Synthesis of Phenylpyridine Iridium(III) Complexes with N-Heterocyclic Carbene as Ancillary Ligands

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Abstract. In this study, [Ir(2,4-F₂ppy)₂(2-(1,2,4-triazol-1-yl)pyridine)]PF₆ (C₁), [Ir(2,4-F₂ppy)₂(2-(2-(4-dimethylbenzyl)-1,2,4-triazol-1-yl)pyridine)]PF₆ (C₂) and [Ir(2,4-F₂ppy)₂(2-(2-hexyl-1,2,4-triazol-1-yl)pyridine)]PF₆ (C₃) complexes were successfully synthesised by refluxing the mixture of dichloro-bridged iridium(III) dimer, [Ir(2,4-F₂ppy)₂(μ-Cl)]₂ and corresponding triazolium salt containing N-heterocyclic carbene (NHC) as ancillary ligands. ¹H NMR of all complexes display well-resolved signals between 10.00-5.00 ppm assign to proton at the aromatic region for penylpyridine and pyridyltriazole. Spectra of C₂ and C₃ also display signals at aliphatic region (singlets) between 0.80-1.50 ppm that proved the presence of methylbenzyl and hexyl substituent on the pyridyltriazole ring. In addition, IR analysis reported the presence of C=C and C=N stretching of pyridine at range 1570-1470 cm⁻¹ and C-H stretching of aromatic pyridine at 2990-3080 cm⁻¹. Besides, UV-Vis absorption data showed that the low-energy metal-to-ligand charge-transfer (MLCT) band in C₂ (364 nm) is significantly blue-shifted compared to C₁ (375 nm) and C₃ (381 nm). Overall, this study reported the synthesis and spectroscopic study of phenylpyridine Ir(III) complexes with various types of pyridyltriazole (NHC ancillary ligands).

1. Introduction

Transition metal complexes such as Pt(II) [1-2], Re(I) [3], Ru(II) [4], Au(I) [5] and Ir(III) [6,7] of N-Heterocyclic Carbene (NHC) ligands have been the subject of interest in modern materials research due to their rich of photophysical properties and big potential in photonic applications such as a good emissive dopants in organic light emitting (OLEDs) devices[8-10], solar energy conversion [11], electroluminescence [12] and sensors [11]. However, compared to other transition metals, Ir(III) complexes are particularly highly tuneable in the colour of the iridium emission. For instance, while common Ru(II) and Os(II) polypyrindines emit in the red or near-infrared (NIR) region, the emission of Ir(III) complexes can shift from the red to the blue region of the spectrum. Generally, Ir(III) complexes containing 2-phenylpyridine are known to exhibit high triplet quantum yields due to the mixing of the singlet and the triplet excited states via a spin-orbit coupling, leading to high phosphorescence efficiencies [13]. In particular, the emission colour of Ir(III) complexes is particularly sensitive to the substituents on the ligand attached to the central metal [14].
Recent studies have shown that an introduction of neutral pyridine-NHC ligands to the Ir(III) complex can form very strong bonds to the transition metals, which shift the metal-carbene antibonding orbitals to high energy and decreasing or eliminating quenching through the ligand field state. Thus, replacing the pyridyl ring with NHC-based group leads to a significant increase in the Lowest Unoccupied Molecular Orbital (LUMO) energy and increases the emission energy of complexes coordinated to these ligands. Hence, it becomes possible to observe efficient blue or near UV phosphorescence at room temperature from Ir(III) complexes that have cyclometalated NHC based ligands[10]. Although there were many reports on the synthesis and characterisation of cationic Ir(III) complexes, there is no studies on the use of the specific pyridyltriazole derivatives reported. Thus, in this paper we report the synthesis and spectroscopic study of phenylpyridine Ir(III) complexes with various types of pyridyltriazole (NHC ancillary ligands).

