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Substituent effect of ancillary ligands on the luminescence of bis[4,6-(di-fluorophenyl)-pyridinato- $N, C^{2'}$]iridium(III) complexes[†]

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Two series of $(dfppy)_2Ir(L_{N^{\wedge}O})$ with different substituents were designed and successfully synthesized and the effect of substitution at the ancillary ligand on the photophysical and electrochemical properties of $(dfppy)_2Ir(L_{N^{\wedge}O})$ were investigated. The results indicate that the electron-donating group of –OMe at $L_{N^{\wedge}O}$ increases the PL quantum efficiencies of $(dfppy)_2Ir(L_{N^{\wedge}O})$ and the electron-withdrawing groups of –CF₃ and –F lower the PL quantum efficiencies.

Introduction

Since the first demonstration of organic light-emitting diode (OLEDs) with organic fluorophores by C. W. Tang in 1987,¹ OLEDs have been developed into an industrially accepted technology for flat panel display and solid-state lighting. Chemists and materials scientists are still deeply involved in discovering and developing novel materials to improve device performance. After the pioneering work by Forrest et al. on using PtOEP as a phosphorescent dopant to greatly improve OLEDs efficiencies in 1998,² a number of heavy metal complexes, such as iridium,^{3–6} platinum,^{2,7–11} ruthenium,^{12–15} osmium,^{16,17} copper^{18,19} *etc.* have been investigated. Among them are iridium(III) complexes most intensively studied and used as dopants in OLED devices^{5,20-23} due to their high quantum efficiencies and broad range of emission colors. While there are many green and red emitters that meet the requirements of device design, the development of blue phosphorescent emitters remains a challenge. Although extensive studies have been carried out and a number of blue emitters have been synthesized and tested, it is a little bit amazing that the initially designed and synthesized iridium(III)bis[4,6-(di-fluorophenyl)-pyridinato- N, C^2]picolinate (FIrpic) is still the most popular blue dopant.^{24–31}

Compared with homoleptic iridium(III) complexes, the synthesis of bis-cyclometalated iridium(III) complexes with ancillary ligands is easier. With the established popularity of FIrpic, a number of works have been focused on the alteration of the ancillary ligand. The ancillary ligands so far explored include

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acetylacetonate,^{32,33} picolinate (pic),^{34,35} picolinamide,³⁶ quinoline-2-carboxylic acid (qui),^{36,37} isoquinoline-1-carboxylic acid,^{36,37} pyrazine-2-carboxylic acid,³⁶ quinoxaline-2-carboxylic acid,³⁶ pyrazine-2-carboxamide,³⁶ *N*-methylsalicylimine,³⁸ diphosphine chelates,³⁹ bis(pyrazolyl)borate ligands,³⁹ triazolate⁴⁰ and tetrazolate derivatives^{41,42} *etc*.

The studies of substitution effects have been focused on the main ligand 2-(2,4-difluorophenyl)pyridine, rather than the ancillary ligands. In designing the ancillary ligands, various steric and electronic effects are taken into consideration.^{20,40,43–46} Furthermore, You *et al.* have demonstrated an inter-ligand energy transfer (ILET) to the "emitting ancillary ligand" in a series of (dfppy)₂Ir($L_{N^{\circ}O}$) complexes (where $L_{N^{\circ}O}$ is an N^{\circ O} chelating ancillary ligand) and provided a novel approach of phosphorescence color tuning.³⁶ The ILET occurs in some (dfppy)₂Ir($L_{N^{\circ}O}$) systems, but not in the well-studied FIrpic. Unfortunately, utilizing the ILET process has not been continued.

It is our objective in this work to systematically compare the effect of substituents of ancillary ligands in two different $(dfppy)_2Ir(L_{N^{\circ}O})$ complexes (Scheme 1), the emission of which are governed by the MLCT³ and an ILET process, respectively. We chose -F, $-CF_3$ and -OMe as the electron-withdrawing and the electron-donating groups, and synthesized two series of $(dfppy)_2Ir(L_{N^{\circ}O})$ complexes, *i.e.* FIrpic-series (MLCT³ mechanism) and FIrqui-series (ILET mechanism). Reported here is how the properties of the photoluminescence (PL), electrochemistry, frontier orbitals and electroluminescence (EL) are influenced by the substituent groups.

Experimental section

Materials

Acetonitrile (spectrophotometric grade) used for measuring UV-Vis absorption and photoluminescent emission spectra was purchased from Sinopharm Chemical Reagent Co., Ltd. Anhydrous acetonitrile (from Acros) and tetrabutylammonium

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Scheme 1 The synthetic route and the chemical structures of $(dfppy)_2 Ir(L_{N^{\wedge}O})$ used in this work.



