

Direct functionalization of the cyclometalated 2-(2'-pyridyl)phenyl ligand bound to iridium(III)

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Abstract

Treatment of $[\text{Ir}(\text{ppy})_2(\mu\text{-Cl})_2]$ and $[\text{Ir}(\text{ppy})_2(\text{dtbpy})][\text{OTf}]$ ($\text{ppy} = 2\text{-}(2'\text{-pyridyl})\text{phenyl}$; $\text{dtbpy} = 4,4'\text{-di-tert-butyl-2,2'-bipyridine}$; $\text{OTf} = \text{triflate}$) with pyridinium tribromide in the presence of Fe powder led to isolation of $[\text{Ir}(4\text{-Br-ppy})(\mu\text{-Br})_2]$ (**1**) and $[\text{Ir}(4\text{-Br-ppy})_2(\text{dtbpy})][\text{OTf}]$ (**2**), respectively. Pd-catalyzed cross-coupling of **2** with $\text{RB}(\text{OH})_2$ afforded $[\text{Ir}(4\text{-R-ppy})_2(\text{dtbpy})][\text{OTf}]$ ($\text{R} = 4'\text{-FC}_6\text{H}_4$ (**3**)), $4'\text{-PhC}_6\text{H}_4$ (**4**), $2'\text{-thienyl}$ (**5**), $4'\text{-C}_6\text{H}_4\text{CH}_2\text{OH}$ (**6**). Treatment of **4** with $\text{B}_2(\text{pin})_2$ ($\text{pin} = \text{pinacolate}$) afforded $[\text{Ir}\{4\text{-(pin)B-ppy}\}_2(\text{dtbpy})][\text{OTf}]$ (**7**). The alkynyl complexes $[\text{Ir}(4\text{-PhC}\equiv\text{C-ppy})_2(\text{dtbpy})][\text{OTf}]$ (**8**) and $[\text{Ir}\{4\text{-Me}_2(\text{OH})\text{C}\equiv\text{C-ppy}\}(4\text{-Br-ppy})(\text{dtbpy})][\text{OTf}]$ (**9**) were prepared by cross-coupling of **2** with $\text{PhC}\equiv\text{CSnMe}_3$ and $\text{Me}_2\text{C}(\text{OH})\text{C}\equiv\text{CH}$, respectively. Ethynylation of $[\text{Ir}(\text{fppy})_2(\text{dtbpy})][\text{OTf}]$ ($\text{fppy} = 5\text{-formyl-2-(2'-pyridyl)phenyl}$) with Ohira's reagent $\text{MeCOC}(\text{N}_2)\text{P}(\text{O})(\text{OEt})_2$ afforded $[\text{Ir}\{5\text{-HC}\equiv\text{C-ppy}\}_2(\text{dtbpy})][\text{OTf}]$ (**10**). The solid-state structures of **2**, **5**, **7**, and **10** have been determined.

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1. Introduction

Iridium(III) complexes containing cyclometalated N^C ligands, notably 2-(2'-pyridyl)phenyl (ppy), have attracted much attention due to their interesting luminescent properties [1]. Of particular interest are Ir(III) bis-ppy complexes that have been used as phosphorescent dopants for organic light-emitting diodes [2], sensors, [3,4] and luminescent labels for biomolecules [5]. In order to develop tailor-made Ir-based luminescent materials and devices, it is desirable to synthesize well-defined polymers based on the $[\text{Ir}(\text{ppy})_2]^+$ building block [6,7].

Organometallic polymers can be prepared by either (i) metal complexation with organic polymers bearing

functional groups in the side chains or (ii) polymerization/copolymerization of pre-functionalized mononuclear metal complexes. The latter approach is of particular interest because a better control of structures and composition of polymers can be achieved. Recently, Arm and Williams synthesized Y-shaped Ir(III)/Ru(II) bimetallic assemblies by cross-coupling of coordinated boronic acid-substituted 2,2'-bipyridine (bpy) ligands with bromo-substituted ppy ligands [8]. Dinuclear Ru(II) complexes with bridging cyclometalated ligands have been prepared by cross-coupling of bromo-substituted Ru(II) cyclometalated complexes with alkynes [9]. These results demonstrate the potential of cross-coupling reactions in the synthesis of well-defined polymeric cyclometalated complexes. This prompted us to investigate the cross-coupling reactions of functionalized Ir(III) bis-cyclometalated complexes. While functionalization of coordinated polypyridyl ligands have been well

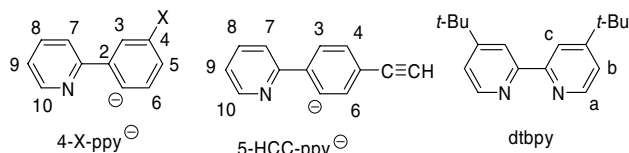
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explored [10], relatively few studies have been made on the ppy analogues [8,9]. Recent works on direct functionalization of ppy ligands bound to Ir(III) [8], Ru(II) [9], and Os(II) [11] suggest that functionalized Ir(III) cyclometalated complexes are easily available and can undergo further chemical transformations. Herein, we describe the bromination of Ir(III) bis-cyclometalated complexes and the Pd-catalyzed cross-coupling of the resulting bromo-substituted Ir(III) ppy complexes. In addition, the synthesis of an Ir(III) ethynylated ppy complex from $[\text{Ir}(\text{fppy})_2(\text{dtbpy})][\text{OTf}]$ (fppy = 5-formyl-2-(2'-pyridyl)phenyl) and Ohira's reagent $\text{MeCOC}(\text{N}_2)\text{-P}(\text{O})(\text{OEt})_2$ is reported.

2. Experimental

2.1. General information

Solvents were purified by standard procedures and distilled prior to use. The ligands 2-phenylpyridine (ppyH) and 2-(2'-pyridyl)benzaldehyde (fppyH) were purchased from Aldrich Ltd. $[\text{Ir}(\text{N}^{\wedge}\text{C})_2\text{Cl}]_2$ [12], $[\text{Ir}(\text{N}^{\wedge}\text{C})_2(\text{dtbpy})][\text{OTf}]$ ($\text{N}^{\wedge}\text{C}$ = ppy [13], fppy [5b]; dtbpy = 4,4'-di-*tert*-butyl-2,2'-dipyridyl; OTf = triflate), and Ohira's reagent $\text{MeCOC}(\text{N}_2)\text{P}(\text{O})(\text{OEt})_2$ [14] were prepared according to literature methods. Hydrogen atom numbering schemes for 4-substituted ppy, 5-substituted ppy, and dtbpy ligands are shown below.



