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### Introduction

Organofluorine chemistry is an active field of research due to the interesting properties that fluorine furnishes to the carbon skeleton.<sup>1</sup> As a consequence, these organofluorine compounds show a broad range of applications in pharmaceutical and material science.<sup>2</sup> For instance, 2-(2,4-difluorophenyl)pyridine (dfppy) has been widely used as a ligand in the synthesis of cyclometalated iridium(III) complexes, which have been intensively studied as emitting materials for organic light-emitting devices (OLEDs).<sup>3–5</sup> Ha *et al.*<sup>6</sup> reported that  $Ir(ppy)_2(dfppy)$  and  $Ir(ppy)(dfppy)_2$  (ppy denotes 2-phenylpyridyl) exhibit emission bands at 502 and 495 nm, respectively, and Thompson<sup>3</sup> confirmed that  $Ir(dfppy)_3$  gave a maximum emission at 468 nm together with a luminescent quantum efficiency of 0.43. The

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## A heteroleptic cyclometalated iridium(III) fluorophenylpyridine complex from partial defluorohydrogenation reaction: synthesis, photophysical properties and mechanistic insights†

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In this paper, a C–F bond activation reaction of a chloro-bridged iridium(III) dimer (dfppy)<sub>2</sub>Ir( $\mu$ -Cl)<sub>2</sub>Ir-(dfppy)<sub>2</sub> (**1**) (dfppy denotes 2-(4,6-difluorophenyl)pyridyl) in the presence of sodium methoxide has been reported, leading to the formation of a heteroleptic cyclometalated iridium(III) fluorophenylpyridine complex **2**. HPLC-mass analysis confirmed the release of formaldehyde in the product mixture. When sodium benzyloxide was used as the base, complex **2** was also generated with the release of a benz-aldehyde derivative. Complex **2** has been fully characterized by <sup>1</sup>H-NMR, <sup>19</sup>F-NMR and X-ray crystallographic methods, confirming the partial loss of one of the fluorine atoms on one of the cyclometalated phenylpyridyl ligands. Photophysical studies of complex **2** show that it has a similar absorption spectrum to that of Ir(III)(dfppy)<sub>3</sub>. However, the emission spectrum shows a red shift maximum emission band at 478 nm due to the loss of a single fluorine atom, highlighting the critical effect of fluorine on the photoluminescence of these Ir(III) complexes. Finally, intensive mechanistic studies including HPLC-mass analysis, <sup>1</sup>H-NMR, and <sup>19</sup>F-NMR studies demonstrate that the formation of complex **2** should involve a critical β-hydride elimination of Ir(III)-alkoxide intermediate and the participation of Ir-hydride and/or Ir-fluoride intermediates.

introduction of fluorine atoms on the ppy backbone leads to significant blue shift of the emission wavelengths compared to the  $Ir(ppy)_3$  complex.<sup>3</sup>

However, owing to the inertness of C-F bonds towards chemical reactions, activation of C-F bonds is challenging and has been the subject of many investigations<sup>7</sup> including the transformation from C-F to C-H, C-C and other bonds. Transition metal complexes have been found to possess a unique ability to react with C-F bonds and a few examples, including both stoichiometric and catalytic activation of aromatic C-F bonds, are reported to occur with palladium,<sup>7e</sup> nickel,<sup>8</sup> rhodium,9 and iridium.10 For instance, Braun et al. reported the selective C-F bond activation in the presence of C-Cl bonds by the treatment of 5-chloro-2,4,6-trifluoropyrimidine with [Ni(COD)<sub>2</sub>]/PCy<sub>3</sub>. The C-F activation product trans-[NiF(4- $C_4N_2ClF_2$  (PCy<sub>3</sub>)<sub>2</sub> was obtained which can further be protonated to obtain the C-H coupling product by hydrochloric acid.<sup>8a</sup> The same group also reported that RhH(PEt<sub>3</sub>)<sub>3</sub> or RhH-(PEt<sub>3</sub>)<sub>4</sub> could react with pentafluoropyridine to afford the C-F activation intermediate Rh(4-C<sub>5</sub>NF<sub>4</sub>)(PEt<sub>3</sub>)<sub>3</sub>, which underwent further reaction with CO and CH<sub>3</sub>I to form the corresponding C-F activation/C-C coupling products.9 Milstein et al. reported an interesting iridium(1)-mediated C-F activation reaction