Scheme 2 The synthetic route of the ligand 4-methoxyquinoline-2-carboxylic acid (qui-OMe) used for synthesizing FIrqui-OMe.

hexafluorophosphate (TBAPF₆, from Fluka) were used for the electrochemical characterization without further treatment. The dicholoro-bridged iridium(III) complex tetrakis(2,4-difluorophenypyridine- C^2 , N)(µ-dichloro)diiridium(III) ([(dfppy)₂Ir(µ-Cl)]₂) was received from SunaTech Inc. Picolinic acid (pic, Alfa Aesar), quinoline-2-carboxylic acid (qui, Alfa Aesar), 5-methoxypicolinic acid (pic-OMe, Fastsyn Inc.), 4-(trifluoromethyl)quinoline-2-carboxylic acid (qui-CF₃, J&K Chemical Ltd) and 6-fluoro-4-(trifluoromethyl)quinoline-2-carboxylic acid (qui-CF₃F, J&K Chemical Ltd) were used as received. 4-methoxyquinoline-2-carboxylic acid (qui-OMe) was synthesized according to Scheme 2.

Measurements

¹H, ¹³C and ¹⁹F NMR spectra were acquired on a VARIAN 400 MHz magnetic resonance spectrometer. The UV-Vis absorption spectra and PL spectra were obtained with a Perkin Elmer Lambda 25 UV/Vis spectrophotometer and a HITACHI F-4600 spectrofluorometer, respectively. Due to oxygen quenching of the photoluminescence of iridium(III) complexes, the acetonitrile solution of $(dfppy)_2Ir(L_{N^O})$ for measuring PL quantum efficiency was prepared in a glove box under nitrogen atmosphere.

The PL quantum efficiencies (Φ) were measured in dilute solutions (10⁻⁵ M) and compared to the standard emitters according to the equation: $\Phi = \Phi_{ref} (I_s/I_{ref})(A_{ref}/A_s)$, where A is the absorbance at the excitation wavelength, I is the integrated intensity of the luminescence and Φ is the PL quantum efficiency. The subscripts s and ref refer to the sample and standard, respectively. Spectrophotometric acetonitrile was deaerated by nitrogen bubbling for 30 min and then stored in a nitrogen glove box. The acetonitrile solutions of $(dfppy)_2 Ir(L_{N \cap O})$ for spectroscopic

characterization were all prepared in glove box under nitrogen atmosphere.

The cyclic voltammetry (CV) was performed with a PARE-STAT 2263 advanced electrochemical system, Princeton Applied Research. Anhydrous acetonitrile was used as the solvent under nitrogen atmosphere and 0.1 mol L^{-1} of TBAPF₆ as the supporting electrolyte. A platinum wire (1 mm in diameter, the electrode area 0.785 mm²) sealed in a PTFE rod was used as the working electrode. A piece of platinum wire and a piece of silver wire were used as counter electrode and quasi-reference electrode, respectively. The potentials were referred to ferrocene/ferrocenium Fc/Fc⁺ redox couple. The potential scan rate in all the experiments was kept at 100 mV s⁻¹.

The EL devices were fabricated by sequentially depositing organic layers using thermal evaporation in one run under high vacuum $(4.5 \times 10^{-4} \text{ Pa})$ onto indium tin oxide (ITO) glass substrates. Prior to use, the substrates were degreased with acetone and cleaned in a UV-ozone chamber for 15 min before it was loaded into the evaporation system. The emitting area was $3 \times 3 \text{ mm}^2$. The thickness of the deposited layer and the evaporation speed of the individual materials were monitored with quartz crystal microbalance monitors. All electrical testing and optical measurements were performed under ambient conditions without further encapsulation. The EL spectra were measured with a Spectra Scan PR655. The current–voltage (*I–V*) and luminance–voltage (*L–V*) relations were characterized with a computer controlled Keithley 2400 Sourcemeter.

Synthesis and characterization

Dimethyl 2-(phenylamino)maleate (1). A solution of phenylamine (50 mmol, 4.7 g) and dimethylacetylene dicarboxylate (50 mmol, 7.1 g) in 180 mL of anhydrous methanol was refluxed for 18 h, and the reaction mixture was roto-evaporated to give the crude product. The pure product **1** was obtained by recrystallization from methanol. Yield: 89%. ¹H NMR (400 MHz, CDCl₃) δ ppm: 9.66 (s, 1 H), 7.30 (m, 2 H), 7.09 (m, 1 H), 6.80–6.92 (m, 2 H), 5.39 (s, 1 H), 3.74 (s, 3 H), 3.69 (s, 3 H). ¹³C NMR (100 MHz, CDCl₃) δ ppm: 169.84, 164.83, 147.96, 140.21, 129.11, 124.20, 120.64, 93.53, 52.75, 52.18.

Methyl 4-hydroxyquinoline-2-carboxylate (2). 1 was added to the solution of diphenyl ether (25 mL) in a 100 mL roundbottomed flask. The reaction mixture was stirred at 250 °C for 4 h. After it was cooled to room temperature, an excess amount of *n*-hexane was added to precipitate the crude solid. After filtration, the solid was washed with ethyl ether 3 times and dried *in vacuo* to provide 3.9 g of gray pale **2**. Yield: 58%. ¹H NMR (400 MHz, CD₃OD) δ ppm: 8.20–8.24 (m, 1 H), 7.82–7.86 (m, 1 H), 7.74–7.77 (m, 1 H), 7.45 (m, 1 H), 6.93 (s, 1 H), 4.03 (s, 3 H).