^1H NMR spectra (300 MHz) were recorded on a Bruker ALX 300 spectrometer. Chemical shifts (δ , ppm) were referenced to SiMe_4 . Infrared spectra were recorded on a Perkin-Elmer 16 PC FT-IR spectrophotometer, UV-visible spectra on a Milton Roy Spectronic 2000 spectrophotometer, emission spectra on a Horiba FluoroMax-3 spectrofluorimeter with 5 nm slit width and 0.5 s integration time and mass spectra on a Finnigan TSQ 7000 spectrometer.

2.2. $[\text{Ir}(4\text{-Br-ppy})_2(\mu\text{-Br})]_2$ (**1**)

To a solution of $[\text{Ir}(\text{ppy})_2(\mu\text{-Cl})_2]$ (0.04 mmol) in CH_2Cl_2 (20 cm^3) at 0 °C was added the pyridinium tribromide (77 mg, 0.24 mmol) in MeOH (1 cm^3) and Fe powder (0.5 mg), and the mixture was stirred at room temperature overnight. The solvent was pumped off and residue was washed with Et_2O and extracted with CH_2Cl_2 . Recrystallization from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}/\text{hexane}$

gave yellow crystals. Depending on experimental conditions, a small amount of $[\text{Ir}(4\text{-Br-ppy})_2(\text{py})\text{Br}]$ was also isolated as side product. Yield: 61 mg, 82%. Anal. Calc. for $\text{C}_{44}\text{H}_{28}\text{N}_4\text{Br}_6\text{Ir}_2 \cdot \text{CH}_2\text{Cl}_2 \cdot \text{Et}_2\text{O}$ C, 35.98; H, 2.47; N, 3.43. Found: C, 36.40; H, 2.12; N, 3.20%. ^1H NMR (CDCl_3): δ 5.72 (d, 4H, J = 8.0 Hz, H^6), 6.70 (d, 4H, J = 8.4 Hz, H^5), 6.92 (t, 4H, J = 7.4 Hz, H^9), 7.60 (s, 4H, H^3), 7.83–7.88 (m, 8H, H^7 and H^8), 9.44 (d, 4H, J = 5.6 Hz, H^{10}).

2.3. $[\text{Ir}(4\text{-Br-ppy})_2(\text{dtbpy})][\text{OTf}]$ (**2**)

This compound was prepared similarly as for **1** using $[\text{Ir}(\text{ppy})_2(\text{dtbpy})][\text{OTf}]$ instead of $[\text{Ir}(\text{ppy})_2(\mu\text{-Cl})_2]$. Yield: 110 mg, 93%. Anal. Calc. for $\text{C}_{41}\text{H}_{38}\text{BrF}_3\text{IrN}_4\text{O}_3\text{S} \cdot 2\text{-H}_2\text{O}$: C, 44.29; H, 3.81; N, 5.04. Found: C, 44.10; H, 3.43; N, 4.94%. ^1H NMR (CDCl_3): δ 1.47 (s, 18H, *t*-Bu), 6.11 (d, 2H, J = 8.4 Hz, H^6), 6.99 (d, 2H, J = 8.4 Hz, H^5), 7.17 (t, 2H, J = 6.3 Hz, H^9), 7.41 (d, 2H, J = 5.7 Hz, H^a or H^b), 7.64 (d, 2H, J = 6.0 Hz, H^a or H^b), 7.77 (s, 2H, H^3), 7.76–7.88 (m, 6H, H^7 , H^8 and H^{10}), 8.54 (s, 2H, H^c). MS (FAB): m/z 927 (M^+).

2.4. $[\text{Ir}(4\text{-R-ppy})_2(\text{dtbpy})][\text{OTf}]$ ($\text{R} = 4'\text{-FC}_6\text{H}_4$ (**3**), $4'\text{-PhC}_6\text{H}_4$ (**4**), *th* (*th* = 2'-thienyl) (**5**), $\text{C}_6\text{H}_4\text{CH}_2\text{OH}$ (**6**))

To a solution of **2** (50 mg, 0.05 mmol) in *N,N*-dimethylformamide (3 cm^3) were added $\text{RB}(\text{OH})_2$ (0.19 mmol), K_2CO_3 (26 mg, 0.19 mmol) and $[\text{Pd}(\text{PPh}_3)_4]$ (3 mg), and the mixture was heat at 110 °C under N_2 for 2 h. The volatiles were removed in vacuo and the residue was purified by column chromatography (silica gel, eluant: $\text{CH}_2\text{Cl}_2/\text{MeOH}$ (1:1)) and recrystallized from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}/\text{hexane}$.

3: Yield: 8 mg (15%). Anal. Calc. for $\text{C}_{53}\text{H}_{46}\text{N}_4\text{F}_2\text{Ir} \cdot 2.5\text{H}_2\text{O}$: C, 62.77; H, 5.07; N, 5.52. Found: C, 62.54; H, 5.22; N, 5.42. ^1H NMR (CDCl_3): 1.54 (s, 18H, *t*-Bu), 6.39 (d, 2H, J = 8.4 Hz, H^6), 7.07–7.13 (m, 6H, $\text{F-C}_6\text{H}_4$ and H^5), 7.21 (t, 2H, J = 5.0 Hz, H^9), 7.42 (d, 2H, J = 5.0 Hz, H^a or H^b), 7.49–7.57 (m, 4H, FC_6H_4), 7.62 (d, 2H, J = 5.8 Hz, H^a or H^b), 7.82–7.90 (m, 6H, H^3 , H^7 and H^8), 8.02 (m, 2H, H^{10}), 9.13 (s, 2H, H^c). ^{19}F NMR (CDCl_3): δ -116. MS (FAB): m/z 957 ($\text{M}^+ + 1$).

4: Yield: 13 mg (22%). Anal. Calc. for $\text{C}_{65}\text{H}_{56}\text{F}_3\text{IrN}_4\text{O}_3\text{S} \cdot 2\text{H}_2\text{O}$: C, 62.04; H, 4.81; N, 4.45. Found: C, 62.24; H, 4.81; N, 4.44%. ^1H NMR (CDCl_3): δ 1.48 (s, 18H, *t*-Bu), 6.45 (d, 2H, J = 7.8 Hz, H^6), 7.18 (t, 2H, J = 5.0 Hz, H^9), 7.37 (d, 2H, J = 7.4 Hz, H^5), 7.43–7.48 (m, 6H, dtbpy and PhC_6H_4), 7.63–7.71 (m, 16H, PhC_6H_4), 7.84 (t, 2H, J = 7.2 Hz, H^8), 7.93 (m, 4H, H^3 and H^7), 8.05 (d, J = 7.8 Hz, 2H, H^{10}), 8.57 (s, 2H, H^c). MS (FAB): m/z 1074 ($\text{M}^+ + 1$).

