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Highly efficient near-infrared emission from binuclear cyclo-metalated platinum complexes bridged with 5-(4-octyloxyphenyl)-1,3,4-oxadiazole-2-thiol in PLEDs

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ABSTRACT

A novel near-infrared-emitting binuclear platinum complex of $(piq)_2Pt_2(\mu\text{-}C_8OXT)_2$ was synthesized and characterized, in which piq is 1-phenylisoquinolinato and C_8OXT is a bridging ancillary ligand of 5-(4-octyloxyphenyl)-1,3,4-oxadiazole)-2-thiol. Its optophysical, electrochemical and electroluminescent characteristics were primary studied. This binuclear platinum complex exhibited an intense UV absorption at about 493 nm from the metal–metal-to-ligand charge transfer transition and a bright near-infrared emission at 721 nm in chloromethane. Using $(piq)_2Pt_2(\mu\text{-}C_8OXT)_2$ as a single dopant, its single-emissive-layer polymer light-emitting devices presented a high-efficiency near-infrared emission peaked at 702 nm with the maximum external quantum efficiency of 6.3% at 7.6 mA cm^{-2}. This work provides an efficient approach to realize high-efficiency near-infrared emission by binuclear platinum complexes.

1. Introduction

Since the first phosphorescent organic light-emitting devices (OLEDs) was reported using 2,3,7,8,12,13,17,18-octaethyl-21H,23H-porphine platinum (II) (PtOEP) as a red-emitting dopant, phosphorescent square-planar platinum (II) complexes have been received a great deal of attention as emitters in OLEDs due to their potential application in both flat-panel displays and solid lighting sources [1]. The high-efficiency visible emission of the red, green, blue and even white have been received from the platinum (II) complexes-based OLEDs [2]. In general, most of the reported platinum (II) complexes are the mononuclear ones and have a potential to aggregate and give the red-shifted excimer emission due to their square-planar configuration [3]. Accordingly, this kind of mononuclear platinum (II) complex attracts an increasing interesting in the near-infrared (NIR) emission [4]. For example, the platinum complexes with porphyrin (or 8-hydroxyquinolate and N^C^N ligands) were developed and exhibited efficient NIR emissions in OLEDs with the maximum external quantum efficiency (*EQE*) of over 10.7% at 720 nm [5].

Compared to the mononuclear platinum complexes, the binuclear ones have an intense metal–metal-to-ligand charge transfer (MMLCT) emission and easily realize long-wavelength red and near-infrared emission by tuning the structure of cyclo-metalated ligands. To date, some binuclear platinum complexes that displayed the long-wavelength orange to red emissions have been reported in OLEDs [6]. Satto group reported a binuclear platinum complex of $(ppy)Pt(\mu\text{-}pyt)_2Pt(ppy)$ as an emitter and exhibited red emission with an external quantum efficiency of 3.4% and a maximum emission peak at 670 nm in an OLED, where ppy is 2-phenylpyridinato-N, $C^{2'}$, and

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pyt is 2-thiopyridyl [7a]. Afterward, Ma group demonstrated another binuclear platinum complexes of (dfppy) Pt(μ-Bu^t-pz)$_2$Pt(dfppy)-based OLEDs with a maximum emission peak at 590 nm and an external quantum efficiency of 6.6%, in which dfppy is 2-(4′,6′-difluorophenyl) pyridinato-N, $C^{2'}$ and Bu^t-pz is 3,5-bis(*tert*-butyl) pyrazole [7b]. However, to our knowledge, few of the binuclear platinum complexes as near-infrared emitting materials have been reported in the OLEDs and polymer light-emitting devices (PLEDs).

