



Syntheses, crystal structure and photophysical property of iridium complexes with 1,3,4-oxadiazole and 1,3,4-thiadiazole derivatives as ancillary ligands



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ABSTRACT

Six iridium complexes with 2-(2-trifluoromethyl)pyrimidine-pyridine as the main ligand and 2-(5-phenyl-1,3,4-oxadiazol-2-yl)-phenol or 2-(5-phenyl-1,3,4-thiadiazol-2-yl)-phenol derivatives as ancillary ligands were synthesized. The crystal structures of the complexes adopted pseudo-octahedral coordination geometry with the conventional *trans*-N, *cis*-C arrangement of main ligand and the ancillary ligand was connected to iridium center by an N atom from 1,3,4-oxadiazole or 1,3,4-thiadiazole group and an O atom from phenol moiety. Electrochemical study confirmed the ancillary ligand variations have effects on the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels. The density functional theory (DFT) calculations suggested that the frontier orbitals and the electronic properties of the complexes can be manipulated by introducing different ancillary ligands. The compositions of LUMO on the 1,3,4-thiadiazole ancillary ligands are higher than that of 1,3,4-oxadiazole derivatives, and the HOMO - LUMO gaps are also decreased. Therefore, the emissions of the complexes with 1,3,4-thiadiazole ancillary ligands are shift from green to red. The organic light-emitting diodes with **Ir3** and **Ir6** as emitters show maximum current efficiencies of 41.08 and 50.92 cd/A, respectively, with mild efficiency roll-off. This work provides a way to tune the emission and device efficiency of Ir^{III} complexes by introducing of 1,3,4-thiadiazole group in ancillary ligand.

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Introduction

Phosphorescent iridium complexes are the favorable choices for organic light-emitting diodes (OLEDs) due to the high efficiency and stability [1–4]. With active design of ligands, phosphorescent Ir^{III} complexes could exhibit a wide emission range from near ultraviolet to red [5–7]. Recently, many efficient single-color and white OLEDs employing Ir^{III} phosphors as emissive dopants have been reported [5–10]. The frontier molecular orbitals (FMOs), especially the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), are crucial for the photophysical properties [11]. According to the density functional theory calculations, the HOMO is basically centered on the Ir^{III}

metal while the LUMO is primarily localized on the heterocyclic rings of the cyclometalated ligands. Therefore some popular strategies aiming to change the HOMO - LUMO gap are adopted to tune the emission color by changing the substitutions of main ligands [12–17].

Although most ancillary ligands do not make contribution to the lowest excited state directly, but some ancillary ligands with strong fields can lower the HOMO energies of cyclometalated Ir^{III} complexes and tune the emissions. For example, the highly efficient phosphorescent blue emitters of iridium(III)bis(4,6-difluorophenylpyridinato)picolate (FIrpic) [18] and iridium(III) bis(4,6-difluorophenylpyridinato)tetrakis(1-pyrazolyl)-borate (FIR6) [19] used picolate and tetrakis(1-pyrazolyl)-borate as ancillary ligands, respectively. In addition, some ancillary ligands also can alter the energy of the excited state by modifying the electron density at the metal center and affect the carrier mobility of the complexes. Thus, the photophysical, electrochemical, and

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electroluminescent properties of Ir^{III} complexes can be tuned through controlling both the cyclometalated and ancillary ligands.

In our group, we have fabricated some efficient devices using tetraphenylimidodiphosphinate and 1,3,4-oxadiazole derivatives as ancillary ligands, which may improve the electron mobility of the Ir^{III} complexes and benefit their OLEDs performances [20,21]. But because these ancillary ligands have no effect on the HOMO/LUMO states of the Ir^{III} complexes, the emission colors were decided by the cyclometalated ligands. In this study, using the novel 2-(2-trifluoromethyl)pyrimidine-pyridine as the main cyclometalated ligand and 1,3,4-oxadiazole derivatives as ancillary ligands we prepared three green Ir^{III} complexes. When the 1,3,4-oxadiazole derivatives were replaced by the 1,3,4-thiadiazole derivatives, the emission colors were tuned from green to red. The results of the density functional theory (DFT) calculation suggested that the frontier orbitals and electronic properties of the complexes can be manipulated by introducing 1,3,4-thiadiazole derivatives.

Experimental section

General information

All chemicals were commercial purchased without further purification. All the reactions were carried out under nitrogen atmosphere. ¹H NMR spectra were measured on a Bruker AM 500 spectrometer. Electrospray ionization mass spectra (ESI-MS) were obtained with ESI-MS (LCQ Fleet, Thermo Fisher Scientific). The high resolution mass spectra (HR EI-MS) were recorded on an Agilent 6540 UHD Accurate-Mass Q-TOF LC/MS. Cyclic voltammetry (CV) curves were measured at room temperature in deaerated mixed solution (CH₂Cl₂: CH₃CN = 1: 1), using a three-electrode cell equipped with a polished Pt plate as working electrode, a Pt wire as counter electrode, and a AgNO₃ (0.1 mol/L)/Ag in CH₃CN as reference electrode on a CHI600E electrochemical workstation using tetra-*n*-butylammomiumperchlorate (0.1 M) as the supporting electrolyte with a potential scan rate of 0.05 V/s. UV–vis absorption and photoluminescence (PL) spectra were measured on a Shimadzu UV-3100 and a Hitachi F-4600 spectrophotometer at room temperature, respectively.