Methyl 4-methoxyquinoline-2-carboxylate (3). A 250 mL, three-neck round flask was charged with **2** (3.7 g, 18 mmol), K₂CO₃ (3.7 g, 27 mmol), and 100 mL of dimethyl sulfoxide. The reaction mixture was stirred at 70 °C for 1 h, then cooled to 35 °C. Methyl iodide (5.1 g, 36 mmol) was added and the reaction was allowed to continue for another 2 h at 35 °C. The mixture was poured into water (300 mL). The solution was filtrated and the precipitate was washed with water. The desired product (2.7 g) was obtained after drying. Yield: 70%. ¹H NMR (400 MHz, CD₃OD) δ ppm: 8.23–8.26 (m, 1 H), 8.13 (dt, J = 8.4, 0.8 Hz, 1 H), 7.81 (m, 1 H), 7.65 (m, 1 H), 7.62 (s, 1 H), 4.16 (s, 3 H), 4.06 (s, 3 H).

4-Methoxyquinoline-2-carboxylic acid (qui-OMe). To a 50 mL anhydrous methanol solution of **3** (at ice bath temperature) was added 50 mL of aqueous NaOH solution (2 wt.%). After 2 h, the methanol in the reaction mixture was removed by roto-evaporation. The remaining solution was diluted with 100 mL of H₂O, washed with 100 mL of dichloromethane three times, the aqueous phase was acidified with concentrated HCl to pH = 3, then a great deal of precipitate appeared. The desired product (1.6 g, yield: 65.5%) was obtained after filtration. ¹H NMR (400 MHz, CD₃OD) δ ppm: 8.38 (ddd, *J* = 8.4, 1.6, 0.8 Hz, 1 H), 8.29 (dt, *J* = 8.8, 0.8 Hz, 1 H), 8.01 (m, 1 H), 7.82 (s, 1 H), 7.79 (m, 1 H), 4.34 (s, 3 H).

General approach to (dfppy)₂**Ir**($L_{N^{\wedge}O}$). The synthetic route of (dfppy)₂Ir($L_{N^{\wedge}O}$) used in this work is demonstrated on Scheme 1. A solution of dichloro-bridged iridium(III) dimer [(dfppy)₂Ir(μ -Cl)]₂, 2.2 equiv. of the corresponding ancillary ligands and 22 equiv. of Na₂CO₃ in 2-ethoxyethanol (for FIrpic-OMe, FIrpic, FIrqui, FIrqui-CF₃, FIrqui-CF₃F) or xylenes (for FIrpic-F and FIrqui-OMe) was refluxed for 24 h. The solvent was roto-evaporated, the residue chromatographed on a silica gel column with CH₂Cl₂/*n*-hexane (various ratios based on the complex properties) eluent to give the pure product. Yield: 53–80%.

FIrpic-OMe. (Yield: 80%, UPLC purity: >99%). ¹H NMR (400 MHz, CDCl₃) δ ppm: 3.87 (s, 3 H), 5.54–5.57 (dd, J = 8.8, 2.4 Hz, 1 H), 5.81–5.84 (dd, J = 8.8, 2.4 Hz, 1 H), 6.36–6.50 (m, 2 H), 6.96–7.00 (m, 1 H), 7.17–7.21 (m, 1 H), 7.37–7.40 (m, 2 H), 7.44–7.47 (m, 1 H), 7.75–7.80 (m, 2 H), 8.23–8.30

(m, 3 H), 8.74–8.76 (m, 1 H). ¹⁹F NMR (376 MHz, CDCl₃) δ ppm: -108.4 (q, J = 9.0), -109.4 (q, J = 9.0), -111.1 (t, J = 11.3), -111.7 (t, J = 11.3).

FIrpic. (Yield: 75%, UPLC purity: >98%). ¹H NMR (400 MHz, CDCl₃) δ ppm: 8.74 (m, 1 H), 8.34 (ddd, J = 8, 1.6, 0.8 Hz, 1 H), 8.26 (m, 2 H), 7.95 (td, J = 7.6, 1.6 Hz, 1 H), 7.77 (m, 3 H), 7.42 (m, 2 H), 7.18 (m, 1 H), 6.97 (m, 1 H), 6.45 (m, 2 H), 5.83 (dd, J = 8.8, 2.4 Hz, 1 H), 5.56 (dd, J = 8.8, 2.4 Hz, 1 H). ¹⁹F NMR (376 MHz, CDCl₃) δ ppm: -108.4 (q, J = 9.0), -109.3 (q, J = 9.0), -111.0 (t, J = 11.3), -111.6 (t, J = 11.3).