In this paper we reported our effort to obtain a high-efficiency near-infrared emitting binuclear platinum (II) complex as a single emitter in PLEDs. The designed binuclear platinum (II) complex consists of a bridging ligand of 5-(4-octyloxyphenyl)-1,3,4-oxadiazole-2-thiolate (C_8OXT) and a common cyclometalated ligand of 1-phenyl-isoquinoline (piq). Its general formula is (piq)Pt(μ-C_8OXT)$_2$Pt(piq). We designed this class of binuclear platinum (II) complex containing an ancillary ligand of 5-aryl-oxadiazole-2-thiol based on the following consideration. Firstly, the C_8OXT is an oxadiazole derivative with excellent electron-transporting property and is expected to improve the optoelectronics property of its binuclear platinum complex. Secondly, the C_8OXT is a bidentate ligand and available to make its platinum complex form a binuclear framework. Thirdly, the resulting binuclear platinum complex of (piq)Pt(μ-C_8 OXT)$_2$Pt(piq) is difficult to construct intermolecular dimers in their neat or doping amorphous thin films due to their steric trammel. Thus, the molecular aggregation and emission annihilation from (piq)Pt(μ-C_8OXT)$_2$Pt(piq) should be efficiently suppressed. Finally, the (piq)Pt(μ-C_8OXT)$_2$Pt (piq) has improved solubility due to the incorporation of an octyloxy group into the bridged ancillary ligand, More importantly, this (piq)Pt(μ-C_8OXT)$_2$Pt(piq) is available to give an emission from the MMLCT, which has significant red-shift compared to that from the metal-to-ligand charge transfer (MLCT) of the mononuclear platinum (II) complexes [8]. Therefore, the (piq)Pt(μ-C_8OXT)$_2$Pt(piq) is expected to provide low-energy near-infrared emission more easily than the mononuclear one. The synthetic route of the (piq)Pt(μ-C_8OXT)$_2$Pt(piq) is shown in Scheme 1. Using (piq)Pt(μ-C_8OXT)$_2$Pt(piq) as a single dopant and a blend of poly (9,9-dioctylflourene) (PFO) and 2-*tert*-butylphenyl-5-biphenyl-1,3,4-oxadiazole (PBD) as a host matrix, we fabricated the PLEDs by solution process and studied the device performances. The device exhibited a near-infrared emission at 706 nm with a maximum external quantum efficiency of 6.3% at 275 mW cm^{-2}. To the best of our knowledge, among the reported near-infrared emitting materials, this binuclear platinum (II) complex of (piq)Pt (μ-C_8OXT)$_2$Pt(piq) displayed the highest external quantum efficiency in the PLEDs up to now [9].

2. Results and discussion

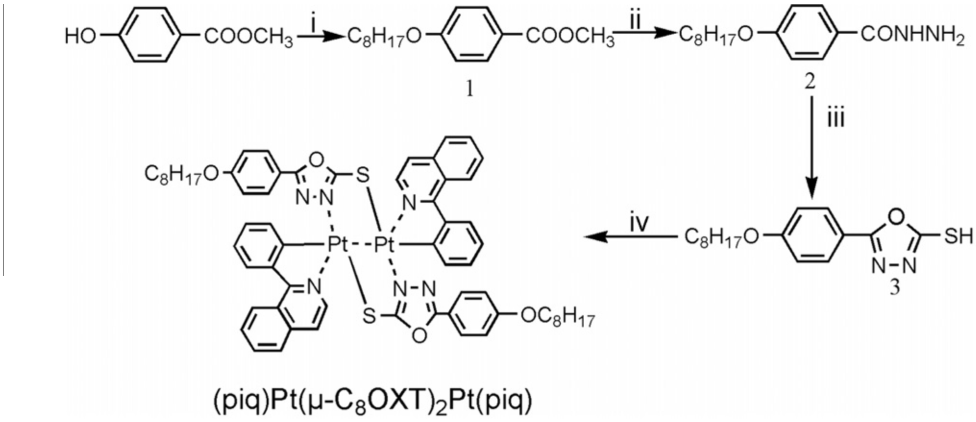
2.1. Synthesis and characterization

The syntheses of compounds **1**, **2** and **3** were prepared according to the literature procedures [10]. The chloride-bridged compound of Pt(piq)(Hpiq)(Cl) was synthesized based on Cho's work [11]. The binuclear platinum (II) complex of (piq)Pt(μ-C_8OXT)$_2$-Pt(piq) was obtained by a debridged reaction between compound **3** and Pt(piq)(H-piq)(Cl) in the presence of sodium carbonate with a moderate yield. Furthermore, it was characterized and confirmed by ^{1}H NMR, ^{13}C NMR, MALDI-TOF mass spectra and element analysis.

