

Luminescent Iridium(III) Complex with Alkoxy-Functionalised 2-Phenylpyridine Ligands: Synthesis, Spectroscopic and Photophysical Studies

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Cyclometalated iridium(III) complexes have garnered considerable interest owing to their exceptional photophysical properties and broad applicability in luminescence-based technologies. This work describes the preparation, spectroscopic analysis, and photophysical characterisation of a new emissive iridium(III) complex, $[\text{Ir}(\text{bFppy})_2(\text{eFppy})]$, incorporating the ligands 2-(2-butoxy-4-fluorophenyl)pyridine (bFppy) and 2-(2-ethoxy-4-fluorophenyl)pyridine (eFppy). The structure identity of the complex was confirmed by ^1H NMR, ^{13}C NMR, and FTIR spectroscopic techniques. In the ^1H NMR spectrum, aliphatic proton signals were observed between δ 1.00–4.09 ppm, corresponding to the ethyl and butyl chain protons, while signals in the δ 5.99–8.81 ppm region were attributed to aromatic protons of the phenylpyridine frameworks. A total of 43 carbon resonances were resolved in the ^{13}C NMR spectrum, in complete accordance with the number of carbon atoms anticipated from the proposed structure. Complementary FTIR data supported these assignments through the observation of C–H, C=C, and C=N stretching bands characteristic of the complex. UV-Vis spectroscopy identified π – π^* intraligand transitions in the ultraviolet region and MLCT transitions extending into the visible range. Steady-state emission measurements revealed that the complex produces intense green phosphorescence in dichloromethane solution at ambient temperature, with an emission maximum at $\lambda_{\text{em}} = 502$ nm, indicative of an emissive pathway dominated by $^3\text{MLCT}$ character. The efficient triplet-state emission exhibited by this complex highlights its promising prospects for applications in optoelectronic devices, such as organic light-emitting diodes (OLEDs).

Keywords: Iridium(III) complex, cyclometalated, luminescent, alkoxy-functionalised, 2-phenylpyridine

Received: February 2026; Accepted: August 2026

In recent decades, luminescent transition metal complexes have gained popularity due to their intriguing photochemical and photophysical properties [1]. The outstanding photophysical and electronic characteristics of luminescent transition metal complexes have attracted considerable research interest, leading to their broad utilisation across numerous applications. These applications include electrochemiluminescence sensing, field-effect transistors, light-emitting diodes, organic electroluminescent devices, photorefractive systems, light-emitting electrochemical cells, and biological labelling agents [2]. The efficiency of light-emitting electrochemical cells (LECs) and organic light-emitting diodes (OLEDs) can be significantly increased by luminescent transition metal complexes, as most of them can utilise both singlet and triplet states simultaneously, unlike classical fluorescent materials that emit light from singlet states [3]. Studies of strongly luminescent complexes of transition metal centres

have mainly focused on transition metal centres with d^6 (for example, osmium(II), rhenium(I), ruthenium(II), or iridium(III)) or d^8 (for example, platinum(II), palladium(II), and gold(III)) [4]. Nevertheless, OLED technology is still struggling with its material systems and the architecture of OLED devices [5], and there is a pressing need for further innovations to improve the efficiency, lifespan, and light output of OLED devices. Red, green, and blue light sources are required for excellent quality in OLED displays and solid-state lighting [6]. However, the development of long-lasting and efficient green emitters remains an obstacle, necessitating ongoing research [7].

Iridium(III) complexes are considered the most favourable emitters in OLED compared to other transition metal complexes because of their remarkable properties, such as relatively high phosphorescence quantum yield, short triplet lifetimes, excellent colour tunability from blue to

deep red, and excellent thermal and electrochemical stability [8]. Notably, iridium(III) was established as the most versatile due to its excellent photophysical properties such as full-colour emission and high efficiency along with durable electrochemical properties [9]. Additionally, cyclometalated iridium(III) complexes can tune the colour over a wide range owing to their other unique photophysical properties, such as large ligand-field splitting, which prevents the thermal formation of non-radiative metal-centred (^3MC) $d-d$ states [10]. Furthermore, iridium(III) complexes also display very quick triplet radiative decay due to their notable spin-orbit coupling which results in extremely high quantum yields for photoluminescence [11]. Iridium(III) complexes differ significantly from lanthanide compounds, other photoluminescent materials, and alternative d^6 or d^8 transition metal complexes. As these compounds exhibit considerably shorter excited-state lifetimes, they facilitate faster signal acquisition and minimise the duration of cellular exposure to the excitation light source [12]. This versatility stems from their capacity to generate highly efficient luminescent emissions, rendering them particularly well-suited for energy transfer processes and photoredox catalytic applications [13].