Firpic-F. (Yield: 60%, UPLC purity: >98%). ¹H NMR (400 MHz, CDCl₃) δ ppm: 8.72 (ddd, J = 5.6, 1.6, 0.8 Hz, 1 H), 8.37 (m, 1 H), 8.28 (m, 2 H), 7.80 (m, 2 H), 7.65 (m, 2 H), 7.44 (ddd, J = 5.6, 1.6, 0.8 Hz, 1 H), 7.21 (m, 1 H), 7.01 (m, 1 H), 6.50 (m, 1 H), 6.40 (m, 1 H), 5.83 (dd, J = 8.8, 2.4 Hz, 1 H), 5.54 (dd, J = 8.8, 2.4 Hz, 1 H). ¹⁹F NMR (376 MHz, CDCl₃) δ ppm: -107.9 (q, J = 9.0), -109.0 (q, J = 9.0), -110.6 (t, J = 11.3), -111.4 (t, J = 11.3), -118.3 (t, J = 5.6).

FIrqui-OMe. (Yield: 53%, UPLC purity: >98%). ¹H NMR (400 MHz, DMSO-d₆) δ ppm: 8.48 (ddd, J = 6, 1.6, 0.8 Hz, 1 H), 8.3 (d, J = 8.8 Hz, 1 H), 8.19 (m, 2 H), 8.05 (td, J = 7.6, 1.6 Hz, 1 H), 7.95 (td, J = 8, 1.6 Hz, 1 H), 7.81 (s, 1 H), 7.79 (ddd, J = 5.6, 0.8 Hz, 1 H), 7.58 (m, 2 H), 7.40 (m, 2 H), 7.23 (m, 1 H), 6.85 (m, 2 H), 5.81 (dd, J = 8.4, 2.4 Hz, 1 H), 5.36 (dd, J = 8.4, 2.4 Hz, 1 H), 4.22 (s, 3 H). ¹⁹F NMR (376 MHz, CDCl₃) δ ppm: -108.6 (q, J = 9.0), -109.0 (q, J = 9.0), -111.9 (t, J = 11.3), -111.7 (t, J = 11.3).

FIrqui. (Yield: 65%, UPLC purity: >99%). ¹H NMR (400 MHz, CDCl₃) δ ppm: 5.43 (dd, J = 8.4, 2.4 Hz, 1 H,), 5.93 (dd, J = 8.8, 2.4 Hz, 1 H), 6.42 (m, 2 H), 6.85 (m, 1 H), 7.12 (m, 1 H), 7.36 (m, 1 H), 7.58 (m, 2 H), 7.71 (m, 2 H), 7.89 (m, 2 H), 8.19 (d, J = 8 Hz, 1 H), 8.30 (m, 1 H), 8.42 (d, J = 8 Hz, 1 H), 8.52 (d, J = 8 Hz, 1 H), 8.66 (m, 1 H). ¹⁹F NMR (376 MHz, CDCl₃) δ ppm: -108.4 (q, J = 9.0), -108.8 (q, J = 9.4), -111.8 (t, J = 11.3), -111.6 (t, J = 11.3).

FIrqui-CF₃. (Yield: 62%, UPLC purity: >98%). ¹H NMR (400 MHz, CDCl₃) δ ppm: 5.40 (dd, J = 8.8, 2.4 Hz, 1 H), 5.93 (dd, J = 8.8, 2.4 Hz, 1 H), 6.50 (m, 2 H), 6.90 (m, 1 H), 7.15 (m, 1 H), 7.47 (m, 1 H), 7.60 (m, 1 H), 7.73 (m, 2 H), 7.79 (m, 1 H), 8.10 (d, J = 4.4 Hz, 1 H), 8.20 (m, 2 H), 8.32 (m, 1 H), 8.63 (m, 1 H), 8.85 (s, 1 H). ¹⁹F NMR (376 MHz, CDCl₃) δ ppm: -62.6 (s), -107.8 (q, J = 9.0), -108.4 (q, J = 9.4), -111.4 (t, J = 11.3), -111.3 (t, J = 11.3).

FIrqui-CF₃F. (Yield: 65%, UPLC purity: >98%). ¹H NMR (400 MHz, CDCl₃) δ ppm: 5.39 (dd, J = 8.8, 2.4 Hz, 1 H), 5.92 (dd, J = 8.8, 2.4 Hz, 1 H), 6.50 (m, 2 H), 6.92 (m, 1 H), 7.17 (m, 1 H), 7.25 (m, 1 H), 7.57 (m, 1 H), 7.78 (m, 3 H), 8.16 (m, 2 H), 8.34 (m, 1 H), 8.61 (m, 1 H), 8.87 (s, 1 H). ¹⁹F NMR (376 MHz, CDCl₃) δ ppm: -63.3 (s), -105.5 (m), -107.4 (q, J = 9.0), -108.2 (q, J = 9.4), -110.0 (t, J = 11.3), -111.1 (t, J = 11.3).