<sup>†</sup>Electronic supplementary information (ESI) available: Details of preparation, spectroscopic and photophysical data. CCDC 903296. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt32800c



Scheme 1 The preparation of partially defluorinated complex 2.

involving the simultaneous cleavage of the P–C bond of the phosphine ligand and P–F bond formation by reacting the methyl iridium(i) complex  $Ir(CH_3)(PEt_3)_3$  with perfluorinated benzene, which produced a pentafluorophenyl iridium(i) complex  $(C_6F_5)Ir(PEt_3)_2(PEt_2F)$ .<sup>10</sup>

Herein, we report an interesting and unexpected example of iridium(m) complex-promoted C–F bond activation coupled with C–H bond formation. Reaction of  $\mu$ -chloro-bridged dimer (dfppy)<sub>2</sub>Ir( $\mu$ -Cl)<sub>2</sub>Ir(dfppy)<sub>2</sub> (1) with NaOCH<sub>3</sub> produced an unprecedented partially defluorinated product (dfppy)<sub>2</sub>Ir(fppy) (2) [fppy denotes 2-(4-fluorophenyl)pyridyl)] (Scheme 1). Synthesis, characterization and photophysical properties for complex 2 are presented. The marked effect of the fluorine atom on the ppy backbone on the photophysical properties of the resulting iridium(m) complex has been recognized. Additionally, a possible mechanism for the formation of complex 2 is also suggested based on evidence derived from HPLC-mass, <sup>1</sup>H-NMR and <sup>19</sup>F-NMR studies.

#### **Results and discussion**

#### Synthesis and characterization of complex 2

Into a Schlenk tube containing 2-ethoxyethanol as solvent, dichloro-bridged dimer **1** [(dfppy)<sub>2</sub>IrCl]<sub>2</sub>, generated from the reaction of dfppy ligand with  $IrCl_3 \cdot 3H_2O$  according to a general procedure (see ESI<sup>†</sup>), and sodium methoxide were added. The mixture was stirred at reflux for 48 h and gave a yellow suspension. A purified yellow crystal of complex **2** was obtained in 46.3% yield after work-up, thin layer chromatography (TLC), and recrystallization using *n*-hexane/CH<sub>2</sub>Cl<sub>2</sub> mixed solvent.

<sup>1</sup>H-NMR signals (Fig. S1 in ESI<sup>†</sup>) provide us with further structural information of **2**: peaks with chemical shifts ranging from 5.74 to 6.60 and 7.50 belong to H atoms of the benzene ring, and peaks with chemical shifts of 6.74, 6.88 and 7.56 to 8.15 belong to H atoms of the pyridine ring. The integral values of these peaks are 7 and 12, respectively, and the total value is 19 which is consistent with the structure of complex **2**.

Furthermore, the signals of <sup>19</sup>F-NMR (Fig. S2 in ESI<sup>†</sup>) indicate that chemical shifts at -109.56 and -110.35 are attributed to the two F atoms of one 2-(2,4-difluorophenyl)pyridyl ligand. Those of -109.70 and -111.58 are attributed to the two F atoms of the other 2-(2,4-difluorophenyl)pyridyl ligand. The single peak at -112.31 is attributed to the 4-F atom of the 2-(4-fluorophenyl)pyridyl ligand.



**Fig. 1** ORTEP diagram of complex **2** with thermal ellipsoids shown at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and bond angles (°): Ir(1)-C(11) 2.007(12), Ir(1)-N(1) 2.032(10), Ir(1)-C(22) 2.098(10), Ir(1)-N(2) 2.098(10), N(1)-C(1) 1.329(16), N(1)-C(5) 1.377(15), N(2)-C(16) 1.371(18), N(2)-C(12) 1.381(15), C(11)-Ir(1)-N(1) 80.4(5), N(2)-Ir(1)-C(22) 79.0(6), F(1)-C(7)-C(8) 118.5(15), F(1)-C(7)-C(6) 118.7(17), F(2)-C(9)-C(8) 119.2(15), F(2)-C(9)-C(10) 117.0(19), C(14)-C(15)-F(3) 125.5(15), C(16)-C(15)-F(3) 115.2(16).