5: Yield: 22 mg (44%). Anal. Calc. for $\text{C}_{49}\text{H}_{44}\text{F}_3\text{IrN}_4\text{O}_3\text{S}_3 \cdot 2\text{H}_2\text{O}$: C, 52.63; H, 4.33; N, 5.01. Found: C,

52.53; H, 4.26; N, 5.30%. ^1H NMR (CDCl_3): δ 1.54 (s, 18H, *t*-Bu), 6.28–6.35 (m, 2H, H^6), 6.91 (t, 2H, $J = 6.6$ Hz, H^9), 7.00–7.08 (m, 2H, H^5), 7.20–7.25 (m, 6H, th), 7.40 (d, 2H, $J = 5.6$ Hz, dtbpy), 7.61–7.79 (m, 2H, dtbpy), 7.81–7.92 (m, 6H, H^3 , H^7 and H^8), 7.97–8.01 (m, 2H, H^{10}), 8.50 (s, 2H, H^c). MS (FAB): m/z 932 ($\text{M}^+ + 1$).

6: Yield: 19 mg (37%). Anal. Calc. for $\text{C}_{55}\text{H}_{52}\text{F}_3\text{IrN}_4\text{O}_5\text{S} \cdot 2\text{H}_2\text{O} \cdot 1/2\text{DMF}$: C, 56.42; H, 4.99; N, 5.24. Found: C, 56.19; H, 4.71; N, 5.36%. ^1H NMR (CDCl_3): δ 1.47 (s, 18H, *t*-Bu), 4.76 (s, 4H, OCH_2), 6.40 (d, 2H, $J = 7.8$ Hz, H^6), 7.15 (m, 4H, H^9 and C_6H_4), 7.30 (s, 2H, H^3), 7.36–7.45 (m, 6H, dtbpy and C_6H_4), 7.45–7.61 (m, 4H, dtbpy and C_6H_4), 7.82 (t, 2H, $J = 7.2$ Hz, H^8), 7.93 (m, 4H, H^5 and H^7), 8.05 (d, 2H, $J = 7.8$ Hz, H^{10}), 8.49 (s, 2H, H^c). MS (FAB): m/z 981 ($\text{M}^+ + 1$).

2.5. $[\text{Ir}\{4\text{-B}(\text{pin})\text{-ppy}\}_2(\text{dtbpy})][\text{OTf}]$ (**7**)

To a solution of **2** (45 mg, 0.05 mmol) in dimethylsulfoxide (2 cm^3) was added bis(pinacolato)diboron ($\text{B}_2(\text{pin})_2$) (47 mg, 0.19 mmol), K_2CO_3 (37 mg, 0.37 mmol), 1,1'-bis(diphenylphosphino)ferrocene (dppf) (5 mg) and $[\text{PdCl}_2(\text{dppf})]$ (7 mg) and the mixture was stirred at 150 °C for 22 h. The volatiles were removed in vacuo and the residue was purified by column chromatography (silica gel, eluant: $\text{CH}_2\text{Cl}_2/\text{acetone}$ (1:1)). Recrystallization from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}/\text{hexane}$ gave yellow crystals. Yield: 35 mg (64%). We have not been able to obtain satisfactory analytical data for the compound. Nevertheless, compound **7** has been characterized by NMR spectroscopy, mass spectrometer, and X-ray crystallography. ^1H NMR (CDCl_3): δ 1.33 (s, 24H, CH_3), 1.46 (s, 18H, *t*-Bu), 6.30 (d, 2H, $J = 7.4$ Hz, H^6), 7.09 (t, 2H, $J = 6.2$ Hz, H^9), 7.28 (s, 2H, H^3), 7.34 (d, 2H, $J = 6.2$ Hz, H^a or H^b), 7.57 (d, 2H, $J = 5.8$ Hz, H^a or H^b), 7.73–7.81 (m, 4H, H^5 and H^8), 8.04 (d, 2H, $J = 7.8$ Hz, H^7), 8.09 (s, 2H, H^{10}), 8.55 (s, 2H, H^c). MS (FAB): m/z 1021 ($\text{M}^+ + 1$).

2.6. $[\text{Ir}(4\text{-PhC}\equiv\text{C-ppy})_2(\text{dtbpy})][\text{OTf}]$ (**8**)

To a solution of **2** (50 mg, 0.05 mmol) in THF (5 cm^3) was added $\text{Me}_3\text{SnC}\equiv\text{CPh}$ (74 mg, 0.28 mmol) and $[\text{Pd}(\text{PPh}_3)_2\text{Cl}_2]$ (6 mg), and the mixture was stirred at 80 °C for 24 h. The volatiles were removed in vacuo, and the residue was purified by column chromatography (silica gel, eluant: $\text{CH}_2\text{Cl}_2/\text{acetone}$ (3:2)). Recrystallization from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}/\text{hexane}$ in air afforded yellow crystals. Yield: 26 mg (50%). Anal. Calc. for $\text{C}_{57}\text{H}_{48}\text{F}_3\text{IrN}_4\text{O}_5\text{S} \cdot \text{H}_2\text{O}$: C, 60.25; H, 4.44; N, 4.93. Found: C, 60.51; H, 4.57; N, 4.80%. ^1H NMR (CDCl_3): δ 1.47 (s, 18H, *t*-Bu), 6.29 (d, 2H, $J = 7.8$ Hz, H^6), 7.05 (t, 2H, $J = 7.8$ Hz, H^9), 7.18 (t, 2H, $J = 6.0$ Hz, H^8), 7.32–7.41 (m, 8H, Ph), 7.52 (m, 4H, Ph and H^a or H^b), 7.65 (d, 2H, $J = 5.6$ Hz, H^a or H^b), 7.79–7.85 (m, 6H, H^3 ,

H^5 and H^7), 7.95 (d, 2H, $J = 7.8$ Hz, H^{10}), 8.57 (s, 2H, H^c). MS (FAB): m/z 969 (M^+).