Fig. 1 Absorption and emission spectra of $(dfppy)_2 Ir(L_{N^{\circ}O})$ in deaerated acetonitrile solutions (40 μ M for absorption spectra and 10 μ M for emission spectra). (A) FIrpic-OMe, FIrpic and FIrpic-F. (B) FIrqui-OMe, FIrqui-CF₃ and FIrqui-CF₃ F. ε is molar extinction coefficient.

Table 1Photophysical data of $(dfppy)_2 Ir(L_{N^{\wedge}O})$ in acetonitrile

	Absorption, $\varepsilon (10^4 \text{ M}^{-1} \text{ cm}^{-1})$	Emission (365 nm excitation)				
Complex/solvent	$\max(a) \lambda$ (nm)	@365 nm	λ_{\max} (nm)	$I_{\rm s}/I_{\rm ref}$	$A_{\rm s}/A_{\rm ref}$	Φ^{a}
FIrpic-OMe/MeCN	4.66@250, 0.45@374	0.43	471	0.69	0.38	0.73
FIrpic/MeCN	4.21@253, 0.49@374	0.47	471	0.70	0.41	0.68
FIrpic-F/MeCN	4.02@253, 0.48@374	0.46	470	0.44	0.40	0.44
FIrqui-OMe/MeCN	5.72@239, 0.48@378	0.53	532	0.26	0.46	0.23
FIrqui/MeCN	5.90@241, 0.48@376	0.53	566	0.07	0.46	0.06
FIrqui-CF ₃ /MeCN	6.37@246, 0.78@361	0.76	_			_
FIrqui-CF ₃ F/MeCN	5.97@246, 0.70@361	0.68				
fac-Ir(ppy) ₃ /MeCN	4.74@241, 4.49@281, 1.17@374	1.14	516	1.00	1.00	0.40
^a Referred to <i>fac</i> -Ir(ppy)	$\sigma_{\rm ref} = 0.4$) in deaerated acetonitrile.					

Results and discussion

Photophysical properties

To confirm the accuracy of our measurement system for quantum efficiency, we firstly measured the PL efficiency of *fac*-Ir(ppy)₃ which has been well characterized in previous studies.^{38,47,48} The PL quantum efficiency of *fac*-Ir(ppy)₃ obtained is 0.42 using quinine sulfate in 0.5 M sulfuric acid as standard $(\Phi = 0.546)^{47,49,50}$ by our measurement system, which is very close to the value (0.4) reported previously.⁴⁸

The absorption and emission spectra of $(dfppy)_2 Ir(L_{N^{\wedge}O})$ in acetonitrile solutions are shown in Fig. 1. Like other heteroleptic iridium(III) complexes reported before, ${}^{39,43,50-54}$ these iridium(III) complexes have strong intra-ligand absorption bands $(\pi - \pi^*)$ in the UV region (below 300 nm, $\varepsilon > 15\,000 \text{ M}^{-1} \text{ cm}^{-1}$) and a featureless MLCT (δ - π *) transition in the near UV and/or blue end of visible light (350–450 nm, $\varepsilon < 6000 \text{ M}^{-1} \text{ cm}^{-1}$). Except FIrqui-CF₃ and FIrqui-CF₃F, all other iridium(III) complexes have shown strong photoluminescence under the excitation of the lights from the whole range of absorption, indicative of their candidacy as phosphorescent dopants in OLEDs. These iridium(III) complexes are grouped into FIrpic and FIrqui series for convenient comparison and their spectroscopic data are summarized in Table 1. Though the substitutes have no influence on the location of intra-ligand transition $(\pi - \pi^*)$ and MLCT $(\delta - \pi^*)$ transition, there are small differences on the extinction coefficient at π - π^* transition and MLCT (δ - π^*) transition. For FIrpic-OMe, FIrpic and FIrpic-F, though the MLCT (δ - π *) transitions are all located at 374 nm, the extinction coefficients vary slightly from between 4500 M⁻¹ cm⁻¹ and 4900 M⁻¹ cm⁻¹. Compared with relative small range of extinction coefficient at the MLCT (δ - π *) transition, the extinction coefficient at π - π * transition exhibits larger variation range from 40 200 M⁻¹ cm⁻¹ of FIrpic-F to $46\,600 \text{ M}^{-1} \text{ cm}^{-1}$ of FIrpic-OMe. Furthermore, substituting H with the electron-donating group of -OMe increases the extinction coefficient (from 42 100 $M^{-1} \text{ cm}^{-1}$ to 46 600 $M^{-1} \text{ cm}^{-1}$) at π - π * transition while substituting H with the electron-withdrawing group of -F decreases the extinction coefficient (from $42\ 100\ M^{-1}\ cm^{-1}\ to\ 40\ 200\ M^{-1}\ cm^{-1}$), as numerically illustrated in Table 1. The same phenomenon was observed in the FIrqui series, i.e. FIrqui-OMe, FIrqui, FIrqui-CF₃ and FIrqui-CF₃F. The extinction coefficients at MLCT (δ - π *) transition range from 4800 M⁻¹ cm⁻¹ to 7800 M⁻¹ cm⁻¹, while at π - π * the transition range is from 57 200 M^{-1} cm⁻¹ to 63 700 M^{-1} cm⁻¹.

