



Synthesis, characterization and photophysical properties of iridium complexes with amidinate ligands



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ABSTRACT

Iridium(III) complexes containing 2-(3-fluorophenyl)-4-methylpyridine and amidinate ligands with alkyl chains were synthesized and characterized by UV/Visible, fluorescence, FTIR, NMR spectroscopies and cyclic voltammetry. Thermal properties of the iridium complexes have been investigated using thermogravimetric analysis (TGA). The influence of alkyl side groups on the photoluminescence spectra of iridium complexes has been investigated. The spectra of all complexes show similar emission which results in the blue region. However, the increase in the solution concentrations of the complexes leads to excimer emission in the amidinate complexes. The effects of different polarities of solvents on photophysical properties have been investigated. The HOMO and LUMO energy levels of the complexes are in the range of 5.32–5.35 eV and 2.48–2.51 eV, respectively. The energy states, thermal and electrochemical stability of the complexes are appropriate for their utilization in OLED applications.

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Introduction

Cyclometalated iridium(III) complexes have attracted attention in organic light emitting diodes (OLEDs) [1], chemosensors [2], biological labeling reagents [3] and catalysts [4] due to their stability, photophysical, photochemical, and electrochemical properties. These properties of iridium(III) complexes can be controlled by cyclometalated ligands variations which cause large d-orbital splitting in iridium atom [5]. OLEDs represent one of the most popular application areas of cyclometalated iridium(III) complexes.

OLEDs have gained great interest in full-color display applications because of their high efficiency, high brightness and, resolution and lower cost [6]. White light emitting OLEDs are becoming increasingly successful in lighting applications. However, there is need for improvement of the efficiency, color purity and stability [1]. Developing new molecules is one of the ways to improve performance and stability of an OLED. Iridium complexes show the best efficiency in this area of technology due to their high quantum efficiency and color tunability [7]. These complexes exhibit high triplet quantum yields due to mixing the singlet and the triplet excited states via spin-orbit coupling, leading to high phosphorescence efficiencies [8]. Iridium complexes usually contain cyclometalated ligands such as phenylpyridyl, phenyl-imidazole for OLED applications [9].

The aim of this study is the synthesis of new iridium complexes containing 2-(3-fluorophenyl)-4-methylpyridine and amidinate ligands with alkyl chains to obtain a wide range of emission. In 2-phenylpyridine ligand, electron withdrawing fluoro unit on the phenyl ring and electron donating methyl group on the pyridyl ring increases the HOMO-LUMO gap and emission energy which leads to blue shifted emission band [10]. Furthermore, polar F atoms and 2-phenylpyridine ligands can induce intermolecular interaction and π - π interaction between molecules [11,12]. The donation from π -electrons on the amidinate ligand to iridium metal can provide chelating bonding mode which increases ligand and metal interaction [13,14].

The influences of different solvent polarities and concentrations of the iridium complexes on photophysical properties are discussed. It is found that molecules show excimer emission with increasing solution concentrations and their energy states, electrochemical and thermal stabilities are appropriate for their utilization in OLED applications.

Experimental section

Materials

3-fluorophenylboronic acid, tetrakis (triphenylphosphine) palladium (0), *N,N*-di-tert-butylcarbodiimide, *N,N*-diisopropylcarbodiimide, sodium carbonate, butyllithium solution (1.6 M in

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hexane) were provided from Aldrich. Iridium (III) trichloride hydrate ($\text{IrCl}_3 \cdot n\text{H}_2\text{O}$), 4-bromotoluene, 1-bromo-4-*n*-propylbenzene, 1-bromo-4-*n*-butylbenzene, 4-bromophenol, 2-ethoxyethanol was obtained from Alfa Aesar. 1-Bromo-3, 5-dimethoxybenzene, 2-bromo-4-methylpyridine were purchased from across. All reactions and manipulations of air-sensitive materials were carried out under argon atmosphere using standard Schlenk techniques. Solvents were dried and freshly distilled prior to use. All other chemicals were used as received.

Measurements

UV–Vis and photoluminescence (PL) spectra were recorded in a 1 cm path length quartz cell using a Shimadzu UV-1601 UV–Vis spectrophotometer and Perkin Elmer LS55 fluorescence spectrometers, respectively. Lifetime measurements were obtained using an Edinburgh FLS920P fluorescence spectrophotometer with an EPL-470 diode laser. Infrared spectra were recorded on a Perkin Elmer Spectrum Two FT-IR Spectrometer with a diamond ATR. NMR spectra were recorded at probe temperature on a Varian Mercury AS 400 NMR instrument. The reported chemical shifts are referenced to tetramethylsilane (TMS). Elemental analyses were performed using a Carlo Erba 1106 elemental analyzer. Mass spectra were recorded on Bruker Microflex LT MALDI-TOF MS. The thermal properties of the complexes were obtained by a Shimadzu DTG-60 equipped with TGA unit. Electrochemical data were obtained using a CH Instrument 660 B Model Electrochemical Workstation.

