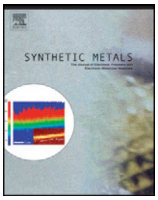
Synthetic Metals 159 (2009) 1308–1312

Contents lists available at ScienceDirect

Synthetic Metals

journal homepage: www.elsevier.com/locate/synmet



Synthesis of bicyclometalated iridium complex containing 1,3,4-oxadiazole-based picolinic acid derivative and its optoelectronic properties in polymer light-emitting devices

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ARTICLE INFO

Article history:
Received 30 July 2008
Received in revised form 19 February 2009
Accepted 23 February 2009
Available online 28 March 2009

Keywords:
Iridium complex
1,3,4-Oxadiazole
Polymer light-emitting device
Photoluminescence
Electrophosphorescence

ABSTRACT

A picolinic acid derivative bearing an 1,3,4-oxadiazole unit and its bicyclometalated iridium complex $(PhOXD)_2Ir(BuPhOXD\text{-}Pic)$ were synthesized and characterized, in which BuPhOXD-Pic is 5-(4′-(5″-(4-*tert*-butylphenyl)-1″,3″,4″-oxadiazol-2″-yl) phenyl) picolinic acid and PhOXD is 2,5-diphenyl-1,3,4-oxadiazole. The optoelectronic properties of this iridium complex were studied in the double-layer polymer light-emitting devices using a blend of poly (9,9-dioctylfluorene) and 5-biphenyl-2-(4-*tert*-butyl) phenyl-1,3,4-oxadiazole as a host matrix. This complex exhibited a maximum luminance efficiency of 7.7 cd/A at 5.6 mA/cm^2 and a peak brightness of 5288 cd/m^2 at 153.7 mA/cm^2 in the devices. Compared to the $(PhOXD)_2Ir(Pic)$ complex, the $(PhOXD)_2Ir(BuPhOXD\text{-}Pic)$ complex displays better optoelectronic properties in the devices. This study provides a convenient way to improve the optoelectronic properties of iridium complexes by modifying an ancillary ligand of picolinic acid (Pic) with an 1,3,4-oxadiazole unit.

1. Introduction

Recently, cyclometalated iridium complexes have attracted great scientific and commercial attention because they have strong spin–orbital coupling of heavy-metal ions and can make full use of both singlet and triplet excitons to emit theoretically with a 100% internal quantum efficiency in organic polymer light-emitting devices (PLEDs) [1–22]. In all reported cyclometalated iridium complexes, the blue-emitting iridium complexes displayed lower efficiency than the green- and red-emitting ones. In order to achieve higher efficient blue-emitting iridium complexes, some ancillary ligands have been developed [16–22]. The reported ancillary ligands contain diketone [16], picolinic acid [17], 1,2,4-triazole [18], tetrazole [19] and tetrakis (1-pyrazolyl) borate [20–22]. However, there is few report on the ancillary ligands tuned directly by functional groups.

As oxadiazole derivatives are good candidates for electron injection and transportation in organic and polymer light-emitting devices [23], they have been introduced into cyclometalated ligands to enhance the optoelectronic properties of their iridium complexes [24–27]. But the effect of oxadiazole units employed in ancillary ligands on the optoelectronic properties of their heteroleptic iridium complexes have not been made clear yet. In order to investigate this effect, an ancillary ligand of picolinic acid is directly modified by an oxadiazole unit in 4-position of pyridyl ring and its heteroleptic iridium complex is made, as well as the optoelectronic properties of this iridium complex are studied in the polymer light-emitting devices using a blend of poly (9,9-dioctylfluorene) (PFO) and 5-biphenyl-2-(4-*tert*-butyl)phenyl-1,3,4-oxadiazole (PBD) as a host matrix. This resulting $(PhOXD)_2Ir(BuPhOXD\text{-}Pic)$ complex is iridium (III) di (2,5-diphenyl-1,3,4-oxadiazole-N, C^2) [5-(4′-(5″-(4-*tert*-butylphenyl)-1″,3″,4″-oxadiazol-2″-yl) phenyl) picolinate]. For comparison, the other $(PhOXD)_2Ir(Pic)$ complex containing an ancillary ligand of picolinic acid (Pic) is also synthesized. The synthetic route of these two iridium complexes is shown in Scheme 1.

