



Note

Charged cyclometalated iridium(III) complexes that have large electrochemical gap

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ABSTRACT

Bis-cyclometalated cationic Ir(III) diimine complexes $[\text{Ir}(\text{C}^{\wedge}\text{N})_2(\text{N}^{\wedge}\text{N})](\text{PF}_6)$ with 1-phenylpyrazoles ($\text{C}^{\wedge}\text{N}$) and 1-(4'-tert-butyl-2'-pyridyl)pyrazole ($\text{N}^{\wedge}\text{N}$) are white solids that have absorption onset below 425 nm and electrochemical gap of up to 3.5 V.

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1. Introduction

Cyclometalated iridium(III) complexes are finding increasing application in electro-luminescent devices as emitters [1–8] and as electronic materials [9–11]. Recently, He et al reported that Ir(III) complexes with 1-(2'-pyridyl)pyrazole (**1**, Chart 1) emit blue-green phosphorescence from a predominantly ligand centered ${}^3(\pi-\pi^*)$ excited state [12]. We considered that the redox and optical properties of **1** could be tuned by replacing a pyridine in the cyclometalating ligand with a pyrazole. We reasoned that the pyrazole is a weaker π -acceptor and a weaker σ -donor than the pyridine [13], and that the pyrazole ligands have $\pi-\pi^*$ transitions at higher energy than the analogous pyridine derivatives [14]. Here, we describe a successful application of this approach to access cationic bis-cyclometalated Ir(III) complexes that have a high-energy absorption onset and a large electrochemical gap.

2. Results and discussion

Scheme 1 shows a new neutral ligand **L** that was prepared by a non-catalyzed C–N coupling reaction of pyrazole with 2-chloro-4-tert-butylpyridine in DMSO, in the presence of potassium tert-butoxide as a base [15]. The pyridyl ring was modified with a bulky tert-butyl group to improve solubility of the Ir(III) complexes and to reduce the intermolecular interaction between them in the solid state.

Two new complexes, **3** (**3H** and **3F**), were prepared by reaction of the neutral ligand with a cyclometalated Ir(III) precursor $[\text{Ir}(\text{C}^{\wedge}\text{N})_2(\mu\text{-Cl})_2]$ (Scheme 1). The complexes were purified by column chromatography (on silica) and by re-crystallization; they were characterized by elemental analysis, ESI⁺ MS, and NMR spectroscopy.

Fig. 1 shows the X-ray molecular structure of complex **3F**. The metal ion is in a distorted octahedral $[\text{Ir}(\text{C}^{\wedge}\text{N})_2(\text{N}^{\wedge}\text{N})]^+$ coordination environment with the two nitrogen atoms of the cyclometalating ligands in trans-position to each other. The Ir–N bonds to the cyclometalating ligand are shorter than those to the neutral ligand (Table 1). The same trend has been previously noted in the structures of **1** and **2H** (Chart 1), and it has been attributed to the strong trans-influence of an anionic phenyl [12,14]. For the neutral ligand in **3F**, the Ir–N bond to pyrazole is shorter by 0.051 Å than that to pyridine (Table 1); in **1**, however, this difference is less than 0.012 Å [12].

The ligands in **3F** are nearly planar: the dihedral angle between their constituent rings is less than 7°. In the solid state, the complexes participate in intermolecular $\pi-\pi$ aromatic stacking that involves only the cyclometalating ligands. The strongest interaction occurs by the overlap of 2,4-difluorophenyl rings at inter-planar distance of 3.245 Å. The bulky neutral ligand does not participate in $\pi-\pi$ aromatic stacking. Inter-metallic communication is likely to be negligible because of the long Ir–Ir distance (8.812 Å).

The redox properties of **3** were studied by cyclic voltammetry in DMF and acetonitrile (Fig. 2 and Fig. S1, Supporting Information). The electrochemical potentials (relative to Fc^+/Fc) and electrochemical gaps (defined as $\Delta E = E_{1/2}^{\text{ox}} - E^{\text{red}}$) of the complexes were found to be solvent-independent (Table 2).