2.2. Thermal and photophysical properties

Thermal property of (piq)Pt(μ-C_8OXT)$_2$Pt(piq) was characterized by thermo-gravimetric analysis (TGA). The onset temperature for 5% weight loss (T_d) is 272 °C, which indicates that this binuclear platinum complex has high thermal stability.

The UV–vis absorption, excitation and photoluminescence (PL) spectra of the (piq)Pt(μ-C_8OXT)$_2$Pt(piq) in



Reagent and conditions: (i) $C_8H_{17}Br$, K_2CO_3, KI, acetone, reflux, 24h; (ii) ethanol, hydrazine hydrate, refluxed, 16h; (iii) CS_2, KOH, ethanol, reflux, 4h (iv) Pt(piq)(Hpiq)(Cl), K_2CO_3, dichloromethane, reflux, 18 h.

Scheme 1. Synthetic route to the binuclear platinum complexes.

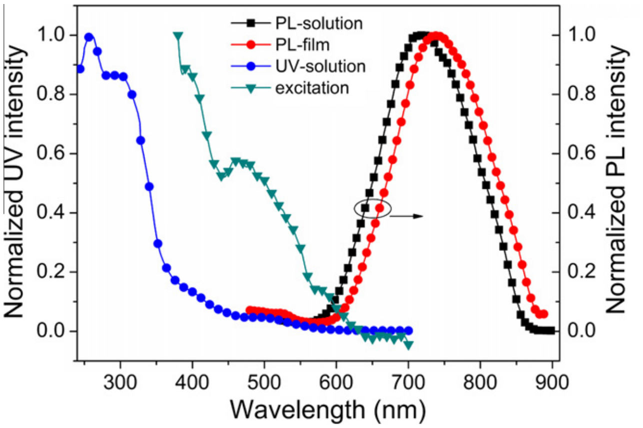


Fig. 1. UV–vis absorption, excitation and emission spectra of the (piq)Pt(μ-C8OXT)$_2$Pt(piq) in DCM and in neat solid film.

dichloromethane (DCM) at 10^{-5} M and room-temperature are shown in Fig. 1. An intense absorption band ($\varepsilon > 2.0 \times 10^4\ M^{-1}\ cm^{-1}$) at high-energy region from 250 nm to 320 nm and a weak absorption band ($\varepsilon < 2.0 \times 10^3\ M^{-1}\ cm^{-1}$) at low-energy region from 450 nm to 550 nm are observed. The intense high-energy absorption band is ascribed to the spin-allowed intraligand π–π^* transitions and the weak low-energy absorption band is assigned to the typical MMLCT transition [12a]. As the corresponding excitation spectrum monitored at 720 nm shows a broad band in the region of 450–550 nm, which is consistent with MMLCT transition, this further evidences the MMLCT transition [12b]. On the other hand, the structured emission peaked at 721 nm is also presented under opto-excitation. Obviously, this binuclear platinum complex gives a near-infrared emission at this time [2b,13].

In order to explore the influence of the aggregating state on emission, the PL spectrum of this binuclear platinum complex in its neat film is simultaneously shown in Fig. 1. A minor red-shifted emission is observed for the platinum complex in the neat film compared to in solution. No excimer emission is exhibited in both PL profiles. This indicates that the aggregating state of (piq)Pt(μ-C$_8$OXT)$_2$Pt(piq) has little effect on the PL profiles. This binuclear platinum complex is very hard to form excimers or dimers in the neat film and solution state. Unlike binuclear platinum complex, the mononuclear platinum (II) complexes often give the emissions from excimers or dimers in the neat films and exhibited different PL profiles in the solution-state in previous works [2f].

