



## Research paper

# Efficient near-infrared emission of $\pi$ -extended cyclometalated iridium complexes based on pyrene in solution-processed polymer light-emitting diode

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## ABSTRACT

A novel iridium complex grafting hole-transporting triphenylamine (TPA) unit onto cyclometalated ligand, namely t-BuPyrPyTPA)<sub>2</sub>Ir(acac), was successfully synthesized and characterized. The photophysical, electrochemical and DFT/TD-DFT calculation, as well as electroluminescence properties of this iridium complex were fully investigated. Meanwhile, the PLEDs employing (t-BuPyrPyTPA)<sub>2</sub>Ir(acac) as dopant presented stable NIR emission peaked at 697 nm and a shoulder at 764 nm with a highest external quantum efficiency (EQE) of 0.56% at 4 wt% dopant concentration. These results demonstrate that expanding the conjugation length of the ligand is an effective way to achieve NIR emission.

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## 1. Introduction

Recently, great progresses have been made to develop near-infrared (NIR) organic/polymer light-emitting diodes (OLEDs/PLEDs) by using phosphorescent transition metal complexes containing osmium (Os), iridium (Ir), or platinum (Pt) as the metal center [1–7]. For transition metal complexes can easily extend the commonly emission to the deep red/near-infrared (NIR) region by utilizing their low energy emissive triplet states through efficient spin orbit coupling (SOC). However, as predicted by the “energy gap law” [8], compared with that of visible emitters, device performance of NIR emitters is less than satisfactory. So far, the relatively higher external quantum efficiency (EQE) obtained by NIR emitters are always platinum complexes [4–7], especially the  $\pi$ -extended platinum porphyrins (9.2%, 773 nm) [6] excimeric platinum complexes (14.5%, 700 nm) [7] and some other platinum complexes species with metal-metal-to-ligand charge transfer (MMLCT) transition formed by intro- or intermolecular stacking [4,5]. However, most of those devices suffered facile efficiency roll-off with increased current densities that

aggravated by their long excited-state lifetimes and square-planar structure, which obstructing in their practical application [9].

Compared to platinum complexes, d<sup>6</sup> octahedral iridium (III) complexes usually have relatively shorter excited-state lifetimes and less triplet-triplet exciton annihilation, their device efficiencies should be more stable at high currents and high doping concentration [10]. Moreover, in some case, iridium complexes with discrete arylpyridine ligands could possess more efficient spin orbit coupling (SOC) and enhanced phosphorescence quantum yields, as compared to their platinum counterparts containing similar ligands [11]. Emission character of iridium complexes could be tuned either by modification of the ancillary ligands [12,13], or by careful decorating the cyclometalated ligands [14–16]. One successful strategy to reduce the band gap and achieve NIR emission of iridium complexes is to expand the conjugation of the cyclometalated ligand. For instance, Qiu et al reported a strategy to synthesize Ir(pbq-g)<sub>2</sub>acac through ring expansion [17], the effective conjugation length of phenylbenzoquinoline derivatives with fused aromatic rings was significantly increased and exhibited an unexpectedly large red shift over 100 nm in wavelength to the NIR region as compared to iridium complexes based on phenylquinoline [18]. Except for complicated ring expansion, by simply connecting large aromatic rings with ligand of phosphorescent emitter also help to effectively extend the  $\pi$ -conjugation and achieve NIR emission. Meanwhile, Cao et al reported a NIR iridium

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phosphor based on diphenylquinoxaline (dpqx) as cyclometalated ligands, through introducing thienyl appendices at the peripheral side of the dpqx ligand, the (thdpqx)<sub>2</sub>Ir(acac)-based device achieved a maximum external quantum efficiency of 3.4% with the emission peak at 702 nm [3], while the initial molecular (dpqx)<sub>2</sub>Ir(acac) is a deep-red phosphorescent emitter emitting at 677 nm, with a maximum EQE of 5.5% [19].

