTA. While the HOMO level of TCTA is very close to that of TAPC, benefiting the hole transporting from the HTL to the EML. The low HOMO energy level of TmPyPB (-6.7 eV) also assures hole confinement in the emitting layers.

The EL spectra, luminance (*L*) versus voltage (*V*), current efficiency (η_c) versus luminance, power efficiency (η_p) versus luminance characteristics of each device are shown in Fig. 6. The key EL data are summarized in Table 2. All devices show typical emission maxima the same as the corresponding complexes **Pt1-Pt4** (504, 512, 495, and 510 nm, respectively) in CH₂Cl₂ solutions, suggesting that the energy can be transferred from TCTA and 2.6DCzPPy to the emitters. However, it is noted that there is a little residual emission from the host 2,6DCzPPy for device **G1**, which means that the energy and/or charge transfer from the host to the phosphor is not complete upon electrical excitation.

All devices display good performances with low turn-on voltages ($V_{turn-on}$) as 3.2-3.3 V. Respectively, the maximum current efficiency and power efficiency for device **G1** are 33.1 cd A⁻¹ and 28.8 lm W⁻¹ with a maximum luminance of over 25000 cd m⁻² at a driving voltage of 7.1 V. The driving voltages to reach the practical brightness of 100 and 1000 cd m⁻² are 3.5 V and 3.9 V, respectively. For **G3** device, the maximum luminance of 24151 cd m⁻² is achieved at a driving voltage of 8.1 V. The maximum current efficiency and power efficiency are 32.6 cd A⁻¹ and 24.4 lm W⁻¹, respectively. The driving voltages to get the practical brightness of 100 and 1000 cd m⁻² are 3.6 V and 4.1 V, respectively. For device **G4**, The maximum current efficiency and power efficiency are 40.6 cd A⁻¹ and 30.1 lm W⁻¹, respectively, with a maximum luminance of 25493 cd m⁻² at a driving voltage of 7.7 V. Among all devices, **G2** fabricated with **Pt2** as the guest material displays the best performances. The maximum luminance for device **G2** is over 39000 cd m⁻². The maximum current efficiency and power efficiency are 41.0 cd A⁻¹ and 31.0 lm W⁻¹, respectively. Additionally, all devices also show low efficiency roll-off. For example, the current efficiency of 37.8 cd A⁻¹ is still maintained for device **G2** as the luminance reaches to 5000 cd m⁻².

Seen from above, it can be found that the EL performances of four devices differ from each other and the complexes with CF₃ units show better results. Compared with **G1**, the maximum current efficiencies of **G2** and **G4** are increased by more than 20%, which suggests that the OLED performances can be really enhanced by the incorporation of bulky CF₃ substituent in Pt(II) complexes. Furthermore, similarly with the PL properties, the complexes with trifluoromethyl groups at different positions on phenyl ring also show different device performances and **Pt2** based device exhibits the best values, indicating that the positions of trifluoromethyl groups at the phenyl ring of ppy greatly affect the EL properties.

The good EL properties should be due to the application of tetraphenylimidodiphosphinate as the ancillary ligand to improve the electron mobility of the complexes. The dopants act as the hole and electron traps to retard the motion of both types of carriers. In our devices, due to the higher hole mobility of the TAPC (1×10^{-2} cm² V⁻¹ s⁻¹) than the electron mobility of the TmPyPB (1×10^{-3} cm² V⁻¹ s⁻¹), and the high energy barrier between TmPyPB and 2,6DCzPPy, the exciton accumulation is expected near the interface between hole blocking layer (TmPyPB) and the emitting layer (Pt complexes (5 wt%) : 2.6DCzPPy) [59-60], which will cause the serious triplet-triplet annihilation (TTA) and triplet-polaron annihilation (TPA) of the platinum

complexes, and high efficiency roll-off consequently. Therefore, the improved electron mobility of the dopants is particularly useful for enhanced OLED performances. Furthermore, the four bulky phenyl and CF₃ groups also lead to a larger spatial separation of the neighboring molecules to suppress TTA and TPA effects. Therefore, the OLEDs with this kind of platinum emitters exhibited high current efficiency and lower efficiency roll-off. Additionally, double light-emitting layers are adopted in the devices, which can broaden the recombination zone, balance the distribution of holes and electrons and reduce leakage current, improved recombination probability, high device efficiency and low efficiency roll-off [61-62].