The PL quantum yields (Φ_f) of (piq)Pt(μ-C$_8$OXT)$_2$Pt(piq) was measured to be 0.18 using Ru(byp)$_3$(PF$_6$)$_2$ as reference ($\Phi_f = 0.062$) in dichloromethane, which are three times higher than that of the binuclear platinum complex of (ppy)Pt(μ-pz)$_2$Pt(ppy) [6b]. and seven times higher than that of the mononuclear platinum (II) (2-(4′,6′-difluorophenyl)pyridinato-C$^{2'}$,N)(2,4-pentanedionate)[FPt] [2b]. Therefore, this type of binuclear platinum (II) complex bridged with 5-aryloxadiazole-2-thiol displayed better emissive property than the reported mononuclear and binuclear platinum (II) complexes. Therefore, an introduction of the bridging ligand of 5-aryloxadiazole-2-thiol in the binuclear platinum (II) complex has an active effect on the emission.

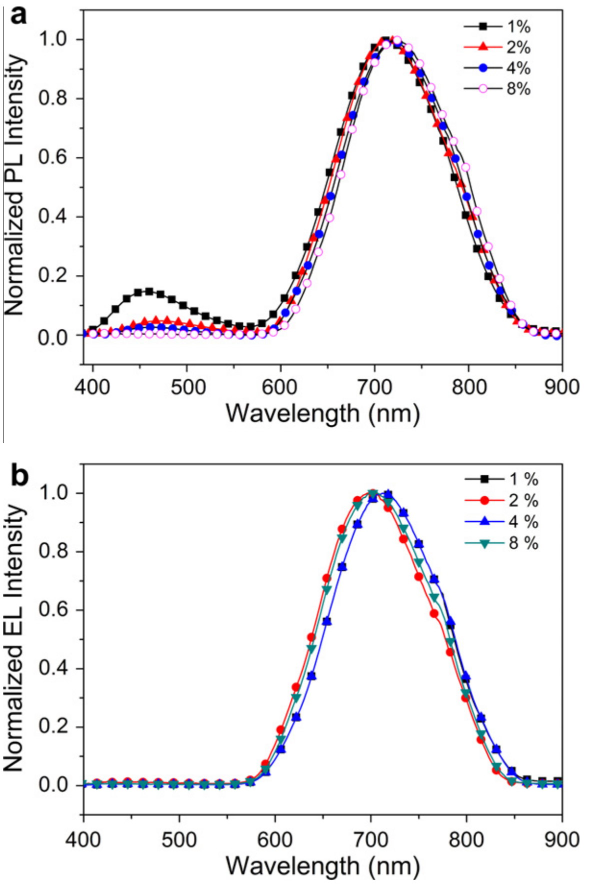


Fig. 2. PL (a) and EL (b) spectra of the (piq)Pt(μ-C$_8$OXT)$_2$Pt(piq)-doped PFO–PBD devices with different dopant concentrations.

Fig. 2a shows PL spectra of the (piq)Pt(μ-C$_8$OXT)$_2$Pt (piq)-doped PFO-PBD films at different dopant concentrations from 1 wt% to 8 wt% at room-temperature. An intense low-energy emission peak is observed at 715 ± 6 nm for all doped films, but a weak high-energy emission peak is only

Table 1
Photophysical, thermal and electrochemical properties of the (piq)Pt(μ-C8OXT)$_2$Pt(piq).

UV[a] nm (ε_{max}/dm^3 mol^{-1} cm^{-1})	PL			E_{HOMO} (eV)[d]	E_{LUMO} (eV)[f]	E_{red} (V)[g]	ΔE (eV)	T_g (°C)[h]	T_d (°C)[h]
	nm[b]	nm[a]	Φ_f[c]						
258(31808), 302(27564), 493(1562)	739	721	0.18	−5.19	−3.03	−1.37	2.16	69	272

[a] Measured in DCM (1×10^{-5} M) at 298 K.
[b] Measured in the neat film.
[c] Ru(bpy)$_3$(PF$_6$)$_2$ in degassed acetonitrile at 298 K ($\Phi_r = 0.062$) was used as reference. Corrections were made due to the change in solvent refractive indices.
[d] $E_{HOMO} = (E_{LUMO} - \Delta E)$ (eV).
[f] $E_{HOMO} = -(E_{red} + 4.4)$ (eV).
[g] The band gap (ΔE) was derived from in CH$_2$Cl$_2$ solution by UV–vis spectrophotometer.
[h] T_g is glass-transition temperature; T_d is decomposition temperature or the onset temperature for 5% weight loss in nitrogen.