For iridium(III) complexes utilising the cyclometalating ligand phenylpyridine, the highest occupied molecular orbital (HOMO) is situated on the phenyl π and iridium $5d$ orbitals, whereas the lowest unoccupied molecular orbitals (LUMO) are found on the π^* orbitals of the pyridyl ring [14].

The incorporation of electron-donating or electron-withdrawing groups can significantly increase the energy gap between the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) [3]. Functionalisation of the phenylpyridine ring of both cyclometalating and auxiliary ligands with alkoxy groups in a single iridium(III) complex has not been previously reported. Notably, an imidazole-based iridium(III) complex (Figure 1) was reported by our research group in 2023 [15] bearing a butoxy group solely on the cyclometalating ligand, emitting at 466 nm, the complex reported in this study exhibited a red-shifted emission at 503 nm. This bathochromic shift suggests that alkoxy functionalisation of the ancillary ligand predominantly raises the HOMO energy level rather than destabilising the LUMO, thereby narrowing the HOMO-LUMO gap relative to cyclometalating-ligand-only substitution. This study highlights the distinct electronic influence of ligand-position-dependent alkoxy substitution on the photophysical behaviour of Ir(ppy)-type complexes, further underscoring the novelty of the dual-ligand functionalisation strategy adopted here.

EXPERIMENTAL

Chemicals and Materials

No further purification was performed on any of the chemicals or solvents used; all were sourced from commercial suppliers and used directly as supplied.

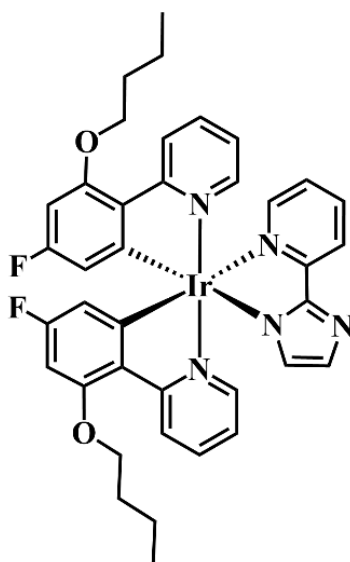


Figure 1. Structure of reported iridium(III) complex, Ir(bFppy) $_2$ (pyim) (bFppy = 2-(2-butoxy-4-fluorophenyl)pyridine and pyim = 2-(1*H*-Imidazol-2-yl)pyridine) [15].

Characterisation Methods

^1H and ^{13}C NMR spectra were acquired at 500 MHz and 126 MHz, respectively, using a JNM-ECX-500 NMR spectrometer. FTIR spectra, recorded over the 4000–400 cm^{-1} range on a Perkin Elmer Spectrum 3 Tri-Range spectrometer, were used to identify the characteristic functional groups of the synthesised compounds. Cary 60 Agilent Technologies UV-Visible spectrophotometer was used to measure the absorption spectrum, while the emission spectrum was obtained using Edinburgh Photoluminescence spectrometer (Model: FLS920) from dichloromethane solution using 1 cm length quartz cuvettes at 298 K.

Synthesis and Characterisation

Preparation of the Ligand 2-(2-butoxy-4-fluorophenyl)pyridine (bFppy)