Finally, to unambiguously elucidate the structure, single crystal X-ray diffraction analysis was done for complex **2**, which presented the most convincing and intuitional evidence, as shown by Fig. **1**. Complex **2** adopts an octahedral geometry with the two dfppy ligands locating in a *cis-C,C'* and *trans-N,N'* manner. The other two coordination positions are occupied by one partially defluorinated ligand 2-(4-fluorophenyl)pyridyl ligand, forming a five-membered metallocycle (for more information, see ESI<sup>†</sup> and the deposited crystal structure CCDC 903296). These intensive characterization studies confirm the structure of complex **2**, especially the partial loss of fluorine atoms on the dfppy ligand.

#### **Photophysical properties**

UV-vis absorption and normalized photoluminescent emission spectra of complex 2 were determined at a concentration of  $10^{-5}$  mol L<sup>-1</sup> in CH<sub>2</sub>Cl<sub>2</sub> solution at 298 K. The absorption spectrum of complex 2 (Fig. 2) shows two intense absorption bands appearing in the ultraviolet range of the spectrum at 239 and 264 nm, respectively, which are assigned to the  $\pi \rightarrow \pi^*$  transitions for the complex. Additional very weak absorption bands at 357, 386 and 459 nm are assigned to the metal-to-ligand charge transfer transitions.<sup>3</sup> Generally, this absorption spectrum is consistent with relevant absorption bands for related Ir(m) ppy or dfppy complexes.

However, the photoluminescent emission spectrum for complex **2** (Fig. 3) shows a significant maximum emission at 478 nm with an excitation wavelength of 264 nm. Compared to iridium(III) complexes  $Ir(ppy)_3$ ,  $Ir(ppy)_2(dfppy)$ ,  $Ir(ppy)(dfppy)_2$  and  $Ir(dfppy)_3$  which show maximum emission wavelengths at 510,<sup>3</sup> 502,<sup>6</sup> 495<sup>6</sup> and 468 nm<sup>3</sup>, respectively, complex **2** displays



Fig. 2 UV-vis absorption spectrum of complex 2 at a concentration of  $10^{-5}$  mol L<sup>-1</sup> in CH<sub>2</sub>Cl<sub>2</sub> solution at 298 K.



Fig. 3 Normalized photoluminescent emission spectrum of complex 2 at a concentration of  $10^{-5}$  mol  $L^{-1}$  in CH\_2Cl\_2 solution at 298 K.

an intermediate emission wavelength between that of Ir(ppy)- $(dfppy)_2$  and  $Ir(dfppy)_3$ . In addition, a quantum yield of 0.14 has been determined for complex 2 at room temperature in degassed dichloromethane solutions using tris(8-hydroxyquinoline) aluminum (Alq<sub>3</sub>) in DMF ( $\Phi_{PL}$  = 0.116) as a reference, which is indicative of a less efficient quantum efficeency compared to a value of 0.43 for Ir(dfppy)<sub>3</sub> reported by Thompson et al. These results highlight the critical electronic effects of the fluorine atoms of the phenylpyridine ligand on the photoluminescence of these Ir(III) complexes3,11,12 and are intrinsically consistent with the accepted consensus that the introduction of fluorine atoms generally stabilizes the HOMO orbital more than the LUMO ortbital of the iridium complexes, leading to an increased HOMO/LUMO gap and shorter emission wavelengths.<sup>11c,e</sup> The lifetime of 9.28 µs for the excited triplet emitting state for complex 2 has also been determined using an excitation wavelength of 264 nm, which is much longer than that for the related  $Ir(dfppy)_3$  complex (1.6 µs). This possibly explains the smaller value of the quantum yield for complex 2 due to a stronger triplet-triplet quenching effect.