2.7. $[\text{Ir}(4\text{-Me}_2\text{C}(\text{OH})\text{C}\equiv\text{Cppy})(4\text{-Br-ppy})(\text{dtbpy})][\text{OTf}]$ (**9**)

To a solution of **2** (50 mg, 0.05 mmol) in NH_4Et_2 (15 cm^3) was added 2-methyl-3-butyn-2-ol (17 mg, 0.19 mmol) and $[\text{Pd}(\text{PPh}_3)_4]$ (3 mg), and the mixture was stirred at 80 °C for 24 h. The volatiles were removed in vacuo and the residue was purified by column chromatography (silica gel, eluant: $\text{CH}_2\text{Cl}_2/\text{acetone}$ (1:1)). Recrystallization from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}/\text{hexane}$ gave yellow crystals that were suitable for X-ray diffraction. Yield: 16 mg (31%). Anal. Calc. for $\text{C}_{46}\text{H}_{45}\text{BrF}_3\text{IrN}_4\text{O}_4\text{S} \cdot 2/3\text{C}_6\text{H}_{14}$: C, 52.84; H, 4.82; N, 4.93. Found: C, 53.11; H, 4.60; N, 5.05%. ^1H NMR (acetone-d_6): δ 1.56 (s, 18H, *t*-Bu), 1.67 (s, 6H, CH_3), 2.95 (s, 2H, OH), 6.37–6.50 (m, 2H, H^6), 7.04 (m, 1H, H^5), 7.18 (t, 1H, $J = 7.0$ Hz, H^9), 7.26–7.34 (m, 2H, H^a or H^b), 7.86 (m, 2H, H^a or H^b), 7.91–7.96 (m, 2H, H^5 and H^9), 8.04–8.15 (m, 2H, H^3), 8.18 (m, 4H, H^7 , H^8 and H^{10}), 8.38 (d, 1H, $J = 8.4$ Hz, H^{10}), 8.48 (t, 1H, $J = 8.0$ Hz, H^8), 9.02 (s, 2H, H^c). MS (FAB): m/z 929 (M^+).

2.8. $[\text{Ir}(5\text{-HC}\equiv\text{C-ppy})_2(\text{dtbpy})][\text{OTf}]$ (**10**)

Ethynylation of the formyl-ppy ligand was carried out according to a literature method [15]. A mixture of $\text{MeCOC}(\text{N}_2)\text{P}(\text{O})(\text{OEt})_2$ (25 mg, 0.10 mmol), $[\text{Ir}(\text{fppy})_2(\text{dtbpy})][\text{OTf}]$ (50 mg, 0.05 mmol) and K_2CO_3 (28 mg, 0.20 mmol) in MeOH (15 cm^3) was stirred at room temperature 4 h. The solvent was pumped off and the residue was washed with Et_2O and then extracted with CH_2Cl_2 . Recrystallization from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}/\text{hexane}$ gave yellow crystals that were suitable for X-ray diffraction analysis. Yield: 31 mg (62%). Anal. Calc. for $\text{C}_{45}\text{H}_{40}\text{F}_3\text{Ir}_3\text{N}_4\text{O}_5\text{S} \cdot \text{H}_2\text{O}$: C, 54.92; H, 4.30; N, 5.69. Found: C, 54.99; H, 4.31; N, 5.87%. ^1H NMR (CDCl_3): δ 1.48 (s, 18H, *t*-Bu), 3.71 (s, 2H, $\text{C}\equiv\text{CH}$), 6.36 (s, 2H, H^6), 7.18 (m, 4H, H^4 and H^9), 7.40 (d, 2H, $J = 5.7$ Hz, H^a or H^b), 7.56 (d, 2H, $J = 5.7$ Hz, H^a or H^b), 7.63 (d, 2H, $J = 8.4$ Hz, H^3), 7.79 (m, 4H, H^7 and H^8), 7.91 (d, 2H, $J = 6.8$ Hz, H^{10}), 8.75 (s, 2H, H^c). MS (FAB): m/z 818 ($\text{M}^+ + 1$).

2.9. X-ray crystallography

A summary of crystallographic data and experimental details for **2**, **5**·1/2 H_2O , **7**, and **10**·2 CH_2Cl_2 ·2 H_2O are compiled in Table 1. Intensity data were collected on a Bruker SMART APEX 1000 CCD diffractometer using graphite-monochromated Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073$ Å) at 100(2) K. The collected frames were processed with the software SAINT [16]. Structures were solved by the direct methods and refined by full-matrix

Table 1

Crystallographic data and experimental details for [Ir(4-Br-ppy)₂(dtbpy)][OTf] (**2**), [Ir(4-th-ppy)₂(dtbpy)][OTf]·1/2H₂O (**5**·1/2H₂O), [Ir{4-(pin)-Bppy}₂(dtbpy)][OTf] (**7**), and [Ir{5-HC≡C-ppy}₂(dtbpy)][OTf]·2CH₂Cl₂·2H₂O (**10**·2CH₂Cl₂·2H₂O)

Compound	2	5 ·1/2H ₂ O	7	10 ·2CH ₂ Cl ₂ ·2H ₂ O
Formula	C ₄₈ H ₅₃ Br ₂ Cl ₂ F ₃ IrN ₄ O ₃ S	C ₄₉ H ₄₅ F ₃ IrN ₄ O _{3.5} S ₃	C ₅₉ H ₇₆ B ₂ F ₃ IrN ₄ O ₈ S	C ₄₇ H ₄₈ Cl ₂ F ₃ IrN ₄ O ₅ S
<i>f</i> _w	1245.92	1091.27	1272.12	1101.05
<i>a</i> (Å)	21.2152(10)	12.1569(8)	14.3945(13)	12.3057(12)
<i>b</i> (Å)	17.4283(9)	34.733(3)	12.2655(11)	30.066(3)
<i>c</i> (Å)	25.7071(13)	10.9504(8)	31.926(3)	12.2968(13)
α (°)	90	90	90	90
β (°)	97.854(1)	109.535(2)	96.250(2)	92.270(2)
γ (°)	90	90	90	90
<i>V</i> (Å ³)	9415.9(8)	4357.6(5)	5603.1(9)	4546.0(8)
<i>Z</i>	8	4	4	4
Cryst system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>I</i> 2/ <i>a</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>C</i> <i>c</i>
ρ _{calc} (g cm ⁻³)	1.758	1.663	1.508	1.609
<i>T</i> (K)	100(2)	100(2)	100(2)	100(2)
μ (mm ⁻¹)	4.750	3.271	2.489	3.164
<i>F</i> (000)	4936	2188	2608	2208
Number of reflections	25,494	24,903	26,821	13,536
Number of independent reflections	9256	8536	9695	7062
<i>R</i> _{int}	0.0334	0.0668	0.0656	0.0499
<i>R</i> ₁ ^a , <i>wR</i> ₂ ^b (<i>I</i> > 2σ(<i>I</i>))	0.0463, 0.1230	0.0727, 0.1613	0.0474, 0.1080	0.0573, 0.1390
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0578, 0.1281	0.1095, 0.1758	0.0738, 0.1162	0.0665, 0.1449
GoF ^c	1.060	1.035	0.996	1.080

