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# Novel cyclometalated platinum (II) complex containing carrier-transporting groups: Synthesis, luminescence and application in single dopant white PLEDs

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ABSTRACT

In order to investigate the influence of carrier-transporting groups on the luminescent properties, especially on excimer/aggregation emission, and to obtain single emissive dopants used in white polymer light-emitting diodes with a single emissive-layer structure, two novel platinum complexes derived from a platinum(II) (2-(4′,6′-difluorophenyl)pyridinato-N,$C^{2\prime}$)(picolinate) unit containing carrier-transporting groups were synthesized and characterized, where a triphenylamino or an oxadiazole-triphenylamino functionalized unit was pending into the picolinate by non-conjugated linkage, respectively. Their optophysical, electrochemical and electroluminescent properties were investigated. Compared to their parent platinum complex, both functionalized platinum complexes exhibited a significantly red-shifted photoluminescent profile in neat film and higher photoluminescent quantum efficiency in dichloromethane at room temperature. Furthermore, the platinum complex with oxadiazole-triphenylamino ambipolar transporting group exhibited better photoluminescent properties and offered potential application as a single dopant in a single emissive-layer-based white polymer light-emitting diode. More stable white light emissions were observed in this platinum complex-doped devices at dopant concentrations of 4–8 wt%. The maximum luminous efficiency of 1.01 cd $A^{-1}$ and the maximum brightness of 2177 cd $m^{-2}$ were obtained in the polyfluorene-hosted devices.



## 1. Introduction

White organic and polymeric light-emitting devices (WOLEDs/WPLEDs) have attracted a great deal of attention because of their potential applications in full color displays, back lighting of flat-panel displays and solid-state lighting [1–4]. To date, white light emission based on polymers and small molecules have been obtained by several methods and technologies [5–14]. There were two device structures to build the small molecule-based WOLEDs by sequential deposition; one is multiple emissive layer (MEL) structure [15–21] and the other is single emissive-layer (SEL) structure [22–24]. However, these WOLEDs fabricated by deposition exhibited problems, such as complicated processes, high cost and poor stability. In order to overcome such problems, WOLEDs and WPLEDs fabricated by solution-processing technique were recently developed, in which all small organic molecules and polymers used as emitters were dissolved in the given solvents and spin-coated to form an emissive layer [25–31].

Using the solution-processing technique, some high-performance white-emitting devices were achieved by a spin-coating process. For example, Wu et al. [32] obtained a WPLED with a power efficiency (PE) of 20.3 lm $W^{-1}$ and a luminescent efficiency (LE) of 42.9 cd $A^{-1}$, in which the blue-emitting small molecules of iridium complexes were spin-coated to form SEL with a blend of poly(*N*-vinylcarbazole) (PVK) and 2,2′-(1,3-phenylene)bis[5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole] (OXD-7). Jen et al. [33] made a WOLED containing PVK, OXD-7, the blue-emitting FIrpic, the green-emitting $Ir(ppy)_3$ and the red-emitting Os-R1 in SEL, which exhibited a maximum external quantum efficiency (EQE) of 5.85%, a PE of 6.15 lm $W^{-1}$ and a LE of 10.9 cd $A^{-1}$. Nevertheless, this class of device obtained by blending various emitters in the SEL structure, could have poor stability and can barely obtain a pure white emission due to phase separation and undesired Förster energy transfer from the high-energy emitter to the low-energy one. In order to decrease the emitter types in the SEL WOLEDs/WPLEDs, a class of emitters used as a single dopant was recently developed, which could present not only high-lying monomer emission, but also low-lying excimer emission in the devices. Meanwhile, our group reported some mononuclear platinum complexes and iridium complexes, as well as dinuclear platinum

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complexes as single emissive dopants in the SEL-based WPLEDs [34]. However, to our best knowledge, the platinum complex containing ambipolar transport groups has not yet been reported in the spin-coated WPLEDs using a single dopant [35].