In contrast to the small influence of substituents on the electronic absorption spectra, $(dfppy)_2 Ir(L_{N^{\circ}O})$ exhibited significant variation of the photoluminescence properties, both in color and PL quantum efficiency.

For the FIrpic series as shown in Fig. 1A and Table 1, because the triplet energy level of the ancillary ligand is higher than that of dfppy-centered MLCT³, the emission is mainly attributed to the phosphorescent decay from the MLCT³ state of dfppy, which



Fig. 2 Cyclic voltammograms of 5 mM of FIrpic-OMe (A), FIrpic (B) and FIrpic-F (C) in acetonitrile solutions with 0.1 M TBAPF_{6} .

is clearly demonstrated by You et al.,36 the emission colors of the FIrpic series have no differences. However, the substitution had significant influence on PL quantum efficiency. Substituting H, meta to the nitrogen in picolinic acid with the electronwithdrawing group -F lowered the PL quantum efficiency from 0.68 to 0.44, while incorporating electron-donating substituent -OMe at the same position of picolinic acid enhanced the PL quantum efficiency of FIrpic-OMe from 0.68 to 0.73. For the FIrqui-series, the phosphorescent decay from the triplet state of the ancillary ligand plays a significant role in emission color. Unlike the FIrpic series, the FIrqui series shows dramatic changes in emission color (Fig. 1B and Table 1). Substituting H at the 4-position of qui with the electron-donating group -OMe caused a blue shift of ca. 34 nm compared with the unsubstituted FIrqui. Just as the negative influence of -F to the PL quantum efficiency of FIrpic-F, the PL intensities of FIrqui-CF3 and FIrqui-CF3F are also very weak compared with FIrqui-OMe and FIrqui, which are shown in Fig. 1B.

Electrochemical properties

Cyclic voltammetry (CV) is a useful tool for characterizing redox active substances, from both the kinetics of the electron transfer reaction and the thermodynamics of the electrode–electrolyte interface. Furthermore, CV can provide HOMO/LUMO information of the cyclometalated iridium(III) complexes. To further investigate the influence of the ancillary ligand on the complexes (dfppy)₂Ir(L_{N^O}), the electrochemical properties of (dfppy)₂Ir(L_{N^O}) were studied by cyclic voltammetry and the voltammograms of (dfppy)₂Ir(L_{N^O}) are presented in Fig. 2 and 3. Considering the issue of electrochemical window, dried acetonitrile was chosen as the solvent and all these electrochemical experiments were completed in a glove box, in which the oxygen and water were kept at less than 1 ppm.



Fig. 3 Cyclic voltammograms of 5 mM of FIrqui-OMe (A), FIrqui (B), FIrqui-CF₃ (C), and FIrqui-CF₃F (D) in acetonitrile solutions with 0.1 M TBAPF₆.

As shown in Fig. 2 and 3, the electron-withdrawing substituents of -F and $-CF_3$ have adverse influence on the reversibility of the first reduction wave of $(dfppy)_2Ir(L_{N^O})$. Furthermore, in both FIrpic and FIrqui series, the electron-withdrawing substituents of -F and $-CF_3$ cause an anodic shift at the first reduction potential compared with $(dfppy)_2Ir(L_{N^O})$ with an unsubstituted L_{N^O} . However, the electron-donating substituent of -OMe led to a cathodic shift at the first reduction potential with respect to $(dfppy)_2Ir(L_{N^O})$ with an unsubstituted L_{N^O} (see Table 2). Accordingly, the LUMOs of $(dfppy)_2Ir(L_{N^O})$ with -F and $-CF_3$ substituted L_{N^O} are lower than that with -OMe. For FIrqui series, the electron-donating substituent of -OMe makes the energy gap between HOMO and LUMO (ΔE) larger. This explains the blue shift of emission wavelength from FIrqui to FIrqui-OMe.

