



Novel iridium complexes containing alkylfluorene functionalized picolinic acid ancillary ligand: Synthesis, optophysics and electroluminescence properties



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ARTICLE INFO

Article history:

Received 9 December 2013

Received in revised form

13 March 2014

Accepted 16 March 2014

Keywords:

Iridium complex

Fluorene

Dispersibility

Concentration quenching

Photophysical properties

OLEDs/PLEDs

ABSTRACT

Two novel green-emitting cyclometalated iridium complexes of (Buppy)₂Ir(Tfl-pic) and (Buppy)₂Ir(Brfl-pic) were synthesized and characterized, in which Buppy is 2-(4-*tert*-butylphenyl)pyridine, Tfl-pic is 6-(6'-(9''-octyl-2'',7''-bi(9,9-dioctylfluoren-2-yl)fluoren-9''-yl)hexyloxy) picolinic acid and Brfl is 6-(6'-(2'',7''-di-bromo-9''-octylfluoren-9''-yl)hexyloxy) picolinic acid. Their thermal property, dispersibility and photophysical properties were investigated. Both iridium complexes present intense UV absorption bands and photoluminescence performance in CH₂Cl₂. Single-emissive-layer polymer light-emitting devices using (Buppy)₂Ir(Tfl-pic) and (Buppy)₂Ir(Brfl-pic) as a single dopant and a blend of poly(vinylcarbazole) and 2-(4-biphenyl)-5-(4-*tert*-butyl-phenyl)-1,3,4-oxadiazole as the host matrix were fabricated. The (Buppy)₂Ir(Tfl-pic)-doped devices exhibited a maximum current efficiency of 2.44 cd A⁻¹. As expected, the phase separation and concentration quenching of these iridium complexes in the devices are efficiently suppressed due to appending bulky fluorene derivatives on the picolinic acid unit by a non-conjugated connection.

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Introduction

Organic/polymer light-emitting diodes (OLEDs/PLEDs) have emerged as the most promising next-generation flat-panel display technology in the decades since the pioneering work of Tang et al. [1]. Correspondingly, considerable novel luminescent materials, playing an important role, have been designed and applied. Among these luminescent materials, third-row transition-metal complexes (Ru^{II}-, Os^{II}-, Ir^{III}- and Pt^{II}-) have been significantly developed and exhibited wide application in OLEDs/PLEDs due to their theoretical internal quantum efficiency of 100% [2–9]. Moreover, cyclometalated iridium complex is the most promising candidate of phosphorescent dyes for its high quantum yields and short lifetime of triplet excited states [5,10]. Up to date, several OLEDs/PLEDs based on highly efficient iridium complexes phosphorescent materials were fabricated [11–24].

However, there are still some challenges for developing the high efficiency OLEDs/PLEDs. For example, phase separation between phosphorescent dyes and host materials and concentration quenching are the bottleneck to the OLEDs/PLEDs. In order to address these issues, several groups focused on designing novel cyclometalated ligand with a steric group via incorporating a bulky, rigid camphor-like unit and dendritic architecture into cyclometalated ligand, which is positive to improve dispersibility and suppress the concentration quenching [25–30]. To our astonishment, an iridium complex containing functionalized ancillary ligand, e.g. picolinic acid and acetylacetonone derivatives, remains scarce [31].

With this in mind, in order to investigate the influence of ancillary ligand on the electroluminescent property of iridium complex, we devoted to design a novel ancillary ligand containing a bulky fluorene unit and expected to improve the dispersibility and suppress concentration quenching. As we know, fluorene derivatives have an excellent carrier-transporting ability and thermal stability, highly efficient photoluminescence (PL) and electroluminescence (EL), as well as easy modification in the C-9 position [26,27,32]. Furthermore, the flexible spacer (aliphatic chains) facilitates the self-assembly in supramolecular architectures leading

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to decrease phase separation and increase the dispersibility [32]. What is more, 2-(4-*tert*-butylphenyl)pyridine is the promising cyclometalated ligand due to a steric effects of *tert*-butyl group, which could achieve an improved luminescent efficiency [25]. In this context, we prepared a cyclometalated iridium complex of (Buppy)₂Ir(Tfl-pic) (Scheme 1), incorporating an alkyltrifluorene-based picolinic acid, in which Buppy is 2-(4-*tert*-butylphenyl)pyridine and Tfl-pic is 6-(6'-(9''-octyl-2'',7''-bi(9,9-dioctylfluoren-2-yl)fluoren-9''-yl)hexyloxy)picolinic acid. For comparison, the cyclometalated iridium complex of (Buppy)₂Ir(Brfl-pic) containing dibromofluorene-based picolinic acid was also synthesized in which, Brfl-picH = 6-(6'-(2'',7''-dibromo-9''-octylfluoren-9''-yl)hexyloxy)picolinic acid. Their optophysical, electrochemical and dispersibility properties were investigated. Single-dopant PLEDs, employing iridium complex as guest and a blend of poly(-vinylcarbazole) (PVK) and 2-(4-biphenyl)-5-(4-*tert*-butyl-phenyl)-1,3,4-oxadiazole (PBD) as a host matrix, were fabricated. The EL properties of both novel iridium complexes were explored.