Triphenylamine (TPA)-based complexes usually possess excellent hole-transporting ability and sufficiently high triplet energy that effectively confine triplet excitons on phosphorescent ligand, commonly used as host materials and phosphorescent dendritic metal complexes [20,21]. In this article, we introduced bulky TPA and tertiary butyl appendices directly into the ligand of a deep red emitter Ir(1-pypr)<sub>2</sub>(acac) [22], and a novel iridium complex (t-BuPyrPyTPA)<sub>2</sub>Ir(acac) with an extended  $\pi$ -conjugation as well as increased energy transfer efficiency and hole-transporting ability was synthesized and characterized. Tertiary butyl was used to increase the solubility of iridium complex. The photophysical, electrochemical and electroluminescence properties of this material were also fully studied. Note that the parent complex Ir(1-pypr)<sub>2</sub>(acac) exhibits an emission peak at 680 nm with a photoluminescence quantum yields (PLQYs) of 0.56% in dichloromethane (DCM) solution [22]. Here, the (t-BuPyrPyTPA)<sub>2</sub>Ir(acac) exhibits an emission peak at 697 nm with a PLQY of 1.92% in similar conditions. The fabricated PLED with a device structure of ITO/PEDOT (40 nm)/PVK:30 wt% OXD-7:4 wt% (t-BuPyrPyTPA)<sub>2</sub>Ir(acac) (60 nm)/TPBi (30 nm)/Ba (4 nm)/Al (100 nm), and exhibited a NIR emission peaked at 698 nm accompanied by a shoulder at 763 nm with a maximum EQE of 0.56% at 2.6 mA cm<sup>-2</sup> and a maximum radiance of 54.3  $\mu$ W cm<sup>-2</sup>.

## 2. Experimental

### 2.1. Measurements and materials

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Bruker Dex-400 NMR instrument using CDCl<sub>3</sub> as a solvent and TMS as an internal standard. Mass spectra (MS) were performed on a Bruker Autoflex TOF/TOF (MALDI-TOF) instrument. The UV-vis absorption and photoluminescence spectra were obtained on a Varian Cray 50 and Perkin-Elmer LS50B luminescence spectrometer, respectively. Excited-state lifetimes were recorded on FLS920 with time-corrected single-photon-counting (TCSPC) measurement. Low temperature phosphorescence spectra were performed in DCM matrix at 77 K on an Edinburgh FLS920 Spectrometer. The  $\Phi_L$  values of iridium complex were measured in degassed CH<sub>2</sub>Cl<sub>2</sub> solutions in accordance with a tris(2,2'-bipyridine) ruthenium(II) standard ( $\Phi_L = 0.062$  in acetonitrile solution at 298 K). Fluorescence quantum yields was calculated using the equation of  $\Phi_s = \Phi_r(\eta_s^2 A_r I_s / \eta_r^2 A_s I_r)$ , where  $\Phi$  stands for the quantum yield,  $\eta$  is the refractive index of the solvent,  $A$  is the absorbance of the sample or the reference at the wavelength of excitation, and  $I$  presents the integrated areas of emission bands, subscript "s" and "r" represents sample and reference, respectively [23]. Cyclic voltammetry was carried out on a CHI600E electrochemical workstation, under nitrogen protection, using tetrabutylammonium hexafluorophosphate (Bu<sub>4</sub>NPF<sub>6</sub>) as electrolyte in acetonitrile solution (0.1 mol/L) at a 100 mV/s scan rate. A micro-platinum spar, a platinum wire and Ag/AgCl electrode were used as the working electrode, counter electrode and reference electrode, respectively.

### 2.2. Theoretical calculations

Density functional theory (DFT) and time-dependent DFT (TD-DFT) were carried out to calculate the ground (singlet) and excited

(triplet) electronic states of the iridium complex. Calculations were carried out using the Gaussian 09 program package at the B3LYP functional [24], with the LANL2DZ basis set for Ir and the 6-31G\* basis set for C, O, N and H. Geometry optimizations of the ground S<sub>0</sub> and the excited T<sub>1</sub> states of the Ir complex were performed using DFT and TD-DFT at the B3LYP/6-31G(d)/LANL2DZ level of theory (spin-unrestricted for T<sub>1</sub>). The electronic density of the molecular orbitals of the ground and excited electronic states of the iridium complex were also performed based on the optimized structures. The calculated absorption spectra were obtained by TD-DFT method with the B3LYP functional.