Theoretical calculations

To compare the experimentally obtained HOMO/LUMO levels with the theoretical calculation, we have used the B3LYP density functional theory (DFT) to calculate HOMO/LUMO energy levels and the electronic ground states for $(dfppy)_2Ir(L_{N^{\land}O})$. As usually done with cyclometalated iridium(III) complexes,^{55–57}

Table 2 Electrochemical data and energy levels of $(dfppy)_2 Ir(L_{N^{\wedge}O})$ used in this work^a

Complex	$E_{a}^{ox}(V)$	$E_{\text{onset}}^{\text{ox}}(V)$	$E_{\rm c}^{\rm re}({\rm V})$	$E_{\text{onset}}^{\text{re}}(V)$	$HOMO^{b}$ (eV)	$LUMO^{c}$ (eV)	$\Delta E (eV)$
FIrpic-OMe	0.97	0.73	-2.42, -2.69	-2.28	-5.53	-2.52	3.01
FIrpic	0.94	0.79	-2.32, -2.75	-2.19	-5.59	-2.61	2.98
FIrpic-F	0.97	0.85	-2.22, -2.73	-2.09	-5.65	-2.71	2.94
FIrqui-OMe	0.96	0.80	-2.09, -2.61	-1.95	-5.60	-2.85	2.75
FIrqui	0.98	0.84	-1.92, -2.78	-1.80	-5.64	-3.00	2.64
FIrqui-CF ₃	1.04	0.88	-1.56, -2.85	-1.38	-5.68	-3.42	2.26
FIrqui-CF ₃ F	1.05	0.87	-1.50, -2.78	-1.32	-5.67	-3.48	2.19

^{*a*} In acetonitrile solution (0.1 M TBAPF₆) and the electrochemical potentials referred to ferrocene/ferrocenium (Fc/Fc⁺) redox couple. ^{*b*} HOMO = $-(E_{\text{onset}}^{\text{re}} + 4.8)$.



Fig. 4 Contour plots of HOMO and LUMO of $(dfppy)_2 Ir(L_{N^{\wedge}O})$ used in this work.

the 6-31G+(d) basis set was chosen for C, N, H, O, the 6-31G-(d, p) basis set for F, and the LANL2DZ basis set for iridium atom.

As we can see from Fig. 4, all $(dfppy)_2Ir(L_{N^{\land}O})$ complexes have similar electron distributions on HOMOs and LUMOs. HOMOs of $(dfppy)_2Ir(L_{N^{\land}O})$ are assigned to an admixture of the d-orbital of metal and π -orbitals of dfppy while LUMOs are assigned to the π -orbitals of the ancillary ligands. Therefore, it is not surprising that with the change of the ancillary ligands, the LUMOs of $(dfppy)_2Ir(L_{N^{\land}O})$ exhibited much bigger change than the HOMOs. Although there are discrepancies between the theoretical data and the electrochemistry based data, the general tendency of the theoretical series is in line with the experimental series (Fig. 5). As already reflected in the electrochemical study, the electron-donating substituent of –OMe increases the energy level of LUMO, while the electron-donating substituents of –F and –CF₃ decrease the LUMO.

The reason why the pic and qui series demonstrated different effects on the photoluminescence of $(dfppy)_2Ir(L_{N^{\wedge}O})$ can be understood by analyzing the energy gaps ΔE of the ligands dfppy and the ancillary $L_{N^{\wedge}O}$. The calculation of ΔE of these ligands showed the following order: pic-F > pic-OMe > pic > dfppy > qui > qui-CF_3F > qui-CF_3 > qui-OMe. For the FIrpic series, due to the lower ΔE of dfppy compared with that of pic-OMe, pic and pic-F, the energy level of dfppy-centered MLCT³ state plays a major role in the emission color, which explains the very small impact the substitution at ancillary ligands had on the



Fig. 5 Theoretical (black) and experimental (red, determined by cyclic voltammetry) energy levels of $(dfppy)_2 Ir(L_{N^{\wedge}O})$.

Table 3 The electronegativity and energy levels of HOMOs and LUMOs for the ligands dfppy and $L_{N^{\wedge}O}$

Ligand	HOMO (eV)	LUMO (eV)	ΔE^a (eV)	Electronegativity $(\chi) (eV)^b$
dfppy	-6.63	-1.71	4.92	4.17
pic-OMe	-7.25	-1.98	5.27	4.62
Pic	-7.46	-2.25	5.21	4.86
pic-F	-7.92	-2.38	5.54	5.15
qui-OMe	-6.50	-2.13	4.37	4.32
qui	-6.85	-2.36	4.49	4.61
qui-CF ₃	-7.24	-2.84	4.40	5.04
qui-CF ₃ F	-7.40	-2.96	4.44	5.18

^{*a*} ΔE is the energy gap between HOMO and LUMO. ^{*b*} $\chi = -(E_{HOMO} + E_{LUMO})/2.^{56,58}$

emission color. However, compared with dfppy, the qui series have lower ΔE , and thus the emission color is mainly determined by the triplet energy level of ancillary ligand. Consequently, the substitution at ancillary ligands has bigger influence on the emission color.