Experimental section

Materials and equipment

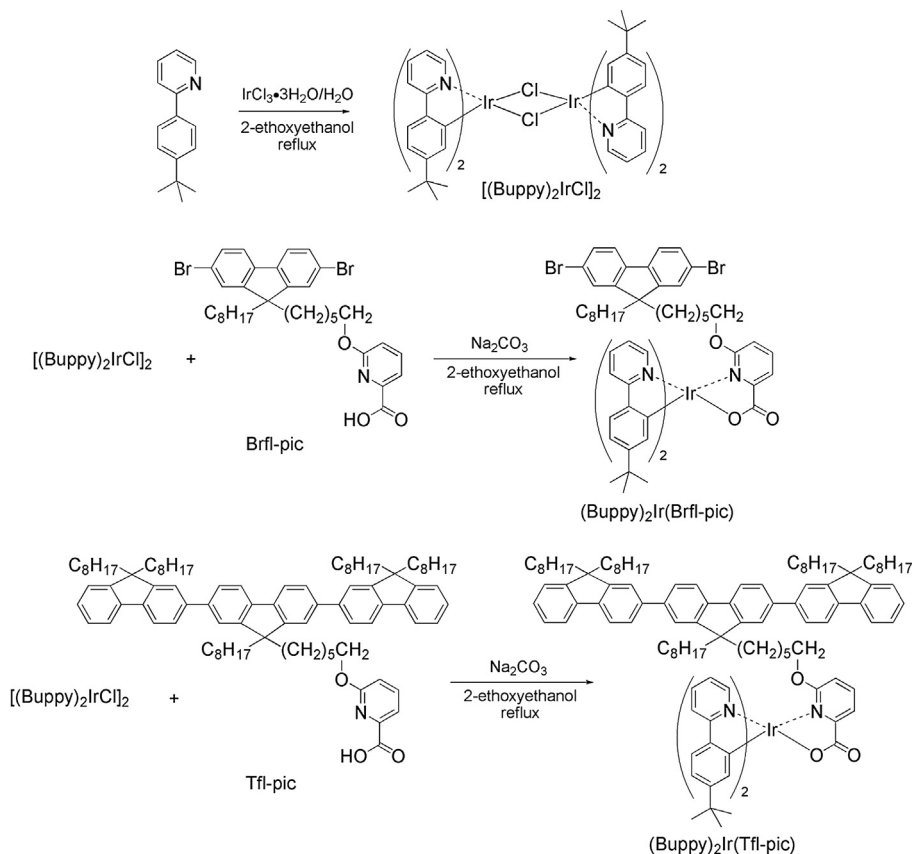
All reagents were purchased from Aldrich, Acros or TCI companies. All reactions and manipulations were carried out under an inert gas atmosphere. ¹H NMR spectra were measured in CDCl₃ solution on a Bruker DPX (400 MHz) NMR spectrometer using tetramethylsilane (TMS) as the internal standard. Cyclic voltammetry was performed on a CHI660A electrochemical work station with a scan rate of 100 mV s⁻¹ at room temperature under argon, in which a Pt disk, Pt plate, and Ag/AgCl electrode were used as

working electrode, counter electrode, and reference electrode in *n*-Bu₄NPF₆ (0.1 M) acetonitrile solution, respectively. For calibration, the redox potential of ferrocene/ferrocenium (Fc/Fc⁺) was measured under the same conditions. PLEDs were fabricated according to the reported procedures [33]. The devices have the following structures: ITO/PEDOT:PSS (50 nm)/iridium complex:PVK + PBD (80 nm)/LiF (1.5 nm)/Al(150 nm). ITO is used as the anode, PEDOT:PSS is used as a hole-injection layer and LiF/Al is employed as a cathode. PBD weight ratio is 30 wt % in the PVK–PBD blend. The doping concentrations for the iridium (III) complex were from 1 wt % to 8 wt % by weight.

Synthesis of (Buppy)₂Ir(Brfl-pic)

To a mixture of IrCl₃·3H₂O (0.30 g, 0.85 mmol) and water (5 mL) was added 2-(4-*tert*-butylphenyl)pyridine (0.55 g, 2.62 mmol) and 2-ethoxyethanol (15 mL). The mixture was refluxed under an inert gas atmosphere for 20 h. After cooled to temperature, the colored precipitate was filtered off and was washed with water, followed by hexane. The resulting dimer of [(Buppy)₂IrCl]₂ was obtained as a yellow solid (0.30 g, 72.3%).

A mixture of the foregoing [(Buppy)₂IrCl]₂ complex (0.20 g, 0.15 mmol), compound Brfl-picH (0.24 g, 0.38 mmol) and Na₂CO₃ (131 mg) were refluxed under an inert gas atmosphere in 2-ethoxyethanol (15 mL) for 15 h. After cooled to room temperature, the mixture was extracted with dichloromethane (CH₂Cl₂) and the combined organic layer was dried over anhydrous magnesium sulfate. The crude product was purified by dry flash silica gel column with petroleum ether (PE)/ethyl acetate (EA) (2:1–0:1) as eluent to gain the target product (0.24 g, 63.2%) as a brown solid. ¹H NMR (CDCl₃, 400 MHz), δ (ppm): 8.70 (d, *J* = 5.4 Hz, 1H), 7.98 (d,



Scheme 1. Synthetic route of the (Buppy)₂Ir(Brfl-pic) and (Buppy)₂Ir(Tfl-pic) complexes.

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