### 2.3. Device fabrication and characterization

The single-emissive-layer devices were fabricated by spin-coating process with a configuration of ITO/PEDOT (40 nm)/PVK:30 wt% OXD-7:x wt% (t-BuPyrPyTPA)<sub>2</sub>Ir(acac) (60 nm)/TPBi (30 nm)/Ba (4 nm)/Al (100 nm) (x = 2, 4, and 8), where indium tin oxide (ITO) acts as anode, poly(ethylenedioxythiophene)/poly(styrene sulfonate) (PEDOT:PSS) acts as hole-injection layer, Ba and Al are employed as cathode layer, respectively. The emitting layer consists of the (t-BuPyrPyTPA)<sub>2</sub>Ir(acac) dopant and a blend of PVK and OXD-7 used as host matrix. The weight ratio of OXD-7 is 30 wt% in PVK-OXD-7 blend. Dopant concentrations vary from 2 wt% to 8 wt%. Electroluminescence (EL) spectra were recorded on Instaspec IV CCD system (Oriel). Luminance was measured with Si photodiode and calibrated by using PR-705 spectrascan spectrophotometer (Photo Research). I-V-characteristics were taken with Keithley 2400 SourceMeter. All device operation was performed inside a nitrogen filled glove-box.

### 2.4. Synthesis and characterization

All solvents were carefully dried and distilled prior to use. Commercially available reagents were used without further purification. All reactions were performed under nitrogen atmosphere. As shown in Scheme 1, the ligand t-BuPyrPyTPA was synthesized according to our previous work [25]. The target iridium complex of (t-BuPyrPyTPA)<sub>2</sub>Ir(acac) was synthesized through a common two-step coordination reaction with a yield of 56.8%. The target complex was fully confirmed with <sup>1</sup>H NMR, <sup>13</sup>C NMR, and MALDI-TOF mass spectrometric (see Electron Supporting Information, ESI, Figs. S1–S3). The detailed synthesis and characterization of the iridium complex are given in the experimental section.

Synthesis of (t-BuPyrPyTPA)<sub>2</sub>Ir(acac). A mixture of t-BuPyrPyTPA (200 mg, 0.33 mmol) and IrCl<sub>3</sub>·H<sub>2</sub>O (30 mg, 0.095 mmol) were dissolved in 2-ethoxyethanol/H<sub>2</sub>O (12 mL/4 mL) (V/V) and heated at 100 °C for 24 h under nitrogen atmosphere. The suspension was filtered and the red solid was washed with water and a small amount of methanol then dried under high vacuum. The product was directly thrown into the next step without any purification. The compounds Ir(t-BuPyrPyTPA)<sub>2</sub>( $\mu$ -Cl)<sub>2</sub> (128 mg, 0.046 mmol), acetylacetone (120 mg, 1.2 mmol), and Na<sub>2</sub>CO<sub>3</sub> (100 mg) were suspended in 2-ethoxyethanol (25 mL) and stirred at 80 °C for 7 h under nitrogen atmosphere. After cooled to room temperature (RT), the mixture was directly poured into methanol and filtered, evaporated in vacuum to give a red solid, the residue was purified by silica gel column chromatography using PE-DCM (V/V, 2/1) as eluent to afford a deep red solid (78 mg, 56.8%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.07 (s, 1H), 8.90 (d, J = 9.2 Hz, 1H), 8.78 (d, J = 8.4 Hz, 1H), 8.17 (d, J = 8.4 Hz, 1H), 8.06 (d, J = 7.6 Hz, 2H), 7.94 (s, 1H), 7.66 (d, J = 8.4 Hz, 1H), 7.61 (d, J = 7.6 Hz, 2H), 7.40 (d, J = 8.4 Hz, 1H), 7.35–7.27 (t, J = 6.8, 4H), 7.17 (m, 6H), 7.06 (t, J = 7.2 Hz, 2H), 6.97 (s, 1H), 5.36 (s, 0.5H), 1.82 (s, 3H), 1.50 (s, 9H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  185.10, 167.22, 148.40, 147.81, 147.43, 147.11, 146.58, 138.84, 134.01, 133.25, 131.15, 130.18, 129.76,

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