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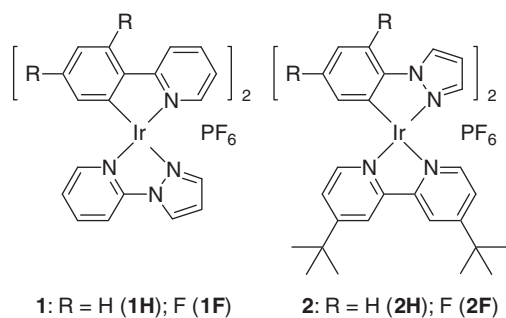
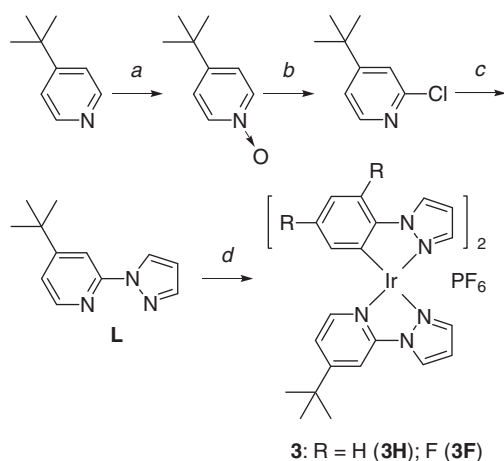
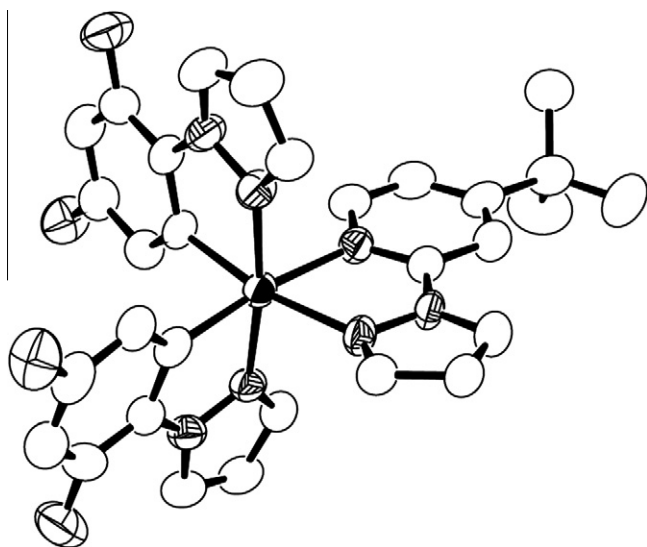


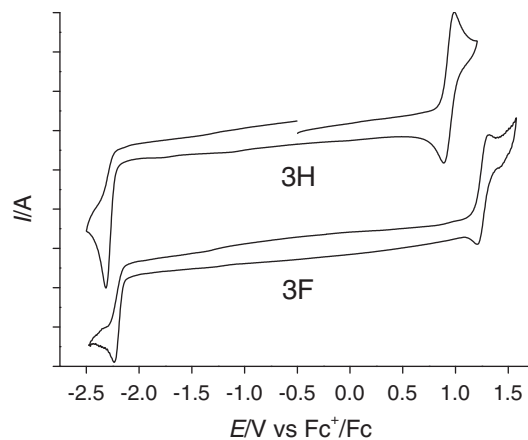
Chart 1. Previously reported Ir(III) complexes [12,14].

Scheme 1. Synthesis of the ligand and Ir(III) complexes: (a) H₂O₂, acetic acid, under air, 80 °C; (b) POCl₃, 'dry finger', under air, 130 °C; (c) pyrazole, KO-*t*-Bu, dry DMSO, under Ar, 140 °C; (d) [Ir(C^N)₂(μ-Cl)]₂, CH₂Cl₂/CH₃OH, under Ar, 40 °C.Fig. 1. Structure of **3F** (50% probability ellipsoids; H atoms, PF₆ anion, and co-crystallized diethyl ether molecule omitted; ORTEP). Heteroatoms are shown as octant ellipsoids: Ir, black; N, shaded; F, clear.