4. Conclusion

In conclusion, four bis-cyclometalated platinum complexes with trifluoromethyl substituents at different positions on the phenyl rings of ppy as main ligand and tpip containing P=O unit as the ancillary ligand have been successfully applied in OLEDs as emitters. The positions of CF₃ substituents on the phenyl rings of ppy can affect the emission color and intensity of these complexes obviously. The devices ITO / TAPC (40 nm) / Pt complexes (5 wt %): TCTA (10 nm) / Pt complexes (5 wt%): 2,6DCzPPy (10 nm) / TmPyPB (40 nm) / LiF (1 nm) / Al (100 nm) show good performances. Especially, device **G2** with **Pt2** complex as emitter show a maximum luminance of over 39000 cd m⁻² and a maximum current efficiency and a power efficiency of 41.0 cd A⁻¹ and 31.0 lm W⁻¹, respectively, with low efficiency roll-off. And a current efficiency of 37.8 cd A⁻¹ is still maintained even at the high luminance of 5000 cd m⁻². The results suggest that all of these complexes with -CF₃ have potential applications in OLEDs.

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Table captions

Table 1. Photophyscial date of platinum complexes.

Table 2. EL performances of the devices G1-G4.

Table 1. Photophyscial date of platinum completion	exes.
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Compound	$T_{\rm d}^{\rm a)}$	$\lambda_{ab}/(nm)^{b)}$	Emission ^{b)}	$ au_{298~\mathrm{K}}^{\mathrm{b}}$	${\cal P}_{\rm P}^{\rm c)}$	$E_{\rm ox}$	HOMO/LUMO ^{d)}	$k_{\rm r} ({\rm s}^{-1})^{\rm e)}$	$k_{\rm nr} ({\rm s}^{-1})^{\rm e)}$
	(°C)	$(\epsilon / 10^5 M^{-1} cm^{-1})$	λ_{max} (nm), 298 K	(µs)	(%)	(V)	(eV)		
Pt1	299	279(0.16), 316(0.06),	504/534	1.9	36.5	0.734	-5.38/-2.50	1.92×10^{5}	3.34×10^{5}
		361(0.05)							
		× /							
Pt2	306	262(0.24), 324(0.06),	512/545	2.0	78.9	0.928	-5.58/-2.80	3.94×10^{5}	1.06×10^{5}
		374(0.05)							
Pt3	268	263(0.29), 317(0.05),	495/526	1.6	28.4	0.832	-5.44/-2.56	1.77×10^{5}	4.48×10^{5}
		364(0.05)			$\langle \gamma \rangle$				
					Y				
Pt4	325	278(0.19), 323(0.05),	510/542	1.5	79.2	0.738	-5.39/-2.55	5.28×10^5	1.38×10^5
		369(0.05)		Y					

^{a)} $T_{\rm d}$: decomposition temperature.

^{b)} Absorption, emission spectra and lifetime were taken in degassed CH₂Cl₂.

^{c)} Φ : emission quantum yields were measured relative to fac-Ir(ppy)₃ ($\Phi = 0.4$) in degassed CH₂Cl₂

solution.

^{d)} 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 CH_2Cl_2 . HOMO (eV) =-(E_{ox} - $E_{1/2,Fc}$)-4.8, LUMO (eV) =HOMO+ $E_{bandgap}$.

^{e)} k_r and k_{nr} were calculated according to the equations, $k_r = \Phi/\tau$ and $k_{nr} = (1/\tau) - k_r$.