2. Experimental section
2.1. Analytical Measurements
$^1$H NMR spectra were recorded at 400 Hz using JEOL, JNM-ECX-500 NMR spectrometer. The FT-IR spectra were measured using Thermo Nicolet Nexus spectrometer in the 4000-600 cm$^{-1}$ regions. UV-Vis absorption spectra were measured in 1 cm path length quartz cell on Cary 60 Agilent Technologies spectrophotometer. Elemental analysis for carbon, hydrogen and nitrogen was carried out by using a CHNO EA 1112 Series Elemental analyser.

2.2. Reagents
All the commercial chemicals and solvents were from reagent quality and were used as received from various suppliers The dimer [Ir(2,4-F$_2$ppy)$_2$(µ-Cl)]$_2$ was prepared according to the literature methods [10].

2.3. Synthesis
2.3.1. Synthesis of [Ir(2,4-F$_2$ppy)$_2$[(2-(1,2,4-triazol-1-yl)pyridine)]PF$_6$(Cl)

2-(1,2,4-triazol-1-yl)pyridine (0.075g, 0.5 mmol, 2.1 equiv), silver(I) oxide (0.07g, 0.29 mmol, 1.2 equiv), and [Ir(2,4-F$_2$ppy)$_2$(µ-Cl)]$_2$ (0.29g, 0.24 mmol, 1.0 equiv) in 12 mL 1,2-dichloroethane were heated to reflux for 18 h. After cooling to ambient temperature, the mixture was filtered through celite to remove silver residues. The filtrate was treated with an aqueous KPF$_6$ solution (55 mg of KPF$_6$ in 40 mL of water per cycle). The combined organic layers were washed with water, dried over Na$_2$SO$_4$, and concentrated in vacuum. The crude product was purified by column chromatography on silica gel using CH$_2$Cl$_2$/acetone (4:1 v/v) as the solvent. After evaporation of the solvent, the pure product obtained was a yellow solid. Yield: 1.27g, 79%. $^1$H NMR (500 MHz, CDCl$_3$): δ 9.91 (1H, d), 9.71 (1H, s), 8.43 (1H, d), 8.30 (1H, t), 8.19 (1H, d), 7.90 (1H, t), 7.90 (1H, t), 7.70 (4H, t), 7.33 (1H, t), 7.09 (1H, t), 6.45 (1H, t), 6.35 (1H, d), 5.82 (1H, d), 5.60 (1H, d). IR: v/cm$^{-1}$ 779 (s, C-H stretch), 1593-1400 (s, C=H, C=N), 3020 (w, C-H from pyridine ring). Anal. Calcd. for C$_{29}$H$_{30}$N$_6$F$_6$Ir: C, 48.33; H, 2.80; N, 11.66%. Found: C, 48.31; H, 2.70; N, 11.61%.

2.3.2. Synthesis of [Ir(2,4-F$_2$ppy)$_2$[(2-(4-dimethylbenzyl)-1,2,4-triazol-1-yl)pyridine)]PF$_6$ (C2)

2-(4-dimethylbenzyl)-1,2,4-triazol-1-yl)pyridine (0.05g, 0.2 mmol, 2.1 equiv), silver(I) oxide (0.027g, 0.12 mmol, 1.2 equiv), and [Ir(2,4-F$_2$ppy)$_2$(µ-Cl)]$_2$ (0.12g, 0.11 mmol, 1.0 equiv) in 12 mL 1,2-dichloroethane were heated to reflux for 18 h. After cooling to ambient temperature, the mixture was filtered through celite to remove silver residues. The filtrate was treated with an aqueous KPF$_6$ solution (55 mg of KPF$_6$ in 40 mL of water per cycle). The combined organic layers were washed with water, dried over Na$_2$SO$_4$, and concentrated in vacuum. The crude product was purified by column chromatography on silica gel using CH$_2$Cl$_2$/acetone (4:1 v/v) as the solvent. After evaporation of the solvent, the pure product obtained was a yellow solid. Yield: 0.09g, 61%. $^1$H NMR (500 MHz, CDCl$_3$): δ 9.90 (1H, s), 8.28 (3H, t), 7.98 (3H, d), 7.98 (3H, t), 7.25 (1H, t) 7.09 (1H, d), 6.98 (1H, d), 6.96 (1H, t), 5.76 (1H, t), 5.50 (1H, t), 2.34 (2H,d), 1.24 (4H, s), 0.92 (3H, t). IR: v/cm$^{-1}$ 824 (s, CH
stretch), 1570-1473 (s, C=H, C=N), 2994 (w, C-H from pyridine ring). Anal. Calcd. for C_{37}H_{30}F_{4}IrN_{6}: C, 53.74; H, 3.66; N, 10.16%. Found: C, 53.68; H, 3.59; N, 10.09%.