The first oxidation process in **3** is quasi-reversible. Although both the forward and the return waves are observed, their peak separation is wider compared to that for the standard (Fc⁺/Fc couple [16]) and strongly depends on the scan rate (Table S2, Support-

Table 1
Selected bond lengths (Å) in complex **3F**^a.

| C ^N | | N ^N | |
|----------------|-----------------------|-----------------------|-----------------------|
| Ir–C | Ir–N(pz) ^b | Ir–N(py) ^b | Ir–N(pz) ^b |
| 2.029(6) | 2.024(6) | 2.162(6) | 2.111(5) |
| 2.036(7) | 2.033(5) | | |

^a Each row corresponds to one ligand in the complex.^b N(py) and N(pz) are nitrogen atoms of pyridine and pyrazole, respectively.Fig. 2. Cyclic voltammograms of the complexes in CH₃CN (0.1 M NBu₄PF₆, 100 mV/s). The unit on the vertical axis is 10 μA. CVs in DMF are provided in the Supporting Information.Table 2
Redox properties of Ir(III) complexes^a.

| Complex | Solvent | E _{1/2} ^{ox} /V | E ^{red} /V | ΔE/V ^b |
|------------------------|--------------------|-----------------------------------|---------------------|-------------------|
| 3H | CH ₃ CN | 0.94 (98) ^c | –2.31 ^d | 3.25 |
| | DMF | 0.91 (146) ^c | –2.33 ^d | 3.23 |
| 3F | CH ₃ CN | 1.26 (112) ^c | –2.24 ^d | 3.50 |
| | DMF | ^e | –2.24 ^d | |
| 1H ^f | CH ₃ CN | 0.88 | –2.19 | 3.07 |
| 1F ^f | CH ₃ CN | 1.20 | –2.15 | 3.35 |
| 2H ^g | CH ₃ CN | 0.95 | –1.89 | 2.84 |
| 2F ^g | CH ₃ CN | 1.25 | –1.83 | 3.08 |

^a Relative to Fc⁺/Fc. On glassy carbon working electrode, in the presence of 0.1 M (NBu₄)PF₆, at scan rate 100 mV/s. Estimated error: ±50 mV. The anodic/cathodic peak separation for the standard, Fc⁺/Fc couple [16], was 68–88 mV in CH₃CN; 83–88 mV in DMF.^b ΔE = E_{1/2}^{ox} – E^{red}.^c Quasi-reversible process; the anodic/cathodic peak separation is given in brackets.^d Irreversible process; the reduction peak potential is reported.^e The process was outside of the electrochemical window of the solvent (>1.0 V relative to Fc⁺/Fc).^f From reference [12].^g From reference [14].

ing Information). The oxidation potential undergoes a positive shift by 320 mV on fluorination of the phenyl ring of the cyclometalating ligand (Table 2). The first reduction is irreversible; its potential undergoes a positive shift by 70–90 mV on fluorination (Table 2).

The redox properties of **3** were compared to those of **1** and **2** [12,14]. The oxidation potential is similar for the complexes that have either a 2,4-difluorophenyl (**3F** ≈ **1F** ≈ **2F** ≈ 1.2 V) or a phenyl (**3H** ≈ **1H** ≈ **2H** ≈ 0.9 V) as an aryl substituent (Table 2). The 300 mV difference in the potential between these two series reflects the strong electron-withdrawing properties of the fluorine and suggests that the oxidation is localized on a metal-aryl fragment.

The reduction potential of the complexes appears to be determined by the neutral ligand: ($\mathbf{3} \approx -2.3 \text{ V}$) < ($\mathbf{1} \approx -2.2 \text{ V}$) < ($\mathbf{2} \approx -1.9 \text{ V}$). We consider the pyridyl ring of ligand **L** to be the main electron acceptor in **3**. The negative shift of the reduction potential of **3** by 90–120 mV with respect to that of **1** [12] arises from the presence of an electron-donating tert-butyl group in the neutral ligand and from the replacement of a pyridine with a pyrazole, a weaker π -acceptor [13], in the cyclometalating ligand.