The luminescence quantum efficiencies were calculated by a comparison of the emission intensities (integrated areas) of a standard sample *fac*-Ir(ppy)₃ and the unknown samples in deaerated CH₂Cl₂ solutions of 5 × 10⁻⁵ mol/L according to the equation [22,23].

$$\Phi_{unk} = \Phi_{std} \left(\frac{I_{unk}}{I_{std}} \right) \left(\frac{A_{std}}{A_{unk}} \right) \left(\frac{\eta_{unk}}{\eta_{std}} \right)^2$$

where Φ_{unk} and Φ_{std} are the luminescence quantum yields of the unknown samples and *fac*-Ir(ppy)₃ solutions ($\Phi_{std} = 40\%$ [22]), respectively. I_{unk} and I_{std} are the integrated emission intensities of the unknown samples and *fac*-Ir(ppy)₃ solutions, respectively. A_{unk} and A_{std} are the absorbance values of the unknown samples and *fac*-Ir(ppy)₃ solutions at their excitation wavelengths, respectively. η_{unk} and η_{std} terms represent the refractive indices of the corresponding acetonitrile (1.345, pure solvent was assumed).

X-ray crystallography

Crystallographic measurements of the single crystals were carried out on a Bruker SMART CCD diffractometer (Bruker Daltonic Inc.) using monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) at room temperature. Cell parameters were retrieved using SMART software and refined using SAINT [24] program in order to reduce

the highly redundant data sets. Data were collected using a narrow-frame method with scan width of 0.30° in ω and an exposure time of 5 s/frame⁻¹. Absorption corrections were applied using SADABS [25] supplied by Bruker. The structures were solved by Patterson methods and refined by full-matrix least-squares on F^2 using the program SHELXS-97 [26]. The positions of metal atoms and their first coordination spheres were located from direct-methods *E*-maps; other non-hydrogen atoms were found in alternating difference.

OLED fabrication and measurement

All OLEDs with the emission area of 0.1 cm² were fabricated on the pre-patterned ITO-coated glass substrate with a sheet resistance of 15 Ω /sq. All chemicals used for devices were sublimed in vacuum (2.2 10⁻⁴ Pa) prior to use. The deposition rate for organic compounds is 1–2 \AA /s. The phosphor and host were co-evaporated from two separate sources. The cathode consisting of LiF/Al was deposited by evaporation of LiF with a deposition rate of 0.1 \AA /s and then by evaporation of Al metal with a rate of 3 \AA /s. The effective area of the emitting diode is 0.1 cm². The characteristics of the devices were measured with a computer controlled KEITHLEY 2400 source meter with a calibrated silicon diode in air without device encapsulation. On the basis of the uncorrected PL and EL spectra, the CIE coordinates were calculated using a test program of the Spectra scan PR650 spectrophotometer.

Syntheses

The syntheses routes of the cyclometalated and ancillary ligands, the corresponding Ir^{III} complexes are shown in Scheme 1. The 2-(5-phenyl-1,3,4-oxadiazol-2-yl)-phenol derivatives (**L1**–**L3**) were reported in our former publication [27].

Syntheses of 2-(2-trifluoromethyl)pyrimidine-pyridine (TPP) ligand [28]

4.4 mmol (1.00 g) 5-Bromo-2-(trifluoromethyl)pyrimidine and 0.22 mmol (0.25 g) tetrakis(triphenylphosphine)palladium(0) were dissolved in 50 mL anhydrous methylbenzene and 4.2 mmol (1.38 g) 2-(tributylstannyl)pyridine was added dropwise, and the solution was refluxed for 24 h in 120 °C. Silica column chromatography purification (petroleum ether: EtOAc = 5:1 as eluent) gave white powder (0.67 g, 2.98 mmol) in 71% yield.

Syntheses of [(TPP)₂Ir(μ -Cl)₂]

IrCl₃·3H₂O (0.49 g, 1.44 mmol) and TPP (0.67 g, 2.98 mmol) were dissolved in 20 mL 2-ethoxyethanol at 60 °C, and then 7 mL H₂O was added. The solution was heated at 100 °C for 14 h. After cooling to room temperature, 20 mL H₂O was added to give yellow precipitate, which was filtered and washed with petroleum ether in 73% yield (0.71 g, 0.55 mmol).

General syntheses of 2-(5-phenyl-1,3,4-thiadiazol-2-yl)-phenol derivatives (**L4** – **L6**)

2-Methoxybenzohydrazide (10 mmol) was dissolved in 50 mL CHCl₃, and benzoyl chloride (10 mmol) was added dropwise for 1 h at room temperature. Then, the solvent was removed under vacuum gave benzoyl-2-methoxybenzohydrazine as pale yellow solid with high yield. Benzoyl-2-methoxybenzohydrazine (3.7 mmol) and phosphorus pentasulfide (4.4 mmol) were stirred in 40 mL dimethylbenzene at 140 °C for 3 h. Water (about 20 mL) was added till no more gas generated. The mixture was washed with water (40 mL × 3 times) and then dried over anhydrous sodium sulfate. Silica column chromatography purification (petroleum ether: EtOAc = 4: 1 as eluent) gave white powder. The powder was

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