Synthesis and characterization

Synthesis of 2-(3-fluorophenyl)-4-methylpyridine (FMepyy)

2-(3-fluorophenyl)-4-methylpyridine was prepared by a Suzuki coupling reaction using a modified literature procedure [15]. 3-

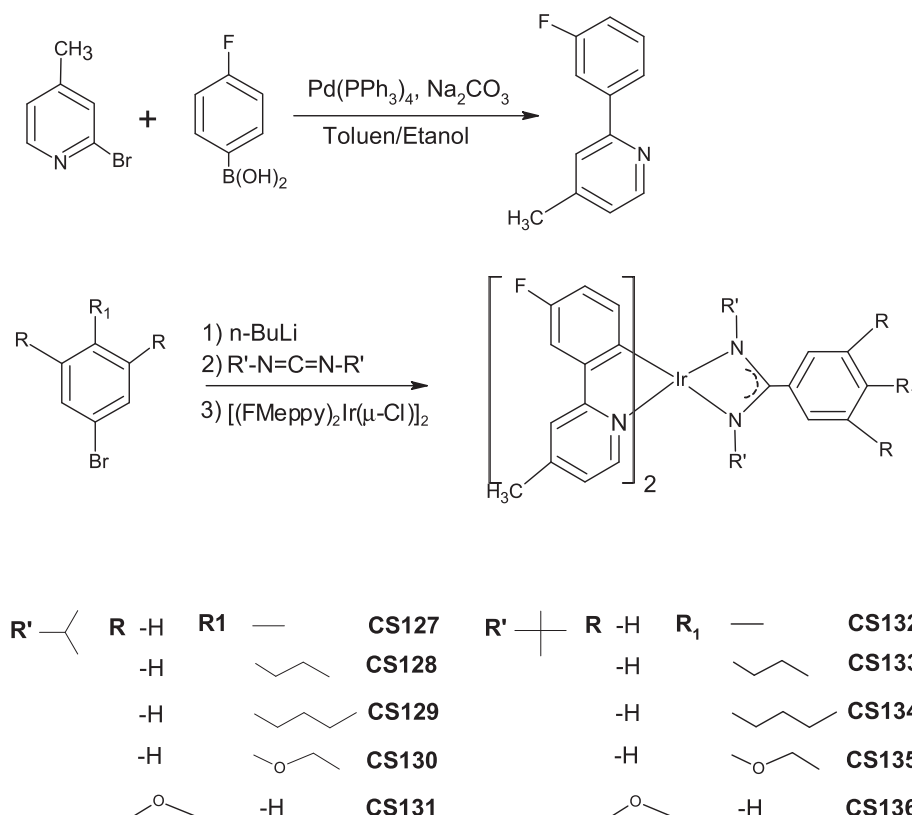
Fluorophenylboronic acid (250 mg, 1.79 mmol) 2-bromo-4-methylpyridine (307.34 mg, 1.79 mmol) and tetrakis (triphenylphosphine) palladium (0) (70.20 mg, 0.061 mmol) were dissolved in a mixture of toluene (12 mL) and ethanol (6 mL). Aqueous sodium carbonate solution (2 N, 12 mL) was added slowly and the reaction mixture was stirred at 80 °C for 24 h. The mixture was cooled to room temperature and extracted with ethyl acetate (2×15 mL). The combined organic phases were dried over anhydrous magnesium sulfate, and were evaporated under vacuum to remove ethyl acetate. The residue was purified by silica gel chromatography using hexane/ethyl acetate (3:1). The collected product was dried under vacuum. The pure product was obtained as yellow liquid with 78% yield. ^1H NMR (CDCl_3) δ ppm: 8.55 (d, $J = 4.8$ Hz, 1H), 7.74 (d, $J = 6.8$ Hz, 1H), 7.70 (dt, $J = 7.6, 0.8$ Hz, 1H), 7.53 (s, 1H), 7.42 (q, 1H), 7.10 (m, 2H), 2.43 (s, 3H).

Synthesis of $[(\text{FMepyy})_2\text{Ir}(\mu\text{-Cl})_2]$

The dimer $[(\text{FMepyy})_2\text{Ir}(\mu\text{-Cl})_2]$ was synthesized according to literature [16]. $\text{IrCl}_3 \cdot \text{XH}_2\text{O}$ (19.1 mg, 0.064 mmol) and 2-(3-fluorophenyl)-4-methylpyridine (30 mg, 0.16 mmol) in a mixture of ethoxyethanol and water (3:1, v/v) were heated at 110 °C for 12 h and then cooled to room temperature. The resulting precipitate was filtered off and washed with diethyl ether and dried to give the yellow solid with 70% yield.

Synthesis of $[\text{Ir}(\text{FMepyy})_2(\text{N,N}'\text{-diisopropyl-4-methyl-benzamide})]$ (CS127)

CS127 was prepared using a modified literature procedure [16]. A solution of butyllithium (1.6 M in hexane, 0.15 mL) was added to a solution of 4-bromotoluene (8.52 mg, 0.050 mmol) in hexane (15 mL). After stirring for 1 h, $\text{N,N}'$ -diisopropylcarbodiimide (6.29 mg, 0.050 mmol) was added dropwise. The solution was stirred for 1 h at room temperature and then the dimer



Scheme 1. The summary of synthetic procedure followed.

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