$$^a R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

$$^b wR_2 = \frac{[\sum w(|F_o|^2 - |F_c|^2)|^2]^{1/2}}{[\sum w|F_o|^2]^{1/2}}$$

$$^c \text{GoF} = \frac{[\sum w(|F_o| - |F_c|)^2 / (N_{\text{obs}} - N_{\text{param}})]^{1/2}}$$

least-squares on *F*² using the SHELXTL [17] software package. Non-hydrogen atoms were refined anisotropically.

3. Results and discussion

3.1. Bromination of Ir(III) bis-cyclometalated complexes

Previously, bromination of the ppy ligands bound to Ru(II) and Ir(III) by *N*-bromosuccinimide has been reported [8,9b]. We found that Ir(III) bis-cyclometalated complexes could be brominated by pyridinium tribromide in good yield according to the method reported by Clark et al. [11]. Thus, treatment of [Ir(ppy)₂(μ-Cl)₂] and [Ir(ppy)₂(dtbpy)][OTf] with pyridinium tribromide in the presence of Fe powder afforded air-stable [Ir(4-Br-ppy)₂(μ-Br)₂] (**1**) and [Ir(4-Br-ppy)₂(dtbpy)][OTf] (**2**), respectively. For the bromination of [Ir(ppy)₂(μ-Cl)₂], a small amount of [Ir(4-Br-ppy)₂(py)Br] that could be separated by fractional recrystallization was also isolated as minor product [18]. X-ray diffraction (Fig. 1) and NMR spectroscopy confirmed that the ppy ligands in **2** were brominated regioselectively at the *para* position with respect to the Ir–C bond. Similar results have been found for the bromination of Os(II) [11], Ru(II) [9b], and Ir(III) [8] ppy complexes. The average Ir–C distance in **2** of 2.022 Å is similar to those in reported Ir bis-ppy complexes [5b,19], indicat-

ing that the bromo substituent in the ppy ligand has little influence on the Ir–C σ bond. The Ir–N(ppy) and Ir–N(dtbpy) distances (2.047 and 2.129 Å, respectively) are not unusual.

3.2. Cross-coupling of **2** with aryl boronic acids

Complex **2** proved to be a versatile starting material for cross-coupling reactions. Thus, Suzuki coupling of **2** with RB(OH)₂ in the presence of Pd(0) catalyst afforded the arylated ppy complexes [Ir(4-*R*-ppy)₂(dtbpy)][OTf] (*R* = 4'-FC₆H₄ (**3**), 4'-PhC₆H₄ (**4**), th (th = 2'-thienyl) (**5**), 4'-C₆H₄CH₂OH (**6**)) (Scheme 1). Complexes **3–6** were purified by column chromatography and characterized by NMR spectroscopy and FAB mass spectrometry. The identity of complexes **5** has been unambiguously established by X-ray diffraction studies. The structure of **5** is shown in Fig. 2, confirming the incorporation of the 2-thienyl groups into the ppy ligands. The average Ir–C distance in **5** of 1.989 Å is similar to that in **2**.

In order to prepare polymeric Ir(III) ppy complexes, the cross-coupling of **2** with diboronic acids was attempted. Treatment of **3** with 1,4-benzenediboronic acid with Pd(0) catalyst yielded an yellow insoluble material, presumably an Ir-containing oligomer, which has yet to be characterized. An alternative approach to polymeric Ir(III) ppy complexes involves the cross-coupling of Ir

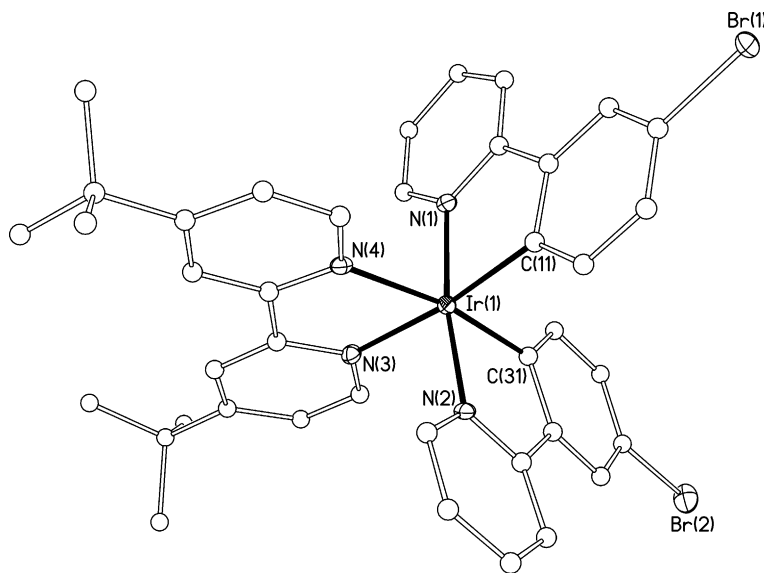
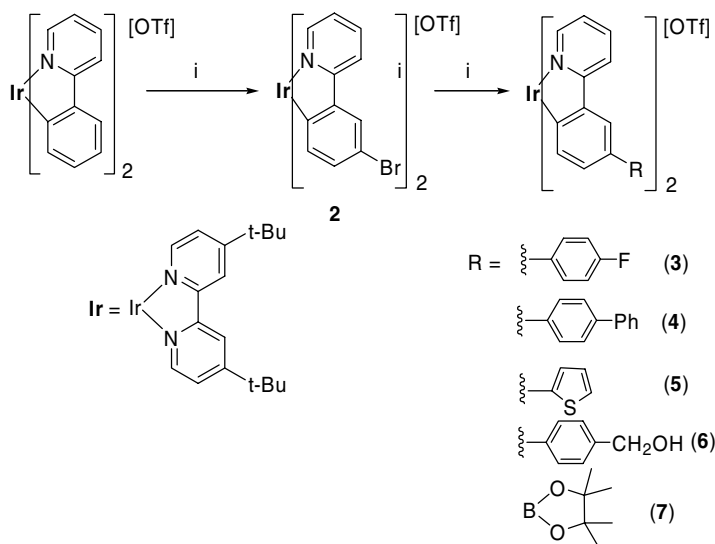


Fig. 1. Perspective view of the cation $[\text{Ir}(4\text{-Br-ppy})_2(\text{dtbbpy})]^+$ in **2**. Selected bond lengths (Å): Ir(1)–C(11) 2.024(6), Ir(1)–C(31) 2.020(7), Ir(1)–N(1) 2.050(5), Ir(1)–N(2) 2.043(5), Ir(1)–N(3) 2.125(5), Ir(1)–N(4) 2.132(5).