The average of HOMO and LUMO (calculated and listed also in Table 3) represents the electronegativity of the ligand.⁵⁶ It is evident that all the ancillary ligands in this work have larger electronegativities than the main ligand dfppy. The HOMO electron distributions of $(dfppy)_2Ir(L_{N^{\circ}O})$ are centered on dfppy and the LUMO electron distributions on $L_{N^{\circ}O}$. Such delocalization

Table 4The summary of EL data in this work

Device	Dopant	PL (nm)	EL (nm)	Current efficiency at peak (cd A^{-1})	Current efficiency at 100 cd m^{-2} (cd A^{-1})	$\text{CIE}_{x,y}$
Ι	FIrpic-OMe	471	468	6.00	3.62	(0.16, 0.31)
II	FIrpic	471	468	8.66	3.01	(0.16, 0.31)
III	FIrqui-OMe	532	512, 531	5.21	1.39	(0.29, 0.55)
IV	FIrqui	566	548	6.21	2.51	(0.39, 0.57)



Fig. 6 Performances evaluation of devices I and II. (A) EL spectrum at 9 V, (B) current efficiency-current density characteristics, (C) current-voltage-luminance characteristics.



Fig. 7 The performance of the device III. (A) EL spectrum at 9 V, (B) current efficiency-current density characteristics, (C) current-voltage-luminance characteristics.

modes, *i.e.* HOMOs centered on the ligand with smaller electronegativity and LUMOs on the ligand with larger electronegativity, is consistent with the results of Shi *et al.*⁵⁶

EL properties

Due to their relatively high PL quantum efficiencies, FIrpic-OMe, FIrqui-OMe and FIrqui were chosen as the dopants for fabricating OLED devices. For the purpose of comparison, FIrpic was also used as dopant in this work. Based on their emission colors, two device structures were designed, *i.e.* ITO/NPB (20 nm)/TAPC (20 nm)/mcp : dopant (25 nm, 7%)/3TPYMB (30 nm)/LiF (1 nm)/Al for FIrpic-OMe and FIrpic (devices I and II), ITO/NPB (30 nm)/CBP : dopant (25 nm, 7%)/TPBi (30 nm)/LiF (1 nm)/Al for FIrqui-OMe and FIrqui (devices III and IV), where the hole-transport materials NPB and TAPC stand for N,N'-bis(naphthalen-1-yl)-N,N'-bis(phenyl)-benzidine and 1,1-bis[4-[N,N'-di(p-tolyl)amino]phenyl]cyclohexane,

respectively. The host materials mcp and CBP represent 1,3-bis(9*H*-carbazol-9-yl)benzene and 4,4'-bis(9*H*-carbazol-9-yl)-biphenyl, respectively. The electron-transport materials 3TPYMB^{22} and TPBi are tris(2,4,6-trimethyl-3-(pyridin-3-yl)-phenyl)borane and 1,3,5-tri(1-phenyl-1*H*-benzo[*d*]imidazol-2-yl)phenyl, respectively.

Table 4 shows the numerical data of the performances of the four devices. Between devices I and II, although device I showed a lower maximum current efficiency than device II, at the brightness of 100 cd m⁻², the current efficiency of device I was higher than that of device II (Fig. 6 and Table 4). Both devices demonstrated no obvious difference on the CIE (the 1931 Commission International de L'Eclairage) and EL spectra.

To the best of our knowledge, no OLED devices using FIrqui-OMe and FIrqui as dopants have ever been reported, although FIrqui has been synthesized by You *et al.* The performances of the devices, *i.e.* III and IV are summarized in Table 4 and detailed in Fig. 7 and 8, respectively. For both dopants, we have



Fig. 8 The performance of the device IV. (A) EL spectrum at 9 V, (B) current efficiency-current density characteristics, (C) current-voltage-luminance characteristics.

noticed blue shifts of emission from their solution photoluminescence to their device electroluminescence. Such blue shifts from solution to solid state has been observed before from $(dfbmb)_2$ Ir- $(fptz)^{20}$ and were considered to be due to the aggregation effect.

The overall performances of these devices are not among the best, though the device structures are not the optimized ones. Nevertheless, these materials and data help enrich the OLED materials research and their high PL efficiencies may allow them to be used in other areas, such as bioimaging.⁵⁹

Conclusions

In summary, two series of $(dfppy)_2 Ir(L_{N^{\wedge}O})$ complexes with different substituents at the ancillary ligand, FIrpic- and FIrquiseries representing MLCT³ and ILET emission mechanisms, respectively, were synthesized and characterized. The substitution of the ancillary ligand, qui, has a significant impact on the ILET governed FIrqui-series, while the MLCT³ governed FIrpicseries were not sensitive to the substitution in terms of the emission wavelength. This work also revealed that, in general, the substitution at ancillary ligands has more significant influence on the first reduction potentials and the LUMOs of (dfppy)₂Ir- $(L_{N^{\wedge}O})$. Compared with $(dfppy)_2 Ir(L_{N^{\wedge}O})$ with unsubstituted pic and qui, the electron-withdrawing substituents of -F and -CF₃ cause an anodic shift of the first reduction potential and lead to lower LUMOs, while the electron-donating substituent of -OMe has a contrary effect. Most importantly, the electron-donating substituent of -OMe at $L_{N^{\wedge}O}$ increased the PL quantum efficiency while the electron-withdrawing substituents of -CF₃ and -F at L_{N^O} lowered the PL quantum efficiency.

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