The 2-(2-butoxy-4-fluorophenyl)pyridine ligand was prepared as previously reported [15] with slight alterations. A 100 mL round-bottomed flask was purged with nitrogen gas to establish an inert atmosphere, ensuring the removal of oxygen, moisture, and any other potential contaminants. A combination of 2-butoxy-4-fluorophenylboronic acid (0.5425 g, 2.6 mmol), 2-bromopyridine (1.2423 g, 7.9 mmol), aqueous potassium carbonate (2.0 M, 4.34 mL), and tetrakis(triphenylphosphine)palladium(0) (0.0300 g, 0.026 mmol, 1 mol%) was prepared in a flask. This mixture was subjected to reflux at 80°C under an inert nitrogen atmosphere for 48 hours, with periodic TLC analysis conducted to track the progress of the reaction. Upon confirmation of reaction completion, water was added to quench the mixture, and the desired products were isolated via extraction with ethyl acetate. The combined organic layers were subsequently washed, dried using anhydrous Na_2SO_4 , filtered, and concentrated under reduced pressure to obtain the crude material. Final purification was achieved using radial chromatography with a chromatotron and a hexane/ethyl acetate eluent system. Gradient elution was applied, starting with 100% hexane and progressively increasing the proportion of ethyl acetate until all fractions were collected. The target compound was obtained as a yellowish oil with a final mass of 0.04290 g (yield > 6.4%). ^1H NMR (500 MHz, CD_3OD) δ 8.55 (d, J = 4.7 Hz, 1H), 7.76 (d, J = 1.7 Hz, 1H), 7.75–7.75 (m, 3H), 7.60–7.56 (m, 1H), 7.29–7.26 (m, 1H), 6.83 (d, J = 11.2 Hz, 1H), 6.76 (t, J = 8.3 Hz, 1H), 1.70–1.63 (m, 2H), 1.38 (h, J = 7.4 Hz, 3H), 0.88 (t, J = 7.4 Hz, 4H). ^{13}C NMR (126 MHz, DMSO- D_6) δ 164.25 (C_q), 162.30 (C_q), 157.59 (C_q), 154.31 (C_q), 149.37 (CH), 135.88 (CH), 132.09 (CH), 124.54 (CH), 100.51 (CH), 68.22 ($-\text{CH}_2-$), 30.57 ($-\text{CH}_2-$), 18.86 ($-\text{CH}_2-$), 13.66 ($-\text{CH}_3$).

Preparation of the Ligand 2-(2-ethoxy-4-fluorophenyl)pyridine (eFppy)

2-(2-ethoxy-4-fluorophenyl)pyridine ligand was synthesised using a modified method reported previously [15]. Radial chromatographic purification of the crude product was performed on a chromatotron using a binary solvent system composed of hexane and ethyl acetate. Elution was performed using a gradient polarity approach, beginning with 100% hexane and gradually increasing the proportion of ethyl acetate until all fractions were successfully collected. This afforded the target compound as a yellowish oil with a final mass of 0.3972 g. ^1H NMR (500 MHz, CD_3OD) δ 8.56 (d, 1H, CH), 7.80 (q, 2H, CH), 7.58 (t, 1H, CH), 7.32 (d, 1H, CH), 6.87 (d, 1H, CH), 6.78 (t, 1H, CH), 4.11–4.05 (m, 2H, $\text{O}-\text{CH}_2$), 1.34 (t, 3H, CH_3). ^{13}C NMR (126 MHz, CD_3OD) δ 165.11 (C_q), 163.15 (C_q), 157.70 (C_q), 155.44 (C_q), 148.44 (CH), 136.45 (CH), 131.80 (CH), 125.48 (CH), 122.04 (CH), 106.67 (CH), 100.16 (CH), 64.27 ($-\text{CH}_2-$), 13.52 ($-\text{CH}_3$).

Preparation of the Iridium(III) Chloro-Bridged Dimer Intermediate $[\text{Ir}(\text{bFppy})_2(\mu\text{-Cl})_2]$

A modified literature procedure [16] was employed to prepare the dimer $[\text{Ir}(\text{bFppy})_2(\mu\text{-Cl})_2]$. To create an inert reaction environment, a 100 mL round-bottomed flask was flushed thoroughly with nitrogen gas, effectively eliminating oxygen, moisture, and other potential impurities before commencing the reaction. The flask was then charged with ligand bFppy (0.0597 g, 2 mmol), iridium trichloride hydrate (0.0271 g, 9 mmol), and 30 mL of a 3:1 mixture of 2-ethoxyethanol and water. The reaction mixture was brought to reflux and stirred for 16 hours under a nitrogen atmosphere, protected from light throughout, and product formation was monitored by TLC. Upon completion, the mixture was allowed to cool to room temperature, and a yellow precipitate was formed. The solid was collected by filtration, washed with water, and dried to give the desired product as a yellow solid in a yield of 0.0726 g (54.03%). ^1H NMR (500 MHz, CDCl_3) δ 9.12 (d, J = 5.7 Hz, 1H), 8.70 (d, J = 8.4 Hz, 1H), 7.70 (t, J = 7.1 Hz, 1H), 6.70 (t, J = 6.6 Hz, 1H), 6.09 (d, J = 11.4 Hz, 1H), 5.13 (d, J = 7.0 Hz, 1H), 4.01–3.94 (m, 2H), 1.92 (p, J = 6.6 Hz, 3H), 1.61 (dd, J = 15.0, 7.5 Hz, 2H), 1.04 (t, J = 7.4 Hz, 3H).