Scheme 1. Reagents and conditions. (i) $[\text{pyH}]\text{Br}_3$, Fe powder, CH_2Cl_2 ; (ii) for **3–5**, $\text{RB}(\text{OH})_2$, $[\text{Pd}(\text{PPh}_3)_4]$, K_2CO_3 , DMF, 150°C , 4 h; for **7**, $\text{B}_2(\text{pin})_2$, $[\text{Pd}(\text{dppf})\text{Cl}_2]$, DMF, 22 h.

(III) bis-borylated ppy complexes with dibromide compounds. Thus, the bis-borylated complex $[\text{Ir}\{4\text{-(pin)B-ppy}\}_2(\text{dtbbpy})][\text{OTf}]$ (**7**) has been prepared by reaction of **2** with $\text{B}_2(\text{pin})_2$ (pin = pinacolate) in the presence of catalytic $[\text{Pd}(\text{dppf})\text{Cl}_2]$. The ^1H NMR spectrum of **7** displays a singlet at δ 1.33 assignable to the pinacolato protons, confirming the addition of the B(pin) groups to the ppy ligands. The structure of **7** has been unambiguously established by X-ray diffraction (Fig. 3). The average Ir–C and Ir–N(ppy) distances in **7** (2.008 and 2.040 Å, respectively) are similar to those in **5**. Unfortunately, Pd-catalyzed cross-coupling of **7** with dibromo compounds such as 1,4-dibromobenzene and 4,4'-dibromo-

biphenyl also yielded insoluble materials that have yet to be characterized.

3.3. Ir(III) alkynyl-ppy complexes

Organometallic dimers and oligomers containing $\text{C}\equiv\text{C}$ linkages have been well developed [20]. In this connection, efforts have been made to synthesize Ir(III) complexes containing ethynyl-ppy ligands that may serve as building blocks for polymers. Pd-catalyzed coupling of **2** with $\text{PhC}\equiv\text{CSnMe}_3$ afforded the phenylethynyl compound $[\text{Ir}(4\text{-PhC}\equiv\text{C-ppy})_2(\text{dtbbpy})][\text{OTf}]$ (**8**) (Scheme 2). In attempts to prepare the Ir(III)

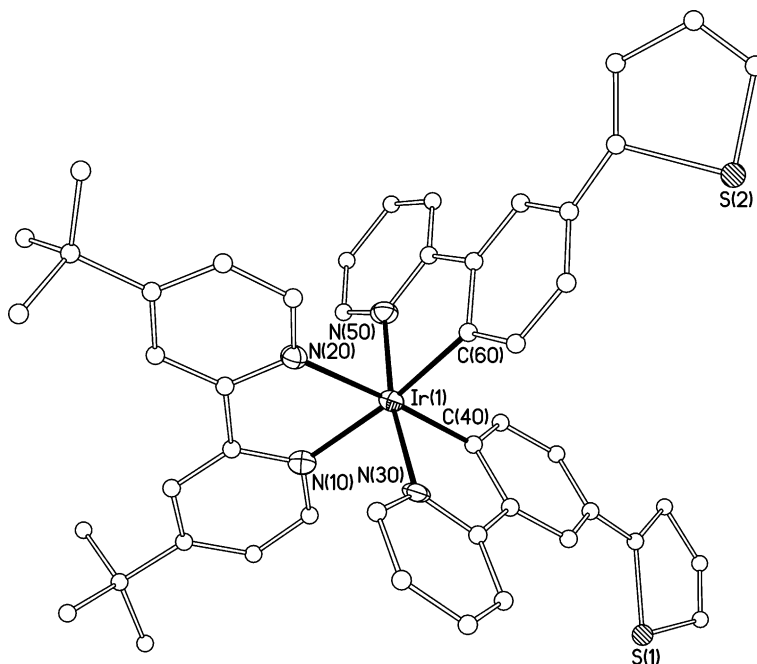


Fig. 2. Perspective view of the cation $[\text{Ir}(4\text{-th-ppy})_2(\text{dtbbpy})]^+$ in **5**. Selected bond lengths (Å): Ir(1)–C(40) 1.988(10), Ir(1)–C(60) 1.990(9), Ir(1)–N(30) 2.038(8), Ir(1)–N(50) 2.056(8), Ir(1)–N(20) 2.131(8), Ir(1)–N(10) 2.131(8).

ethynyl-ppy complex, Sonogashira's coupling of **2** with protected acetylenes such as $\text{Me}_3\text{SiC}\equiv\text{CH}$ and $\text{HC}\equiv\text{CC}(\text{OH})\text{Me}_2$ was attempted. Although we were not able to isolate the coupling product from **2** and $\text{Me}_3\text{-}$

$\text{SiC}\equiv\text{CH}$, Pd-catalyzed cross-coupling of **2** with $\text{HC}\equiv\text{CC}(\text{OH})\text{Me}_2$ afforded the mono-ethynyl compound $[\text{Ir}\{4\text{-Me}_2(\text{OH})\text{CC}\equiv\text{C-ppy}\}(4\text{-Br-ppy})(\text{dtbbpy})][\text{OTf}]$ (**9**). As expected, the ^1H NMR spectrum of **9** shows