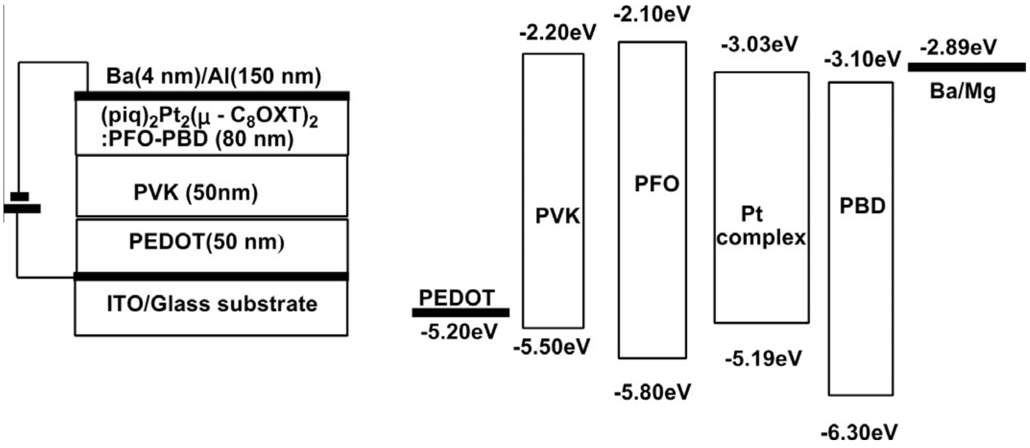


Fig. 3. Energy level diagram of the EL devices and molecular structure of the binuclear platinum complex.

found at about 455 nm in the doped films at 1 wt% and 2 wt% dopant concentrations. This means that an effectively energy transfer from the PFO-PBD host matrix to this dinuclear complex under opto-excitation.

2.3. Electrochemical properties

The electrochemistry of (piq)Pt(μ-C$_8$OXT)$_2$Pt(piq) was examined by cyclic voltammetry, and the electrochemical data are summarized in Table 1. A reversible reductive potential (E_{red}) of −1.37 eV (versus Fc$^+$/Fc) was observed. The lowest unoccupied molecular orbital (LUMO) energy (E_{LUMO}) is calculated according to an empirical formula: $E_{LUMO} = -(E_{red} + 4.4)$ eV [14]. However, the electrochemical oxidation potentials (E_{ox}) of this binuclear platinum complex is typically an irreversible process [7a]. Thus, the E_{ox} had to be estimated based on the UV–vis absorption spectral edge and the E_{red} level [15]. The highest occupied molecular orbital (HOMO) energies (E_{HOMO}) can be calculated according to an empirical formula: $E_{HOMO} = -(E_{ox} + 4.4)$ eV [14]. The resulting E_{HOMO} and E_{LUMO} data are shown in Fig. 3. In order to further understand the EL process, the HOMO and LUMO energy levels for the other used materials in the devices were obtained from the literatures and also presented in Fig. 3 [16]. As the LUMO and HOMO energy levels of PFO reported in literature are −2.1 eV and −5.8 eV, respectively, this binuclear platinum complex exhibits a matched energy levels with the PFO host and is available to play a carrier trap role in the PFO-hosted PLEDs.

2.4. Electroluminescent properties

Fig. 2b shows the electroluminescent (EL) spectra of the binuclear platinum (II) complex-doped devices at different dopant concentrations from 1 wt% to 8 wt%. A near-infrared emission with a maximum peak at 706 nm and a CIE coordinates (0.68, 0.31) is observed for these devices under electric field. Furthermore, these EL spectra are similar to the PL spectrum and independent of the dopant concentrations and driving voltages. What is more, no emissions from the aggregated state and excimer are observed for all these devices. This implies that the emissions of these devices are dominated by the rigid binuclear platinum complex.