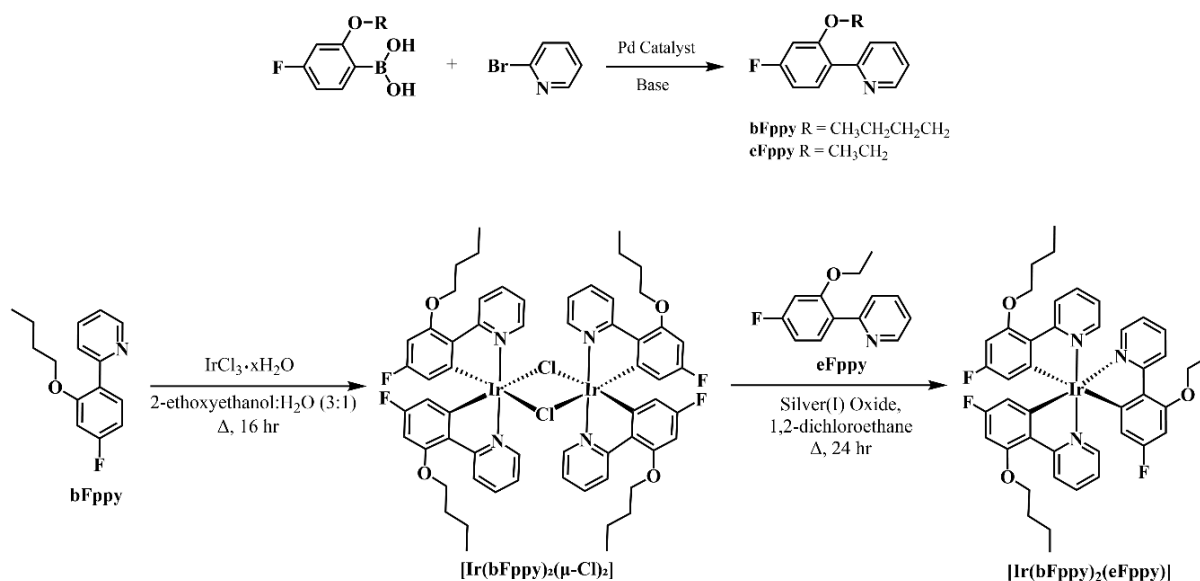
Preparation of the Complex $\text{Bis}(2-(2-butoxy-4-fluorophenyl)pyridine)(2-(2-ethoxy-4-fluorophenyl)pyridine)\text{iridium(III)}$, $[\text{Ir}(\text{bFppy})_2(\text{eFppy})]$

The complex $[\text{Ir}(\text{bFppy})_2(\text{eFppy})]$ was prepared in an inert atmosphere. Prior to use, a 100 mL round-bottomed flask was purged with nitrogen gas to eliminate oxygen, moisture, and other impurities