2. Experimental

Benzoyl chloride, 4-*tert*-butylbenzoic acid, 4-bromobenzoic acid, 5-bromo picolinic acid, phosphorus (III) oxychloride and hydrazine hydrate were purchased from some reagent plants in China. 2-Ethoxyethanol and iridium trichloride hydrate were obtained from ARCOS. 2,5-Diphenyl-1,3,4-oxadiazole (PhOXD)

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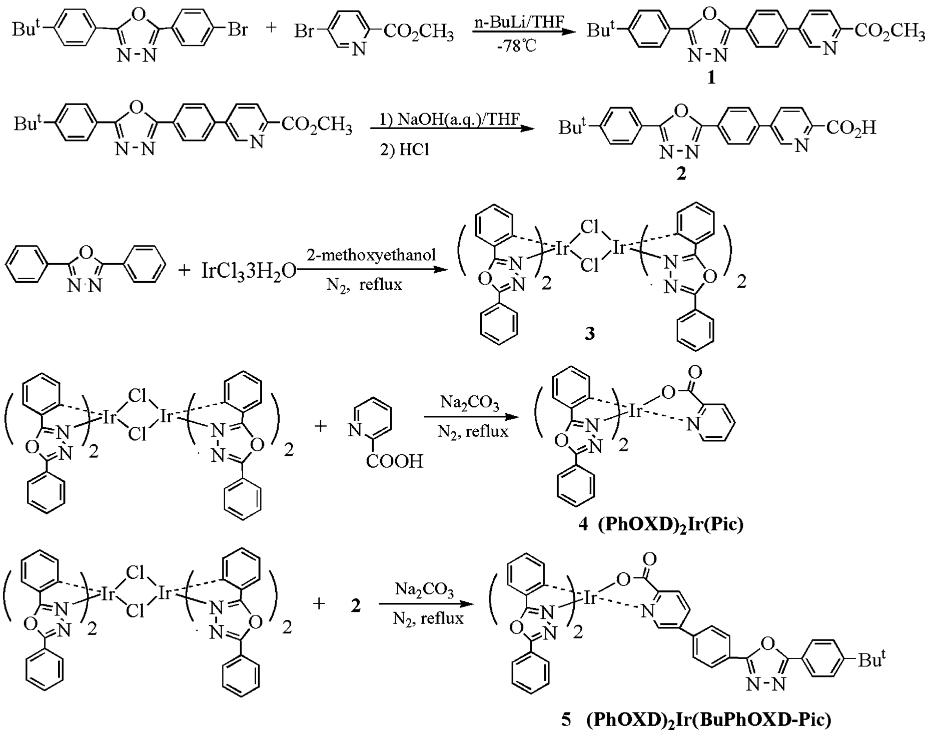
doi:10.1016/j.synthmet.2009.02.034



Scheme 1. Synthetic route of the iridium complexes.

and 2-(4-bromophenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (BuPhOXDPhBr) were synthesized according to the literature procedures [28,29].

All ^{1}H NMR spectra were acquired at a Bruker Dex-400NMR instrument using $CDCl_3$ as solvent. Elemental analysis was performed on a Harrios elemental analysis instrument.