The external quantum efficiency (*EQE*) versus current density characteristic of the binuclear platinum complex-doped devices is shown in Fig. 4 at different dopant concentrations from 1 wt% to 8 wt%. The turn-on voltages increase with increasing dopant concentrations from 1 wt% to 8 wt% in these devices. The device performance data are summarized in Table 2 for comparison. This result is consistent with the charge trapping role of the binuclear platinum complex. We note that the *EQE* also increases with increasing dopant concentrations from 1 wt% to 8 wt%. The

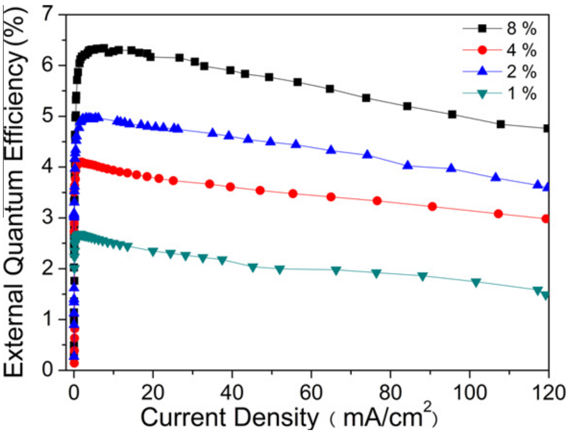


Fig. 4. The external quantum efficiency versus current density characteristics of the (piq)Pt(μ-C_8OXT)$_2$Pt(piq)-doped PFO–PBD devices with different dopant concentrations.

Table 2
Electroluminescence data of the (piq)Pt(μ-C8OXT)$_2$Pt(piq)-doped PLEDs.

	1 wt%	2 wt%	4 wt%	8 wt%
V_{on} (V)	6.1	6.5	9.5	9.8
λ_{EL} (nm)	692	698	712	706
EQE_{max} (%)	2.7	4.1	5.0	6.3
J (mA cm^{-2})[a]	1.8	2.2	5.5	7.6
EQE (%)[b]	1.78	3.15	3.94	5.01
B_{max} (mW cm^{-2})	3229	3228	3230	3229
CIE (x, y)	(0.63, 0.31)	(0.65, 0.31)	(0.66, 0.31)	(0.68, 0.31)

V_{on}: turn-on voltage, λ_{EL}: the maximum EL emission peak, EQE_{max}: the maximum external quantum efficiency.

[a] Current density data at EQE_{max}.

[b] EQE at 100 mA cm^{-2}, B_{max} is maximum brightness, CIE is the Commission International de L'Eclairage.

concentration annihilation here was effectively suppressed. The best device performances were observed in the device at 8 wt% dopant concentration. The maximum *EQE* of 6.3% at 7.6 mA cm^{-2} and a maximum brightness of 3229 mW cm^{-2} at 120.7 mA cm^{-2} were obtained in the device. More importantly, all of these devices showed a gradually decreased external quantum efficiency with an increase of current density. It is suggested that the luminescence and concentration quenching for this binuclear platinum (II) complex was effectively controlled in the devices [17,18]. Based on the PL spectra of the (piq)Pt(μ-C_8OXT)$_2$Pt(piq)-doped PFO-PBD films and the electro-chemical data of the (piq)Pt(μ-C_8OXT)$_2$Pt(piq), we think the good device performance of the (piq)Pt(μ-C_8OXT)$_2$Pt(piq)-doped PLEDs should be related to the charge trapping role of this binuclear platinum complex and the effective energy transfer between the host and guest at the same time.

3. Conclusions

A near-infrared emitting binuclear platinum (II) complex of (piq)Pt(μ-C_8OXT)$_2$Pt(piq) was obtained. The (piq)Pt(μ-C_8OXT)$_2$Pt(piq)-doped device displayed the best device performances with an *EQE* as high as 6.3% at 7.6 mA cm^{-2}. Highly efficient near-infrared emission are realized from the binuclear platinum (II) complex bridged with 5-(4-octyloxyphenyl)-1,3,4-oxadiazole-2-thiolate in PLEDs.