#### Mechanistic studies for the formation of complex 2

To provide some insights into the formation of complex 2, some preliminary mechanistic studies were performed. To determine the release of formaldehyde during this process,



**Scheme 2** The preparation of complex **2** with the release of *m*-nitro benzaldehyde.

the product mixture was treated with Sawicki's reagent (3-methyl-2-benzothiazolinone hydrazone hydrochloride monohydrate). Subsequent HPLC-mass analysis of the resulting solution shows that apparent ion peaks around 192 (Fig. S12 in ESI<sup>†</sup>) are present which are assigned to formaldehyde-2-(3-methyl-2-benzothiazolylidene)hydrazone, the condensation product of formaldehyde and Sawicki's reagent (Fig. S12 and S13<sup>†</sup>). Moreover, under identical conditions, when sodium methoxide was replaced by sodium *m*-nitrobenzyloxide (Scheme 2), the expected *m*-nitrobenzaldehyde was observed as a <sup>1</sup>H-NMR signal at 9.895 ppm (Fig. S5 in ESI<sup>+</sup>). From these results, it is proposed that sodium alkoxide or benzyloxide reacted with the dimer to give the iridium alkoxide or benzyloxide complex initially, and produced the aldehyde through a subsequent B-H elimination process. Relevant studies involving this β-hydride elimination of Ir-alkoxide have already been reported previously by Bergman et al., and Milstein et al.<sup>13,14</sup>

Further mechanistic evidence from spectroscopic studies is presented below. Firstly, the <sup>1</sup>H-NMR spectrum for one of the bands of TLC analysis of the product mixture shows typical signals at -15.517(20) and -15.871 ppm (Fig. S6 in ESI<sup>+</sup>), which are assigned to the chemical shifts of the hydride moiety of Ir-H bonds. Similar values were previously reported for relevant Ir(III) 2-phenylpyridyl hydride complexes by the Chong, Sung and Young group.<sup>15</sup> Secondly, for another band of TLC analysis, the <sup>19</sup>F-NMR spectrum (Fig. S7 in ESI<sup>†</sup>) shows characteristic signals of the fluorine atom in the Ir-F bond at -61.982 and -61.986 ppm, respectively, as well as the conventional C-F bonds on the aromatic rings. Finally, HPLC-mass analysis of the product mixture (Fig. S8, S9, S10 and S11 in the ESI<sup>†</sup>) shows four different ion peaks at 192, 174, 573 and 555, which are assigned to 2-(2,4-difluorophenyl)pyridine, 2-(4difluorophenyl)pyridine,  $[(dfppy)_2Ir]^+$  and  $[(dfppy)Ir(fppy)]^+$ , respectively. These studies indicate that iridium hydride and iridium fluoride intermediates should be involved during the formation of complex 2.

Based on these studies, a probable mechanistic proposal for the formation of complex 2 is presented in Fig. 4. The chloride-bridged dimer 1 reacts with sodium methoxide to form Ir-alkoxide intermediate 3,<sup>11,16</sup> which undergoes  $\beta$ -hydride elimination to form Ir hydride intermediate 4 with the release of formaldehyde. Intermediate 4 could undergo reductive elimination to afford intermediate 5 and compound 6 (compound 6 has been detected by our HPLC-MS ion peaks at around 192, *vide supra*). Similar reactivity has also been reported before.<sup>17</sup> Oxidative addition of intermediate 5 with



Fig. 4 The proposed mechanism for the formation of complex 2.

the C–F bond of compound 6 would generate complex 7. Transmetalation of complex 7 with complex 4 would deliver directly the target complex 2, with the concurrent formation of complex  $8.^{18}$ 

#### Conclusions

We report herein the synthesis and characterization of a heteroleptic Ir(III) fluorophenylpyridyl complex 2. The results demonstrate the involvement of a partial hydrodefluorination of the cyclometalated fluorophenylpyridine ligand. Studies on photophysical properties for complex 2 show that it has a similar MLCT excitation process to analogous  $Ir(III)(dfppy)_3$  or  $Ir(III)(ppy)_3$  complexes, but exhibits a notable blue shift relative to  $Ir(III)(ppy)_3$  and red shift relative to  $Ir(III)(dfppy)_3$ . In addition, a mechanistic proposal has also been presented for the formation of complex 2 based on a series of mechanistic studies characterizing the relevant intermediates.

#### Experimental

#### General considerations

IrCl<sub>3</sub>·3H<sub>2</sub>O, *m*-nitrobenzaldehyde, sodium methoxide, sodium borohydride and other chemicals were obtained from commercial sources and used without further purification. All solvents were dried and purified by known procedures and freshly distilled under nitrogen from appropriate drying agents prior to use. All manipulations and reactions involving air and/or moisture-sensitive organometallic compounds were performed under an atmosphere of dry nitrogen using standard Schlenk techniques.