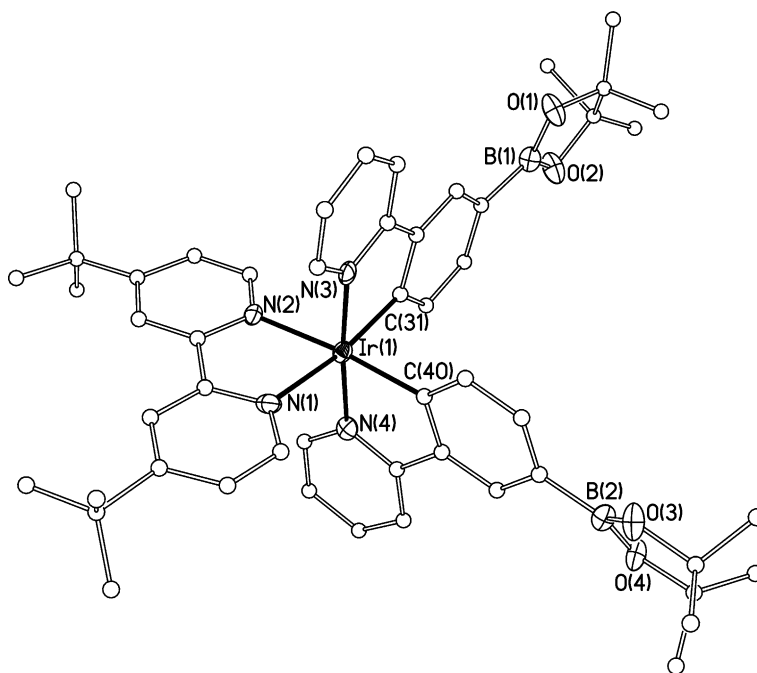
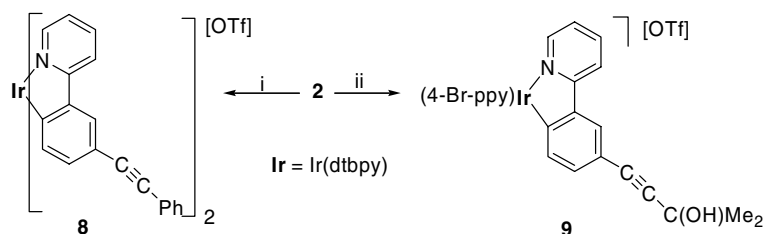
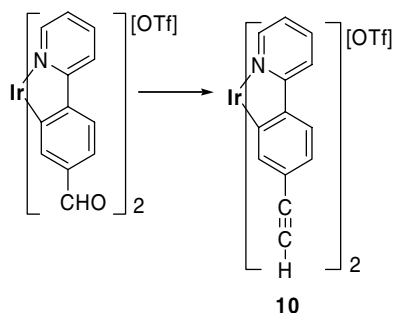


Fig. 3. Perspective view of the cation $[\text{Ir}\{4\text{-(pin)B-ppy}\}_2(\text{dtbbpy})]^+$ in **7**. Selected bond lengths (Å): Ir(1)–C(40) 2.007(5), Ir(1)–C(31), 2.009(6), Ir(1)–N(1), 2.131(5), Ir(1)–N(2) 2.146(5), Ir(1)–N(3) 2.029(5), Ir(1)–N(4) 2.051(5).



Scheme 2. Reagents and conditions. (i) $\text{Me}_3\text{SnC}\equiv\text{CPh}$, $[\text{Pd}(\text{PPh}_3)_4]$, THF, 80°C , 24 h. (ii) $\text{Me}_2(\text{OH})\text{CC}\equiv\text{CH}$, $[\text{Pd}(\text{PPh}_3)_4]$, NH_4Et_2 , 80°C , 24 h.



Scheme 3. Reagent and conditions. $\text{MeCOC}(\text{N}_2)\text{P}(\text{O})(\text{OEt})_2$, K_2CO_3 , MeOH, RT, 4 h.

two sets of resonances for the non-equivalent cyclometalated ligands. The FAB mass spectrum shows the molecular ion for **9** at m/z 929. Despite several attempts, we were not able to synthesize the bis-ethynylated complex even excess $\text{HC}\equiv\text{CC}(\text{OH})\text{Me}_2$ was used.

Recently, Bunz and coworkers [15] synthesized ethynylated π -cycloolefin complexes by treatment of formylcycloolefin complexes with $\text{MeCOC}(\text{N}_2)\text{P}(\text{O})(\text{OEt})_2$ according to Ohira's protocol. This prompted us to

investigate Ohira's ethynylation of $[\text{Ir}(\text{fppy})_2(\text{dtbbpy})][\text{OTf}]$. Treatment of $[\text{Ir}(\text{fppy})_2(\text{dtbbpy})][\text{OTf}]$ with $\text{MeCOC}(\text{N}_2)\text{P}(\text{O})(\text{OEt})_2$ afforded $[\text{Ir}(5\text{-HC}\equiv\text{CH-ppy})_2(\text{dtbbpy})][\text{OTf}]$ (**10**) as an air-stable yellow solid (Scheme 3). Although ethynylation of π -formylcycloolefin complexes have been well explored, to our knowledge, this is the first report on direct ethynylation of a σ -formylaryl complex. The ^1H NMR spectrum of **10** displays a singlet at δ 3.71 assignable to the ethynyl protons, indicating the addition of the ethynyl groups to the ppy ligands. The structure of **10** has been unambiguously established by X-ray diffraction study. Fig. 4 shows the molecular structure of **10**. The average Ir–C and Ir–N distances of 2.07(2) and 1.88(3) Å are comparable to those in **5**. The C–C distance of 1.10(3) Å is consistent with a $\text{C}\equiv\text{C}$ triple bond. Attempts to synthesize polynuclear Ir(III) complexes with $-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-$ linkages by Cu-mediated homo-coupling of the *meta* –CCH groups in **10** were not successful presumably because of steric effects. Currently efforts are being made to synthesize the less hindered 4-ethynylppy derivative starting from the Ir(III) 4-formylppy complex.

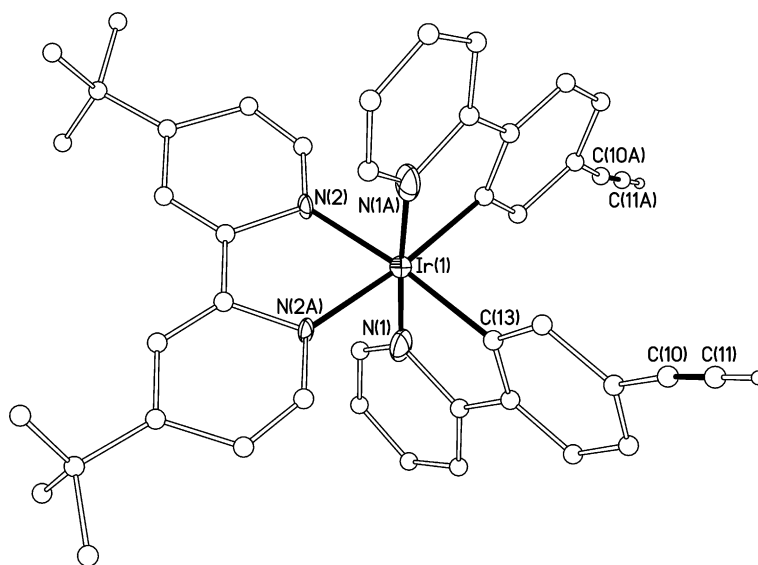


Fig. 4. Perspective view of the cation $[\text{Ir}(5\text{-HC}\equiv\text{C-ppy})_2(\text{dtbbpy})]^+$ in **10**. Selected bond lengths (Å): Ir(1)–C(13) 2.07(2), Ir(1)–N(1) 1.88(3), Ir(1)–N(2) 2.029(13), C(10)–C(11) 1.10(3).