4. Experimental

4.1. General information

^{1}H NMR, ^{13}C NMR spectra were recorded with a Bruker Dex-400 NMR instrument using $CDCl_3$ as a solvent. Elemental analysis was carried out with a Harrios elemental analysis instrument. Mass spectrum was recorded on a Voyager Depro MALDI-TOF spectrometer (Applied Biosystems). UV absorption and fluorescence spectra were recorded with a Shimadzu UV-265 spectrophotometer and a Perkin-Elmer LS-50 luminescence spectrometer, respectively. PL quantum yields (Φ_f) were measured in DCM using Ru(bpy)$_3$(PF$_6$)$_2$ as reference in degassed acetonitrile (Φ_r = 0.062) [19]. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were conducted under a dry nitrogen gas flow at a heating rate of 20 °C min^{-1} on a Perkin-Elmer TGA 7 and a TA-DSC Q100 instruments. Cyclic voltammetry was performed on a CHI660A electrochemical workstation in dry acetonitrile containing n-Bu$_4$NPF$_6$ (0.1 M) with a scan rate of 50 mV S^{-1} at room temperature under argon, using a Pt disk (2 mm diameter) as the working electrode, a Pt wire as the counter electrode, and an aqueous saturated calomel electrode (SCE) as the reference electrode. Ferrocene was used for potential calibration. The PL properties were measured based on the literature [20].

4.2. PLEDs fabrication

The (piq)Pt(μ-C_8OXT)$_2$Pt(piq)-doped PLEDs were made according to our previous work [21]. The device configuration is ITO/PEDOT:PSS, 50 nm/PVK, 40 nm/dopants + PFO-PBD, 80 nm/Ba, 4 nm/Al, 150 nm, where PEDOT:PSS is poly(3,4-ethylene dioxythio-phene):poly(styrenesulfonate) and used as an anode buffer layer at the interface between indium tin oxide (ITO) and hole-transporting layer, PVK is poly(vinylcarbazole) and used as hole-transporting layer. The emitting layer consists of the binuclear platinum complex and a blend of PFO and PBD. The dopant concentrations are varied from 1 wt% to 8 wt%. The PBD weight ratio is 30% in the PFO-PBD blend.

4.3. Synthesis of (piq)Pt(μ-C_8OXT)$_2$Pt(piq)

C_8OXT (125 g, 0.408 mmol) and K_2CO_3 (0.50 g) were added into a DCM solution of Pt(piq)(Hpiq)(Cl) (105 mg, 0.163 mmol). The mixture was refluxed for 18 h, and then evaporated to remove DCM. The resulting mixture was passed through a column of silica gel using DCM as an eluent and crystallized from methanol to give dark-red crystals (110.2 mg, 48%). m.p. 125–127 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, J = 8.60 Hz, 2H), 7.96 (d, J = 8.68 Hz, 4H), 7.82 (d, J = 6.36 Hz, 2H), 7.76 (d, J = 7.56 Hz, 2H), 7.61 (d, J = 5.28 Hz 4H), 7.41 (d, J = 6.48 Hz, 2H), 7.11 (d, J = 7.68 Hz, 2H), 6.95 (d, J = 8.52 Hz, 6H), 6.50 (dd, J = 7.44, 7.32 Hz, 2H), 6.42 (dd, J = 7.40, 7.56 Hz, 2H), 4.00

(dd, J = 6.64, 6.48 Hz, 4H), 1.79 (m, 4H), 1.29 (m, 20H), 0.86 (dd, J = 4.81, 6.80 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.58, 166.55, 164.83, 161.78, 145.93, 142.59, 140.79, 137.54, 134.14, 130.72, 129.05, 128.46, 128.32, 127.98, 127.29, 127.08, 126.97, 124.85, 122.21, 119.64, 116.09, 114.91, 68.31, 31.80, 29.69, 29.21, 29.14, 25.99, 22.65, 14.07. MS (MALDI-TOF for $C_{62}H_{62}N_6$-$O_4Pt_2S_2$), m/z: calcd. 1409.36, found 1408.25 (M^+-1). Anal. calcd. for $C_{62}H_{62}N_6O_4Pt_2S_2$: C, 52.83%; H, 4.43%; N, 5.96%; S, 4.55%; found: C, 52.54%; H, 4.73%; N, 5.46%; S, 4.153%.

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