#### Characterization methods

IR spectra were recorded on a FTLA2000 spectrometer by dispersing samples in potassium bromide. Absorption spectra

were measured using a UV-Vis spectrophotometer (Model TU-1901). Photoluminescence spectra were obtained using an RF-5301PC fluorescence spectrophotometer (Shimadzu, Japan) connected to a photomultiplier tube with a xenon lamp as the excitation source. The quantum efficiency measurement was carried out at room temperature in degassed dichloromethane solutions, using tris(8-hydroxyquinoline) aluminum (Alq<sub>3</sub>) in DMF ( $\Phi_{\rm PL}$  = 0.116) as a reference. Phosphorescence lifetime measurement was performed on an Edinburgh instrument LFS920 spectrometer equipped with a microsecond xenon flash lamp as the excitation source in degassed dichloromethane solutions at room temperature. The data were analyzed by iterative convolution of the luminescence decay profile with the instrument response function using the software package provided by Edinburgh Instruments. NMR spectra were collected on a Bruker AVANCE III 400 spectrometer with deuterated dichloromethane and deuterated chloroform as solvents and tetramethylsilane as the internal standard. X-Ray data for complex 2 were collected using a HER-CURY-AFC8 CCD area detector using monochromated Mo-Ka radiation ( $\lambda = 0.71073$  Å). The crystal **2** was measured at 223(2) K. Elemental analyses (C, H, N) were carried out on a Vario EL III elemental analyzer (Elementar, Germany). Mass spectra were recorded on a Waters MALDI SYNAPT QT mass spectrometer. HPLC analysis was performed on a high pressure liquid chromatograph (Waters 515) using water and acetonitrile as the mobile phase.

#### Reaction of (dfppy)<sub>2</sub>Ir(µ-Cl)<sub>2</sub>Ir(dfppy)<sub>2</sub> with sodium methoxide

Two different bases were used to react with 1 and generated the same product (dfppy)<sub>2</sub>Ir(fppy) (2) as shown in Schemes 1 and 2. Thus, herein, a typical procedure for the production of 2 is described as follows: [(dfppy)<sub>2</sub>IrCl]<sub>2</sub> (0.183 g, 0.15 mmol) and NaOCH<sub>3</sub> (0.083 g, 1.54 mmol) were added into a 100 mL three-necked flask. After being vacuumed by a vacuum pump and refilled with dry nitrogen three times, ethoxy-ethanol (10 mL) was then added to the mixture. The resulting mixture was stirred at 373.15 K (100 °C) for 48 h, then dried in vacuo and the residue was extracted with water and dichloromethane. The organic layer was separated by TLC to afford 2 as a yellow crude powder, which was further recrystallized in hexane/dichloromethane and a desired yellow cuboid crystal product 2 was obtained. IR (KBr): 3087 m, 1604 1479 s, 1430 m, 1405 s, 1295 1249 m, 848 831 m, 756 m. <sup>1</sup>H-NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C): δ 5.74 (dd, J = 2.4, 2.4 Hz, 1H), 5.94 (dd, J = 2.4, 2.4 Hz, 1H), 6.38 (m, 1H), 6.41 (m, 1H), 6.60 (td, J = 8.8, 2.7 Hz, 2H), 6.74 (m, 2H), 6.88 (m, 1H), 7.50 (m, 1H), 7.56 (d, J = 0.9 Hz, 2H), 7.62 (d, J = 1.6 Hz, 1H), 7.70 (d, J =3.4 Hz, 1H), 7.77 (d, J = 5.6 Hz, 1H), 7.82 (d, J = 8.2 Hz, 1H), 7.97 (d, J = 5.9 Hz, 1H), 8.15 (m, 2H). <sup>19</sup>F-NMR (377 MHz,  $CD_2Cl_2$ , 25 °C):  $\delta$  -109.56 (d, J = 9.6 Hz), -109.70 (d, J = 10.0 Hz), -110.35 (d, J = 9.6 Hz), -111.58 (d, J = 9.9 Hz), -112.31 (s). Anal found C 53.13 H 2.59 N 5.55 Cald C 53.22 H 2.57 N 5.64. MS (m/z): 746  $[M + H^+]^+$ .

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