Table 2
Absorption and emission spectral data for functionalized cyclometalated Ir(III) complexes in CH₂Cl₂ at room temperature

Complex	Absorption $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/10^3 \text{ M}^{-1} \text{ cm}^{-1}$) ^a	Emission ^a $\lambda_{\text{max}}/\text{nm}$
2	287 (15.0), 368 sh (11.5), 392 (8.77), 418 (7.82), 475 sh (1.34)	554
3	301 (13.0), 346 (11.2), 375 (7.20), 425 (4.53)	581
4	299 (10.9), 376 (7.15), 427 (4.26)	591
5	296 (12.7), 309 sh (11.6), 378 (2.35), 422 (1.76)	585
6	278 (16.1), 312 sh (12.1), 381 (5.00), 424 (3.66)	571
7	283 (11.3), 375 (8.35), 414 (4.33), 466 sh (1.35)	555
8	295 (10.1), 344 sh (6.17), 372 (4.04), 422 (2.18)	560
9	279 (15.1), 309 sh (12.3), 348 (7.70), 418 (5.23), 418 (5.23)	572
10	278 (14.6), 298 (12.8), 309 sh (10.1), 329 (9.17), 348 sh (8.12), 405 (6.52), 422 (5.94)	538, 574

^a Samples were excited at 397 nm.

3.4. Absorption and emission spectra

The absorption and emission spectral data are summarized in Table 2. In general, the UV–visible absorption spectra for the functionalized Ir(III) bis-cyclometalated complexes show intense absorptions at 287–296 nm and weaker absorptions at 324–466 nm. With reference to previous studies on related cyclometalated Ir(III) di-imine complexes [1b,2a,5,21] these absorptions are attributed to intra-ligand (IL) ($\pi \rightarrow \pi^*$) (ppy and dtbpy) and spin-allowed metal-to-ligand charge transfer ¹MLCT [$d\pi(\text{Ir}) \rightarrow \pi^*(\text{ppy}$ and dtbpy)] transitions, respectively. The weak absorptions at lower energy region ($\lambda_{\text{max}} > 450 \text{ nm}$) are probably due to the spin-forbidden ³MLCT [$d\pi(\text{Ir}) \rightarrow \pi^*(\text{ppy}$ and dtbpy)] transition.

Similar to reported cyclometalated Ir(III) di-imine complexes [1a,5,21], the arylated Ir(III) bis-cyclometalated complexes are luminescent in fluid solutions at room temperature. The emission spectra for complexes 3–6 in CH₂Cl₂ are shown in Fig. 5. The emission maxima for these complexes at 571–591 nm are comparable to that for [Ir(ppy)₂(bpy)]⁺ (ca. 600 nm) [21]. Previously, the luminescence of [Ir(ppy)₂(bpy)]⁺ has been attributed to the MLCT [$d\pi(\text{Ir}) \rightarrow \pi^*(\text{ppy})$] excited state [1b]. We therefore believe that the luminescence of 3–6 also originates from the MLCT [$d\pi(\text{Ir}) \rightarrow \pi^*(\text{ppy})$] excited state. For complexes 2 and 7 that contain electron-withdrawing substituents in the ppy ligand, the emission was observed at higher energies (554 and 555 nm, respectively). A similar emission blue-shift has been found for the electron-poor formyl-ppy compound [Ir(fppy)₂(bpy)]⁺ ($\lambda_{\text{max}} = 529, 563 \text{ nm}$) [5b]. Previously, the luminescence

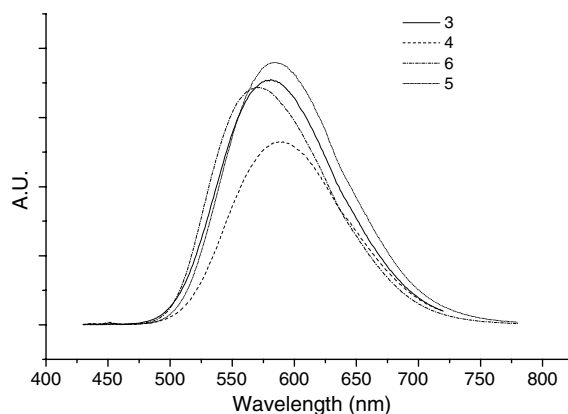


Fig. 5. Emission spectra for complexes 3–6 in CH₂Cl₂ at room temperature.

for [Ir(fppy)₂(bpy)]⁺ has been attributed primarily to the ³IL ($\pi \rightarrow \pi^*$) (fppy) excited state [5b]. We therefore tentatively assign the emission of 2 and 7 to the ³IL ($\pi \rightarrow \pi^*$) excited state. It seems likely that the emission for the bis-ethynyl compound 10 at 554 and 571 nm also originates from an excited state of ³IL character. Additional photophysical studies are required to elucidate the nature of the excited state(s) involved in the photoluminescence of these compounds.

4. Conclusion

In summary, we have demonstrated that the cyclometalated ppy ligands bound to Ir(III) could be functionalized by bromination and subsequent cross-coupling with reagents including aryl boronic acids, ethynylstannane, and butynol, which are commonly used for cross-coupling of organic compounds. In addition, an Ir(III) ethynyl-ppy complex has been synthesized via direct Ohira's ethynylation of the coordinated formyl-ppy ligand. Similar to reported cyclometalated Ir(III) di-imine complexes, arylated and alkynylated Ir(III) ppy complexes are luminescent in solution. The synthesis of well-defined, soluble oligomers based on functionalized cyclometalated Ir(III) complexes is underway.

5. Supporting information available

Crystallographic data for 2, 5·1/2H₂O, 7, and 10·2CH₂Cl₂·2H₂O have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 261427, 261428, 261430, and 261431, respectively, in CIF format. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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