2.3. Synthesis of [Ir(2,4-F_{2}ppy)\(_2\)\(2\)-(2-hexyl-1,2,4-triazol-1-yl)pyridine]\PF_{6}(C3)

2-(2-hexyl-1,2,4-triazol-1-yl)pyridine (0.08 g, 0.35 mmol, 8.4 equiv), silver(I) oxide (0.011 g, 0.05 mmol, 1.2 equiv), and [Ir(2,4-F_{2}ppy)\(_2\)(µ-Cl)]\(_2\) (0.05 g, 0.04 mmol, 1.0 equiv) in 12 mL 1,2-dichloroethane were heated to reflux for 18 h. After cooling to ambient temperature, the mixture was filtered through celite to remove silver residues. The filtrate was treated with an aqueous KPF\(_6\) solution (55 mg of KPF\(_6\) in 40 mL of water per cycle). The combined organic layers were washed with water, dried over Na\(_2\)SO\(_4\), and concentrated in vacuum. The crude product was purified by column chromatography on silica gel using CH\(_2\)Cl\(_2\)/acetone (4:1 v/v) as the solvent. After evaporation of the solvent, the pure product obtained was a yellow solid. Yield: 0.19 g, 45%. \(^{1}\)H NMR (500 MHz, CDCl\(_3\)): δ 9.90 (1H, d), 9.71 (1H, s), 8.37 (1H, d), 8.30 (1H, t), 8.20 (1H, d), 7.60 (1H, d), 7.35 (1H, t), 7.34 (t, 1H), 7.10 (1H, s), 6.43 (1H, t), 6.33 (1H, t), 5.82 (1H, d), 5.62 (1H, d), 1.24 (8H, t), 0.85 (5H, d). IR: ν/cm\(^{-1}\) 782 (s, C-H stretch), 1595-1459 (s, C=H, C=N), 3057 (w, C-H from pyridine ring). Anal. Calcd. for C\(_{35}\)H\(_{34}\)F\(_4\)IrN\(_6\): C, 52.10; H, 4.25; N, 10.42%. Found: C, 52.05; H, 4.15; N, 10.36%.

3. Results and Discussion

Complexes of bis(phenylpyridine) iridium(III) pyridyltriazole ligands were successfully synthesised by reacting the dichloro-bridged iridium(III) dimer, [Ir(2,4-F\(_2\)ppy)\(_2\)(µ-Cl)]\(_2\) in 1,2-dichloroethane solvent with the presence of silver oxide which gave [Ir(2,4-F\(_2\)ppy)\(_2\)(2-(2-hexyl-1,2,4-triazol-1-yl)pyridine)]PF\(_6\) (C3). The schematic pathway leading to the phenylpyridine iridium(III) pyridyltriazole complexes was depicted in scheme 1.
Scheme 1. Synthesis of bis(phenylpyridine) iridium(III) pyridyltriazole complexes C1-C3.