3H has an electrochemical gap of 3.2 V that on fluorination increases to 3.5 V in **3F** (Table 2). To our knowledge, the value of the electrochemical gap in **3F** is the highest reported for a cationic bis-cyclometalated Ir(III) complex with a neutral diimine ligand (Table 2) [12,14,17,18].

The complexes **3** are white solids and give colorless solutions in polar organic solvents. The electronic absorption spectra of **3** in dichloromethane do not have strong transitions in the visible range (Table 3, Fig. 3 and Fig. S2, Supporting Information). The absorption onset, defined as a wavelength above which $\epsilon < 0.1\% \epsilon_{\text{max}}$, is observed at 425 nm in **3H**; it is blue-shifted to 400 nm in the fluorinated complex **3F** (Fig. 3). The shorter wavelength of an absorption onset (Table 3) corresponds to a larger value of the electrochemical gap (Table 2); therefore, we assign the lowest energy transition in the complexes ($\lambda > 350 \text{ nm}$; $\epsilon < 10^3 \text{ M}^{-1} \text{ cm}^{-1}$; Fig. 3) to the (metal and aryl)-to-pyridyl charge transfer.

3 do not display luminescence at 400–700 nm in 10^{-4} M dichloromethane solutions at room temperature under near-UV excitation; the upper limit of their quantum yield is 0.05%. We attribute the lack of luminescence of **3** to the quenching of a ligand-centered or charge-transfer excited state by proximate non-emissive $d-d$ metal states; the same deactivation mechanism has been suggested for the cyclometalated Ir(III) complexes with 1-phenylpyrazoles [19–22].

In conclusion, 1-(4'-tert-butyl-2'-pyridyl)pyrazole and 1-(2',4'-R₂-phenyl)pyrazole (R = H or F) form cationic bis-cyclometalated

Table 3
Optical absorption of new compounds^a.

| Compound | $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/10^3 \text{ M}^{-1} \text{ cm}^{-1}$) | $\lambda_{\text{onset}}/\text{nm}^b$ |
|-----------|---|--------------------------------------|
| L | 253 (11), 281 (10), 305 (0.9, sh) | 330 |
| 3H | 258 (39), 310 (12, sh), 377 (1.1, sh) | 425 |
| 3F | 253 (44) | 400 |

^a In CH_2Cl_2 , at room temperature, in the range 250–500 nm. Estimated errors: $\pm 1 \text{ nm}$ for λ_{max} ; $\pm 5 \text{ nm}$ for λ_{onset} ; $\pm 5\%$ for ϵ .

^b Defined as a wavelength above which $\epsilon < 0.1\% \epsilon_{\text{max}}$.

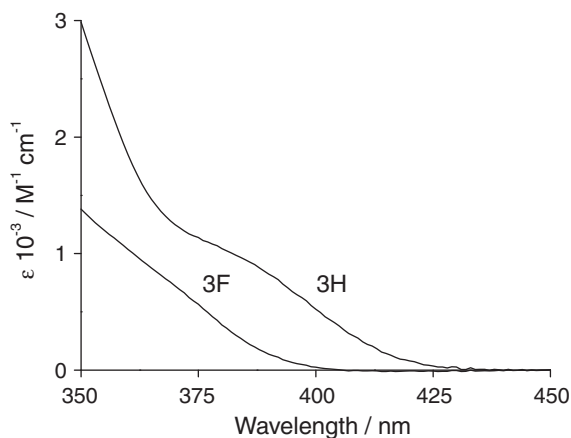


Fig. 3. Absorption spectra of the complexes **3H** ($8.63 \times 10^{-5} \text{ M}$) and **3F** ($9.28 \times 10^{-5} \text{ M}$) in CH_2Cl_2 . Additional absorption spectra are provided in the Supporting Information.

Ir(III) complexes $[\text{Ir}(\text{C}^{\wedge}\text{N})_2(\text{N}^{\wedge}\text{N})]^+$ that have high-energy absorption onset and large electrochemical gap. A facile modification of these ligands opens opportunities for the development of functional Ir(III) complexes.