Device	Emitter	V _{turn-on} ^{a)} (V)	$L_{\rm max}({\rm Voltage})^{\rm b)}$ (cd m ⁻² (V))	$\eta_{\rm c} ({\rm voltage})^{\rm c}$ (cd A ⁻¹ (V))	$\eta_{\rm c, L5000}^{d)}$ (cd A ⁻¹)	$EQE_{max}^{e)}$ (%)	$\eta_{\rm p} ({\rm voltage})^{\rm f)}$ (lm W ⁻¹⁽ V))	CIE (x,y)
G1	Pt1	3.2	25203(7.1)	33.1(3.7)	27.0	9.8	28.8(3.8)	(0.28,0.60)
G2	Pt2	3.2	39196(9.0)	41.0(4.2)	37.8	10.8	31.0(4.0)	(0.34,0.61)
G3	Pt3	3.2	24151(8.1)	32.6(4.3)	27.3	10.1	24.4(3.8)	(0.25,0.60)
G4	Pt4	3.3	25544(7.7)	40.6(4.1)	27.1	12.0	30.1(4.0)	(0.27,0.62)

Table 2. EL performances of the devices G1-G4.

^{a)} $V_{\text{turn-on}}$: Turn-on voltage recorded at a luminance of 1 cd m⁻².

^{b)} L_{max} : maximum luminance.

^{c)} $\eta_{c,max}$: maximum current efficiency.

 $^{d)}\eta_{c,5000}$: current efficiency at 5000 cd m⁻².

^{e)} EQE_{max} : maximum external quantum efficiency.

^{f)} $\eta_{p,max}$: maximum power efficiency.

Scheme and figure captions:

Scheme 1. Synthetic route of Pt1-Pt4.

Scheme 2. Device structure and energy level diagram of HOMO and LUMO levels (relative to vacuum level) for materials investigated in this work and their molecular structures.

Fig. 1. Oka Ridge Thermal Ellipsoidal plot (ORTEP) diagrams of **Pt2** (CCDC No. 1509842), **Pt3** (CCDC No. 1509841) and **Pt4** (CCDC No. 1509840) complexes with the atom-numbering schemes. Hydrogen atoms are omitted for clarity. Ellipsoids are drawn at 50% probability level.

Fig. 2. TGA spectra of Pt1-Pt4.

Fig. 3. The cyclic voltammograms spectra of Pt1-Pt4.

Fig. 4. HOMO/LUMO electron-state-density distributions of Pt1-Pt4.

Fig. 5. UV/vis absorption (a) and PL spectra (b) of **Pt1-Pt4** in degassed CH_2Cl_2 (5 × 10⁻⁵ M) at room temperature

Fig. 6. Characteristics of devices with configuration ITO / TAPC (40 nm) / **Pt1-Pt4**: TCTA (10 nm, 5 wt%) / **Pt1-Pt4**: 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-G4**.



Scheme 1. Synthetic route of Pt1-Pt4.



Scheme 2. Device structure and energy level diagram of HOMO and LUMO levels (relative to vacuum level) for materials investigated in this work and their molecular structures.



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Fig. 2. TGA spectra of Pt1-Pt4.



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Fig. 5. UV/vis absorption (a) and PL spectra (b) of **Pt1-Pt4** in degassed CH_2Cl_2 (5 × 10⁻⁵ M) at room temperature.



Fig. 6. Characteristics of devices with configuration ITO / TAPC (40 nm) / **Pt1-Pt4**: TCTA (10 nm, 5 wt%) / **Pt1-Pt4**: 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-G4**.

Highlights

- Four Pt(II) complexes containing trifluoromethyl-substituted 2-phenylpyridine and tetraphenylimidodiphosphinate ligands were synthesized.
- The identification of structures, photophysical property, thermal stability, theoretical calculation, electrochemical and electroluminescent properties were investigated.
- Devices showed a maximum luminance of over 39000 cd m⁻² and a maximum current efficiency and a power efficiency of 41.0 cd A⁻¹ and 31.0 lm W⁻¹, respectively, with low efficiency roll-off.
- The positions of CF₃ on the phenyl rings of phenylpyridine affect the photophysical and electroluminescent properties greatly.