from the flask. A mixture comprising 2-(2-ethoxy-4-fluorophenyl)pyridine ligand (0.0163 g, 4 mmol), chloro-bridged iridium(III) dimer $[\text{Ir}(\text{bFppy})_2(\mu\text{-Cl})_2]$ (0.0382 g, 1 mmol), and silver(I) oxide (0.0080 g, 1.24 mmol) was prepared and transferred into a flask, with 30 mL of 1,2-dichloroethane serving as the reaction solvent. Reflux conditions at 85°C were applied to the reaction mixture for 24 hours under inert nitrogen atmosphere and protected from light exposure, with TLC analysis periodically conducted to track progress. Upon confirmation of reaction completion, the mixture was cooled and filtered through a Celite bed to eliminate any undissolved material. A chromatotron was then used for the radial chromatographic purification of the crude product, with the eluent composition incrementally adjusted from pure hexane to hexane/ethyl acetate ratios of 100:1, 100:2, and ultimately 100:3. The target complex was isolated in a yield of 0.0234 g (54.51%). ^1H NMR (500 MHz, CDCl_3) δ 8.80 (d, J = 8.6 Hz, 1H), 8.69–8.63 (m, 2H), 8.04 (d, J = 5.2 Hz, 1H), 7.90 (d, J = 5.7 Hz, 1H), 7.86 (d, J = 8.0 Hz, 1H), 7.80 (t, J = 7.7 Hz, 1H), 7.71 (t, J = 7.7 Hz, 2H), 7.60–7.57 (m, 1H), 7.54–7.44 (m, 2H), 7.21 (t, J = 6.0 Hz, 1H), 6.78 (d, J = 8.6 Hz, 1H), 6.70 (d, J = 10.9 Hz, 1H), 6.24–6.18 (m, 1H), 5.75 (d, J = 7.4 Hz, 1H), 5.60 (d, J = 6.9 Hz, 1H), 4.09–4.01 (m, 6H), 1.95–1.89 (m, 4H), 1.58 (q, J = 7.3 Hz, 4H), 1.41 (t, J = 6.9 Hz, 6H), 1.02 (t, J = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3): δ = 13.84 (–CH₃), 14.07 (–CH₃), 14.69 (–CH₃), 19.65 (–CH₂–), 22.80 (–CH₂–), 29.81 (–CH₂–), 31.40 (–CH₂–), 63.80 (–CH₂–), 67.90 (–CH₂–), 68.02 (–CH₂–), 100.25 (CH), 100.46 (CH), 107.56 (CH), 107.73 (CH), 120.28 (CH), 121.16 (CH), 121.30 (CH), 121.78 (CH), 123.09 (CH), 123.28 (CH), 123.85 (CH), 125.14 (CH), 132.38 (CH), 132.46 (CH), 134.52 (CH), 135.77 (CH), 136.02 (CH), 136.55 (CH), 147.52 (C_q), 149.17 (C_q), 151.12 (C_q), 153.02 (C_q), 155.12 (C_q), 157.57 (C_q), 157.65 (C_q), 159.95 (C_q), 163.03 (C_q), 165.00 (C_q), 166.50 (C_q), 166.60 (C_q), 168.62 (C_q), 181.32 (C_q), 184.12 (C_q). IR (ATR): ν = 2957 (w) cm^{-1} (C–H_{aromatic}); 2925 (w) cm^{-1} (C–H_{methyl}); 2853 (w) cm^{-1} (C–H_{methylene}); 1571 (vs) cm^{-1} (C=C_{aromatic}); 1463 (s) cm^{-1} (C=N_{pyridine}); 1160 (s) cm^{-1} (C–N); 1042 (s) cm^{-1} (C–O_{alkyl}). UV/Vis (CH_2Cl_2) λ_{max} (ϵ) = 292 nm (7399 $\text{mol}^{-1} \text{dm}^3 \text{cm}^{-1}$), 336 nm (3363 $\text{mol}^{-1} \text{dm}^3 \text{cm}^{-1}$), and 463 nm (740 $\text{mol}^{-1} \text{dm}^3 \text{cm}^{-1}$); fluorescence (CH_2Cl_2): λ_{ex} = 378 nm; λ_{em} = 502 nm.

RESULTS AND DISCUSSION

The synthetic route for the newly developed bis-cyclometalated iridium(III) complex is outlined in Scheme 1. The synthesis of $[\text{Ir}(\text{bFppy})_2(\text{eFppy})]$ was structured into three discrete phases. The opening phase centred on constructing the alkoxy-bearing 2-phenylpyridine ligand framework, yielding 2-(2-butoxy-4-fluorophenyl)pyridine (bFppy) and 2-(2-ethoxy-4-fluorophenyl)pyridine (eFppy). Both ligands were synthesised via Suzuki-Miyaura cross-coupling reactions, in which the corresponding 2-(2-alkoxy-4-fluorophenyl)boronic acids were coupled with 2-bromopyridine in the presence of a palladium catalyst and potassium carbonate as the base in tetrahydrofuran. This approach efficiently afforded the desired fluorinated phenylpyridine derivatives through the formation of a new C–C bond between phenyl and pyridyl moieties. In subsequent complexation steps, bFppy served as the primary cyclometalating (C^N) ligand, and eFppy was incorporated as the ancillary ligand. The ortho-substituted and electron-rich nature of 2-butoxy-4-fluorophenylboronic acid, which is known to be prone to protodeboronation and homocoupling side reactions, contributed to the moderate yield of ligand bFppy (>6.4%). To counteract these competing routes, a three-fold excess of 2-bromopyridine was used in the reaction. In addition, purification by radial chromatography further contributed to the overall reduced isolated yield [17], as the product was obtained as an oil rather than a crystalline solid. In the second phase, the synthesised ligand bFppy was reacted with iridium(III) chloride hydrate through a cyclometalation reaction in a 3:1 (v/v) mixture of 2-ethoxyethanol and water under an inert atmosphere. The mixture was refluxed for 16 hours, yielding the cyclometalated iridium(III) μ -chloride bridged dimer, $[\text{Ir}(\text{bFppy})_2(\mu\text{-Cl})_2]$. The $[\text{Ir}(\text{C}^{\text{N}})_2(\mu\text{-Cl})]_2$ core structure was formed via a conventional Nonoyama chloro-bridged dimerisation pathway [18] in this reaction. The reaction of the chloro-bridged iridium(III) dimer $[\text{Ir}(\text{bFppy})_2(\mu\text{-Cl})_2]$ with the eFppy ligand constituted the final synthetic phase, furnishing the desired neutral cyclometalated complex $[\text{Ir}(\text{bFppy})_2(\text{eFppy})]$ as the final product.