3. Experimental

Purification, crystal growth, and handling of all compounds were carried out under air. All products were stored in the dark. Chemicals from commercial suppliers were used without purification. Chromatography was performed on a column with an i.d. of 30 mm on silica gel 60 (Fluka, Nr 60752). The progress of reactions and elution of products were followed on TLC plates (silica gel 60 F₂₅₄ on aluminum sheets, Merck).

3.1. Synthesis of the ligand **L**

The reaction was performed under argon. Pyrazole (440 mg, 6.46 mmol, excess, Aldrich) and potassium tert-butoxide (714 mg, 6.36 mmol, excess, Acros) were dissolved at RT in dry and degassed DMSO (3 mL, Acros, 99.8%, ExtraDry, over Molecular Sieves, AcroSeal[®]). 2-Chloro-4-tert-butylpyridine (1 g, 5.89 mmol) [23,24] was added. The reaction mixture was stirred at 140 °C for 9 h to give orange solution. It was cooled to RT. It was extracted with water and ether. Organic layer was washed with water to extract DMSO. Purification by chromatography (run twice; silica, 2 × 25 g) removed the starting material (hexane/ CH_2Cl_2 ; 3/1–1/1) and recovered the product (0.5% CH_3OH in CH_2Cl_2). The product was isolated as colourless oil that crystallized to a pale yellow solid after a week of standing: 923 mg (4.59 mmol, 78%). *Anal.* Calcd for $\text{C}_{12}\text{H}_{15}\text{N}_3$ (MW 201.27): C, 71.61; H, 7.51; N, 20.88. Found: C, 72.13; H, 7.54; N, 20.71. ¹H NMR (400 MHz, CDCl_3 ; py = pyridine; pz = pyrazole): δ = 8.58 (dd, J = 2.8, 0.8 Hz, 1H, pz), 8.32 (dd, J = 5.6, 0.4 Hz, 1H, py), 8.00 (m, 1H, py), 7.76 (m, 1H, pz), 7.20 (m, 1H, py), 6.47 (m, 1H, pz), 1.39 (s, 9H, tert-butyl) [25,26]. ¹³C NMR (100 MHz, CDCl_3): δ = 163.54 (C, py), 152.03 (C, py), 148.02 (CH, py), 141.97 (CH, pz), 127.36 (CH, pz), 119.04 (CH, py), 109.52 (CH, py), 107.78 (CH, pz), 35.38 (tert-butyl, C), 30.72 (tert-butyl, CH_3) [25,26]. GC-EI⁺ MS: m/z 201 (M^+ , 100%), 186 ($\{\text{M}-\text{CH}_3\}^+$, 95%).

3.2. Synthesis of the complexes **3**

The reactions were performed under argon and in the absence of light. The solvents were de-oxygenated by bubbling with Ar, but they were not dried. Cyclometalated precursor $[\text{Ir}(\text{C}^{\wedge}\text{N})_2(\mu\text{-Cl})_2]$ [27] was dissolved in CH_2Cl_2 (40 mL) at RT. After addition of CH_3OH (5 mL) and ligand **L** (excess), the reaction mixture was stirred at 40 °C overnight to give colourless or pale brown solution. It was evaporated to dryness. The work-up and further synthetic details are provided below. The complexes are air- and moisture-stable white solids; to the naked eye they appear to be non-emissive at RT under excitation with 365 nm light in the solid state, in CH_2Cl_2 solution, or on silica TLC plate.

3H: The reaction was performed with $[\text{Ir}(\text{ppz})_2(\mu\text{-Cl})_2]$ (100 mg, 0.097 mmol; ppz = 1-phenylpyrazole- $N^2, C^{2'}$) and **L** (50 mg, 0.25 mmol, excess). Purification by chromatography (silica, 15 g) removed the impurities (1–3% CH_3OH in CH_2Cl_2) and recovered the product as colourless eluate (4–6% CH_3OH in CH_2Cl_2). The target fractions were evaporated. Dry residue was dissolved in CH_3OH (4 mL), and the complex was precipitated by KPF_6 (305 mg, 1.66 mmol, in 10 mL of water, excess, Alfa Aesar). More water (15 mL) was added. The resulting suspension was stirred (30 min) and filtered. The complex was washed with water and ether. It was re-crystallized by pouring its solution in CH_2Cl_2 (2 mL) to ether (30 mL). The product was filtered and washed with