2.1. Synthesis of methyl 5-(4′-(5″-(4-tert-butylphenyl)-1″,3″,4″-oxadiazol-2″-yl) phenyl) picolinate

n-Butyllithium/hexane (14.5 mL,1.60 M, 23.4 mmol) was added dropwise in a solution of 2-(4-bromophenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (8.36 g, 23.4 mmol), anhydrous THF (120 mL) at −78 °C under nitrogen atmosphere in a 500 mL three-neck flask for 1 h under stirring and continued to react for 30 min. A solution of $ZnCl_2$ (3.14 g, 23.4 mmol) and THF (38 mL) was then added into the above mixture at −45 °C. While the reaction temperature rose to room temperature, a solution of methyl 5-bromo-picolinate (5.0 g, 23.4 mmol), $Pd(PPh_3)_4$ (1.2 g, 0.78 mmol) and THF (120 mL) was added dropwise into the mixture and continued to stir for 2 h. The present mixture was distilled under vacuum and the precipitate was formed. The precipitate was collected and washed respectively with THF, anhydrous ethanol and petroleum ether to obtain 2.0 g pale yellow solid with a yield of 20.3%. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ ppm: 9.07 (s, 1H), 8.30 (d, J = 8.14 Hz, 2H), 8.16 (s, 2H), 8.09 (d, J = 6.6 Hz, 2H), 7.82 (d, J = 8.16 Hz, 2H), 7.57 (d, J = 8.20 Hz, 2H), 4.07 (s, 3H), 1.39 (s, 9H). Anal calcd for $C_{25}H_{23}N_3O_3$: C, 72.62%; H, 5.61%; N, 10.16%. Found: C, 72.26%; H, 5.58%; N, 10.12%.

2.2. Synthesis of 5-(4′-(5″-(4-tert-butylphenyl)-1″,3″,4″-oxadiazol-2″-yl)phenyl) picolinic acid

A solution of methyl 5-(4′-(5″-(4-*tert*-butylphenyl)-1″,3″,4″-oxadiazol-2″-yl) phenyl) picolinate (0.74 g, 1.8 mmol), THF (60 mL), ethanol (95%, 10 mL) and NaOH aqueous solution (40%, 20 mL) was heated to 60 °C and stirred for 30 min. Then it was allowed to cool to room temperature and stirred for 30 h. The mixture was evaporated to remove the solvent and mixed with 5 mL water, further was acidified to pH 1 with concentrated HCl. The resulting pale yellow precipitate was filtered, then washed respectively with water, ethanol and petroleum ether to obtain 0.71 g white solid with a yield of 98.3%. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ ppm: 8.93 (s, 1H), 8.36 (s, 2H), 8.31 (s, 2H), 8.11 (d, J = 6.88 Hz, 2H), 7.81 (s, 2H), 7.57 (d, J = 7.44 Hz, 2H), 1.39 (s, 9H). Anal calcd for $C_{24}H_{21}N_3O_3$: C, 72.16%; H, 5.30%; N, 10.52%. Found: C, 71.91%; H, 5.25%; N, 10.46%.

2.3. Synthesis of $(PhOXD)_2Ir(Pic)$

A mixture of iridium trichloride hydrate (183 mg, 0.52 mmol), 2,5-diphenyl-1,3,4-oxadiazole (351 mg, 1.58 mmol), sodium chloride (100 mg, 1.71 mmol) and 2-ethoxyethanol (30 mL) was refluxed for 24 h under nitrogen atmosphere and then evaporated under vacuum to remove a majority of 2-ethoxyethanol. The residue was allowed to cool to room temperature and formed the precipitate. The precipitate was collected, and then washed respectively with water, ethanol and dichloromethane to afford 300 mg chlorine-bridged iridium dimer $(PhOXD)_4Ir_2Cl_2$ as a yellow powder. The dimer was directly used in the following procedure.

A mixture of the $(PhOXD)_4Ir_2Cl_2$ dimer (300 mg, 0.224 mmol), picolinic acid (160 mg, 1.30 mmol), Na_2CO_3 (512 mg, 4.83 mmol) and 2-ethoxyethanol (20 mL) was refluxed for 21 h under nitrogen atmosphere, then was allowed to cool to room temperature and mixed with 4 mL water to present a yellow precipitate. The precipitate was collected, washed with water and dried, then was purified by chromatography using dichloromethane as eluent to provide 190 mg solid as a yellow powder with a yield of 56.0%. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ ppm: 8.30 (s, 1H), 8.19 (d, J = 7.36 Hz, 2H), 8.00 (d, J = 7.32 Hz, 2H), 7.87 (d, J = 3.8 Hz, 2H), 7.67 (d, J = 7.45 Hz,1H), 7.50 (m, 8H), 6.87 (m, 5H), 6.73 (s, 1H). Anal calcd for $C_{34}H_{22}IrN_5O_4$: C, 53.96%; H, 2.93%; N, 9.25%. Found: C, 53.52%; H, 2.85%; N, 9.17%.