As triphenylamine (TPA) and oxadiazole (OXD) are well-known hole- and electron-transporting moieties, respectively, applied in the fields of OLEDs and organic solar cells [36], they can form ambipolar transport groups and are suggested to be available to improve the optoelectronic properties of their resulting platinum complexes while they are simultaneously introduced into the platinum complex as substituent groups. In order to investigate the influence of the ambipolar transport groups on the luminescent properties, especially on excimer/aggregation emission of these platinum complexes and further to obtain a class of single emissive dopants used in the SEL-based WPLEDs, a novel platinum complex with ambipolar transporting groups of TPA and OXD, i.e. FPt(OXD6TPA6Pic), was designed and synthesized, where FPt is a platinum(II) (2-(4′,6′-difluorophenyl) pyridinato-N,$C^{2\prime}$) unit, and OXD6TPA6Pic is an oxadiazole-triphenylamino functionalized picolinate, respectively. For comparison, another platinum complex with only a hole-transporting group of TPA, i.e. FPt(TPA6Pic), was also synthesized, where TPA6Pic is a triphenylamino functionalized picolinate. The photophysical, electrochemical and thermal properties, as well as electroluminescent properties for both platinum (II) complexes were studied. As expected, the pending carrier-transporting groups have exhibited a significant influence on the luminescent properties of their corresponding platinum complexes. The FPt(OXD6TPA6Pic) with ambipolar transport groups can be used as a single dopant to obtain WPLEDs containing a polymer matrix of PVK or poly(9,9-dihexylfluorene) (PFO), respectively. The best device performance with a maximum LE of 1.0 cd $A^{-1}$ and brightness of 855 cd $A^{-2}$ was obtained in the FPt(OXD6-TPA6Pic)-doped PFO device at dopant concentrations of 8 wt% and a white emission with a stable CIE coordinate of (0.30, 0.38) was observed at the same time.

## 2. Experimental section

### 2.1. Materials and equipment

All solvents were carefully dried and distilled prior to use. Commercially available reagents were used without further purification unless otherwise stated. 3-(6-(4-(Diphenyl-amino)benzyloxy) hexyloxy)picolinic acid (TPA6PicH) and 3-(6-(4′-((4-((6-(4-(5-(4-methyl)-1,3,4-oxadiazole-2-yl)phenoxy)hexyloxy)methyl)phenyl)(-phenyl) amino) biphen-yl-4-yloxy)hexyloxy)picolinic acid (OXD6T-PA6PicH) were prepared according to the reported process, respectively [37]. For further comparison, platinum (II) (4′,6′-(difluoro-phenyl) pyridinato-N,$C^{2\prime}$) (picolinate) [FPt(pic)] was also made based on our previous work [34]. All reactions were performed under nitrogen atmosphere and were monitored by thin-layer chromatography (TLC). Flash column chromatography and preparative TLC were carried out using silica gel from Merck (200–300 mesh). All $^1$H NMR spectra were acquired at a Bruker Dex-400NMR instrument using $CDCl_3$ as a solvent. Elemental analysis was performed on a Harrios elemental analysis instrument. Time-of-flight mass spectrometry (TOF-MS) was performed in the positive ion mode with a matrix of dithranol on a Bruker-autoflex III smart-beam. The UV absorption and photoluminescence (PL) spectra were measured with a Varian Cary 50 and Perkin–Elmer LS50B Luminescence Spectrometer, respectively. EL spectra and CIE coordinates were recorded with an Insta-Spec IV CCD system (Oriel). Luminance and luminous efficiency–current density (LE–$J$) data were measured with a Si photodiode and calibrated by using a PR-705 spectrascan spectrophotometer (Photo Research).

### 2.2. Synthesis of FPt(TPA6Pic)

To a mixture of $K_2PtCl_4$ (0.3 g, 0.84 mmol) and water (5 mL) was added 2-(2,4-difluorophenyl)pyridine (0.4 g, 2.1 mmol) and 2-ethoxyethanol (15 mL). The mixture was stirred vigorously at 100 °C under inert gas atmosphere for 20 h. After cooling to room temperature (RT), the colored precipitate was filtered off, washed with water and hexane, respectively. A red solid of dimer of $[FPtCl]_2$ was obtained (0.42 g, 78.0%). Then a mixture of the dimer (0.2 g, 0.24 mmol), compound TPA6PicH (0.30 g, 0.60 mmol) and sodium carbonate (90 mg, 0.85 mmol) in 2-ethoxyethanol (15 mL) at about 80–90 °C was stirred vigorously under inert gas atmosphere for 24 h. After cooling to RT, the mixture was extracted with dichloromethane ($CH_2Cl_2$) and the resulting organic layer was dried over anhydrous magnesium sulfate. The solvent was removed and the residue was purified by a dry flash silica gel column using $CH_2Cl_2$ as eluent to gain FPt(TPA6Pic) (0.22 g, 53.0%) as a brown red solid. $^1$H NMR ($CDCl_3$, 400 MHz), $\delta$ (ppm): 9.14–9.15 (d, $J$ = 4.8 Hz, 1H), 8.63–8.64 (d, $J$ = 5.2 Hz, 1H), 7.97–7.99 (d, $J$ = 5.8 Hz, 1H), 7.86–7.89 (t, 1H), 7.65–7.67 (d, $J$ = 5.4 Hz, 1H), 7.52–7.53 (t, 1H), 6.85–7.21 (m, 15H), 6.84–6.86 (d, $J$ = 5.8 Hz, 1H), 6.58–6.59 (t, 1H), 4.42 (s, 2H), 4.16–4.18 (t, 2H), 3.49–3.52 (t, 2H), 1.96–2.03 (m, 2H), 1.90–1.92 (m, 2H), 1.63–1.65 (m, 2H), 1.47–1.50 (m, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ ppm: 170.11, 158.09, 149.89, 147.85, 147.26, 141.39, 139.54, 132.97, 129.20, 128.85, 128.14, 125.12, 124.16, 124.02, 122.70, 114.63, 114.45, 99.50, 70.39, 67.65, 29.16, 28.81, 25.76, 25.53. Anal. Calcd for $C_{42}H_{37}F_2N_3O_4Pt$: C 57.27, H 4.23, N 4.77. Found: C 57.32, H 4.20, N 4.81. MALDI-TOF ($m/z$): calcd for $[M]^+$ 880.24, found $[M]^+$ 880.20.