In each case, the elemental analysis is consistent with the expected molecular formula. IR spectra exhibit C=N and C=C ring stretching of pyridine for all complexes at 1595-1400 cm$^{-1}$(C1); 1570-1473 cm$^{-1}$(C2); 1595-1473 cm$^{-1}$(C3). In addition, the weak C-H stretching of aromatic pyridine shows at 2990-3080 cm$^{-1}$ for all complexes and for complex C3 indicates the presence of C-H from hexyl substituent [18] and this show that introduction of different ancillary ligand to the complex affected the shift of IR wavenumber to the right or to the left. In general, there is no significant change in IR spectral pattern between the starting dichloro-bridged iridium(III) dimer and the complexes C1C3. The clear comparison for C3 shown in Figure 1.
Figure 1. FT-IR Comparison of complex C3 and the starting dichloro-bridged Ir(III) dimer.

$^1$H NMR spectroscopy used to characterise all three complexes. $^1$H NMR spectra of C1-C3 were recorded in deuterated CDCl$_3$ are presented in Table 1 and Table 2, with their labeling scheme in Figure 2. Assignments of proton resonances for C1-C3 were made by comparison to the $^1$H NMR spectra of dichloro-bridged iridium(III) dimer and their ligands. All the $^1$H NMR spectra display well-resolved signals and a similar pattern to each other in the aromatic region between 10.00 and 5.00 ppm that assigned to penylpyridine and pyridyltriazole proton but slightly different pattern at the aliphatic region due to the ancillary ligand modification. The spectrum of C2 displays 5 well-resolved signals at aliphatic region (singlets) between 1.00-1.50 ppm corresponding to the proton that attached to the aromatic ring in the ancillary ligand, while the spectrum of C3 displays 13 well-resolved signals at aliphatic region (singlets) assigned to the hexane substituent that attached to triazolium. Additionally, the coupling between hydrogen and fluorine (spin $\frac{1}{2}$) is very strong. Therefore, the proton signals of H7 and H8 are split into a triplet because of coupling with two fluorine nuclei [4].

Figure 2. The molecular structure of complexes C1-C3 with their labeling scheme.
Table 1. $^1$H NMR for H1-H12 for C1-C3 and starting dimer in deuterated CDCl$_3$

| Complexes | Structural position (ppm), Group |
|-----------|----------------------------------|
|           | H1     | H2     | H3     | H4     | H5     | H6     | H7     | H8     | H9     | H10    | H11    | H12    |
| C1        | 8.53   | 8.43   | 8.30   | 9.91   | 9.71   | 7.90   | 7.90   | 7.70   | 7.70   | 8.19   | 7.33   |
|           | d      | d      | d      | s      | -      | t      | t      | t      | d      | d      |
| C2        | 8.00   | 7.98   | 7.98   | 8.00   | 9.90   | 8.28   | 8.28   | 8.28   | 7.98   | 7.25   | 8.28   |
|           | d      | d      | t      | s      | s      | s      | t      | t      | t      | d      | d      |
| C3        | 8.57   | 8.37   | 9.30   | 9.90   | 9.71   | 7.80   | 7.80   | 7.80   | 7.60   | 8.20   | 7.10   |
|           | d      | d      | t      | d      | s      | t      | t      | t      | d      | d      |
| Starting  |        |        |        |        |        | 7.90   | 6.90   |         |         | 9.10   | 8.31   |
| dimer     |        |        |        |        |        | t      | t      | -      | -      | d      | t      |

s = singlet, d = doublet, t = triplet

Table 2. $^1$H NMR for H13-H24 for C1-C3 and starting dimer in deuterated CDCl$_3$