ether. White solid: 124 mg (0.15 mmol, 77%). *Anal.* Calcd for $C_{30}H_{29}F_6IrN_7P$ (MW 824.78): C, 43.69; H, 3.54; N, 11.89. Found: C, 43.23; H, 3.45; N, 12.27. 1H NMR (400 MHz, CD_2Cl_2): δ = 8.69 (d, J = 2.8 Hz, 1H), 8.19–8.15 (m, 2H), 7.91 (d, J = 1.2 Hz, 1H), 7.87 (d, J = 6.0 Hz, 1H), 7.42 (d, J = 2.0 Hz, 1H), 7.37–7.31 (m, 3H), 7.14–6.99 (m, 4H), 6.94–6.84 (m, 2H), 6.82 (dd, J = 3.2, 2.0 Hz, 1H), 6.63–6.60 (m, 2H), 6.37–6.31 (m, 2H), 1.43 (s, 9H, tert-butyl). ^{19}F NMR (376 MHz, CD_2Cl_2): δ = –73.1 (d, J_{P-F} = 710 Hz, 6F, PF_6). ^{31}P NMR (162 MHz, CD_2Cl_2): δ = 144.5 (septet, PF_6 , J_{P-F} = 710 Hz). ESI⁺ TOF MS: m/z 680.21 ($\{M-PF_6\}^+$, 100%).

3F: The reaction was performed with $[Ir(dfppz)_2(\mu-Cl)]_2$ [100 mg, 0.085 mmol; $dfppz$ = 1-(2',4'-difluorophenyl)pyrazole- N^2 , C^6] and **L** (47 mg, 0.23 mmol). Dry residue was dissolved in CH_3OH (5 mL), and the complex was precipitated by KPF_6 (250 mg, 1.36 mmol, in 5 mL of water, excess). More water (10 mL) was added. The resulting suspension was stirred for 30 min and filtered. The complex was washed with water and ether. White solid: 130 mg (0.145 mmol, 85%). *Anal.* Calcd for $C_{30}H_{25}F_{10}IrN_7P$ (MW 896.74): C, 40.18; H, 2.81; N, 10.93. Found: C, 40.26; H, 2.76; N, 10.86. 1H NMR (400 MHz, $DMSO-d_6$): δ = 9.51 (d, J = 3.2 Hz, 1H), 8.63 (m, 2H), 8.43 (d, J = 1.6 Hz, 1H), 7.71 (d, J = 6.0 Hz, 1H), 7.61 (d, J = 2.0 Hz, 1H), 7.55 (dd, J = 6.0, 1.6 Hz, 1H), 7.45 (d, J = 2.4 Hz, 1H), 7.37 (d, J = 2.4 Hz, 1H), 7.18–7.05 (m, 2H), 6.94 (t, J = 2.4 Hz, 1H), 6.82–6.77 (m, 2H), 5.68–5.58 (m, 2H), 1.36 (s, 9H, tert-butyl). ^{19}F NMR (376 MHz, CD_2Cl_2): δ = –72.9 (d, J_{P-F} = 710 Hz, 6F, PF_6), –112.3 (d, J_{F-F} = 6 Hz, 1F), –112.8 (d, J_{F-F} = 6 Hz, 1F), –123.8 (d, J_{F-F} = 6 Hz, 1F), –124.2 (d, J_{F-F} = 6 Hz, 1F). ^{31}P NMR (162 MHz, CD_2Cl_2): δ = 144.5 (septet, PF_6 , J_{P-F} = 710 Hz). ESI⁺ TOF MS: m/z 752.18 ($\{M-PF_6\}^+$, 100%).

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Appendix A. Supplementary material

CCDC 833460 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The

Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.ica.2011.10.052](https://doi.org/10.1016/j.ica.2011.10.052).

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