### 2.3. Synthesis of FPt(OXD6TPA6Pic)

This was prepared according to the synthetic procedure of FPt(TPA6Pic). A brown red solid was obtained with a yield of 36.0%. $^1$H NMR ($CDCl_3$, 400 MHz), $\delta$ (ppm): 9.19–9.20 (d, $J$ = 5.2 Hz, 1H), 8.66–8.68 (d, $J$ = 5.4 Hz, 1H), 8.00–8.06 (m, 5H), 7.85–7.87 (t, 1H), 7.78–7.76 (d, $J$ = 5.8 Hz, 1H), 7.52–7.58 (m, 1H), 7.46–7.48 (d, $J$ = 8.5 Hz, 2H), 7.40–7.42 (d, $J$ = 8.4 Hz, 2H), 7.32–7.34 (d, $J$ = 8.0 Hz, 2H), 7.23–7,27 (t, 4H), 7.16–7.18 (t, 1H), 7.08–7.12 (m, 6H), 7.00–7.02(d, $J$ = 8.8 Hz, 3H), 6.93–6.95 (d, $J$ = 8.4 Hz, 2H), 6.76–6.77 (d, $J$ = 6.4 Hz, 1H), 6.54–6.60 (t, 1H), 4.46 (s, 2H), 4.20–4.21 (t, 2H), 4.01–4.06 (t, 4H), 3.51–3.55 (t, 2H), 2.45 (s, 3H), 1.99–2.05 (m, 2H), 1.84–1.87 (m, 4H), 1.61–1.78 (m, 10H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ ppm: 170.21, 164.37, 164.27, 161.88, 158.41, 150.04, 147.74, 147.22, 146.47, 142.01, 141.33, 139.66, 135.16, 133.01, 132.90, 129.24, 128.89, 128.65, 127.64, 126.80, 124.23, 116.36, 114.98, 114.83, 99.68, 72.71, 70.36, 68.18, 67.84, 29.73, 29.18, 29.14, 26.05, 25.92, 25.49, 21.66. Anal. Calcd for $C_{69}H_{63}F_2N_5O_7Pt$: C 63.39, H 4.86, N 5.36. Found: C 63.42, H 4.87, N 5.32. MALDI-TOF ($m/z$): calcd for $[M]^+$ 1306.43, found $[M]^+$ 1306.38.

### 2.4. Fabrication of PLEDs

The devices were made based on the following standard procedure. The ITO glass substrate was cleaned by ultrasonic bath sequentially in acetone, detergent, deionized water and isopropanol, and baked at 80 °C. A 40 nm-thick layer of poly(ethylendioxy-thiophene):poly(styrene sulfonic acid) (PEDOT:PSS, Baytron P4083, Bayer AG) was spin-coated onto the precleaned ITO-glass substrates after an $O_2$ plasma treatment and dried in a vacuum box for over 8 h. In the PFO-hosted devices, a 40 nm thick layer of PVK (10 mg/mL in dichlorobenzene) was spin-coated on the top of PEDOT and baked at 120 °C for 30 min. Then a mixture of the platinum complex with PVK + PBD (or PFO) was, respectively, spin-coated onto the top of PPEDOT (or PVK) to form the emitting layer from the solution in