| Complexes | Structural position (ppm), Group |
|-----------|----------------------------------|
|           | H13    | H14    | H15    | H16    | H17    | H18    | H19    | H20    | H21    | H22    | H23    | H24    |
| C1        |        |        |        |        |        |        |        |        |        |        |        |        |
|           | 7.09   | 5.82   | 5.60   | 6.35   | 6.45   | -      | -      | -      | -      |
|           | t      | d      | d      | t      | t      | -      | -      | -      | -      |
| C2        |        |        |        |        |        |        |        |        |        |        |        |        |
|           | 7.09   | 6.96   | 6.96   | 5.76   | 5.50   | 6.98   | 2.34   | 7.24   | 0.92   |
|           | d      | d      | t      | t      | t      | t      | s      | s      | s      |
| C3        |        |        |        |        |        |        |        |        |        |        |        |        |
|           | 7.35   | 5.82   | 5.62   | 6.43   | 6.33   | -      | -      | -      | 1.24   |
|           | t      | d      | d      | t      | t      | -      | -      | -      | s      |
| Starting  |        |        |        |        |        |        |        |        |        |
| dimer     |        |        |        |        |        |        |        |        |        |
|           | 6.30   | 5.30   | -      | -      | -      | -      | -      | -      | -      |
|           | t      | d      | -      | -      | -      | -      | -      | -      | -      |

s = singlet, d = doublet, t = triplet

Table 3 shows the comparison of UV/Vis absorption data for C1-C3 in dichloromethane solution at 298K. As with most iridium(III) complexes, the absorption spectra can be divided into two regions; the short wavelength π–π* transitions of the ligands in the UV region, and the longer wavelength metal-to-ligand charge-transfer (MLCT) dπ(M)→π*(L-ligand) transitions in the visible region [6,11,14,16].

Table 3. The summary of UV-Vis spectral data for all the complexes.

| Compound | $\lambda_{\text{max}}$/nm($10^{-3}$)E/M$^{-1}$cm$^{-1}$ |
|----------|------------------------------------------------------|
| [Ir(2,4-F$_2$ppy)$_2$(L1)]PF$_6$ (C1)                | 262 (17), 375(5.7)                                    |
| [Ir(2,4-F$_2$ppy)$_2$(L2)]PF$_6$ (C2)                | 262 (12), 364 (6.6)                                   |
| [Ir(2,4-F$_2$ppy)$_2$(L3)]PF$_6$ (C3)                | 261 (14), 381 (5.6)                                   |

Complexes of C1-C3 show very similar absorption spectra to each other, in which less intense absorptions at lower energy have a mixture of ligand centred (LC) π–π* and metal-to-ligand chargetransfer (MLCT) character ($\epsilon$ between 5500 and 6800 M$^{-1}$ cm$^{-1}$) in the region 360-385 nm [16], and the expected strong π–π* transitions associated with aromatic ligands occur in the UV region. In
particular, the low-energy MLCT band in C2 (364 nm) is significantly blue-shifted compared to C1 (375 nm) and C3 (381 nm). The low-lying transitions in the spectral properties of iridium(III) phenylpyridine complexes are categorised as MLCT transitions, though the metal orbitals have a significant mixture of ligand π character, and the high-energy bands above 280 nm are assigned to the intraligand (IL) π–π* transition of 2-phenylpyridine [14]. The absorption spectra of C1-C3 complexes are shown in Figure 3.

![Absorption spectra of complexes C1-C3 in dichloromethane at 298K](image)

**Figure 3.** Absorption spectra of complexes C1-C3 in dichloromethane at 298K

4. Conclusion
A series of phenylpyridines iridium(III) complexes with various types of pyridyltriazole ancillary ligands were successfully synthesised and characterised to gaining a better understanding into reasons behind the varying of electronic properties. This study demonstrated that complexes of C1-C3 display comparable absorption spectra to each other with a mixture of ligand centred (LC) π–π* and metal-toligand charge-transfer (MLCT) character in the region 364 nm (C2), 375 nm (C1) and 381 nm (C3). Therefore, further photophysical study will be done in order to prove that the luminescence properties of cyclometalated iridium(III) complexes can be tuned by the ligand modification.

5. References
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