Scheme 1. Synthetic route for the preparation of the new bis-cyclometalated iridium(III) complex $[\text{Ir}(\text{bFppy})_2(\text{eFppy})]$.

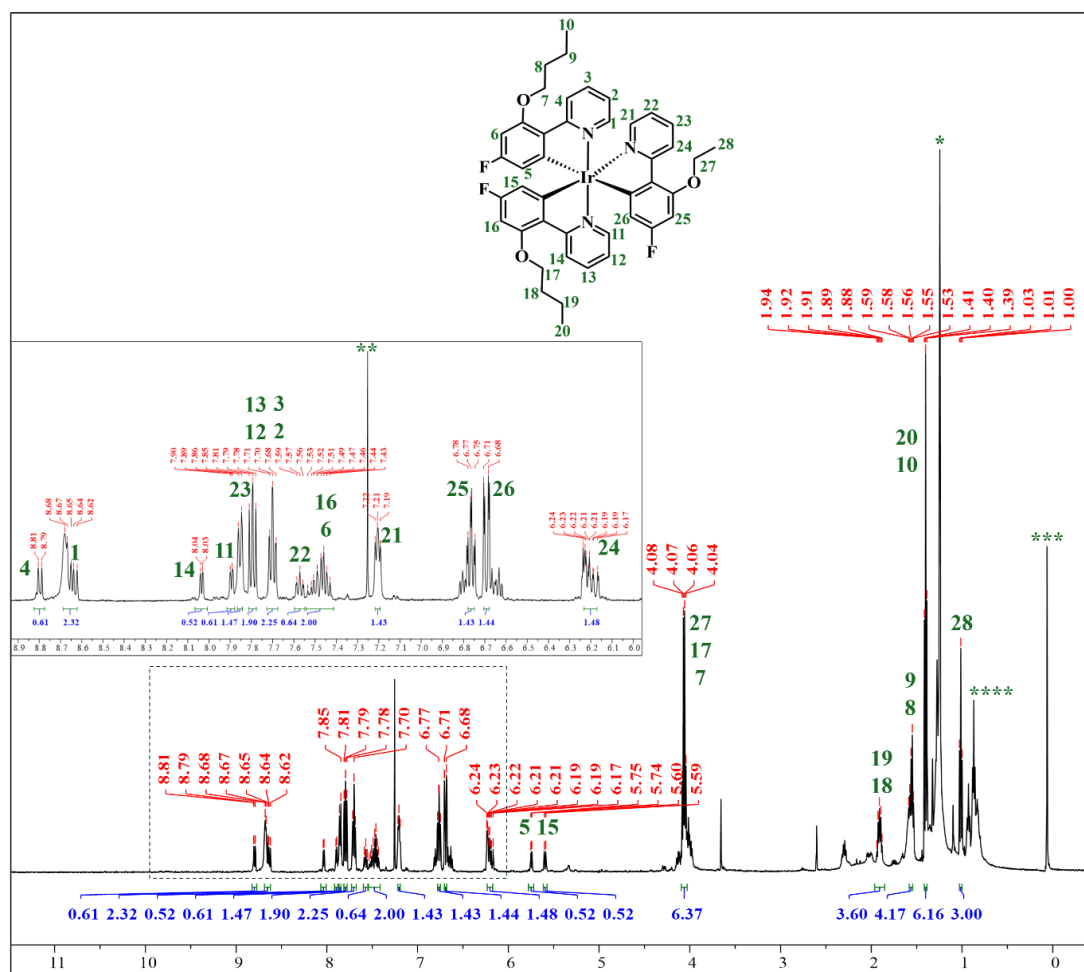


Figure 2. ^1H NMR spectrum of complex $[\text{Ir}(\text{bFppy})_2(\text{eFppy})]$. The residual solvents are labelled accordingly: H_2O is marked with *, CDCl_3 is marked with **, grease is marked with *** and n-hexane residual is marked with ****
Inset: chemical structure of the complex with its atom numbering scheme.

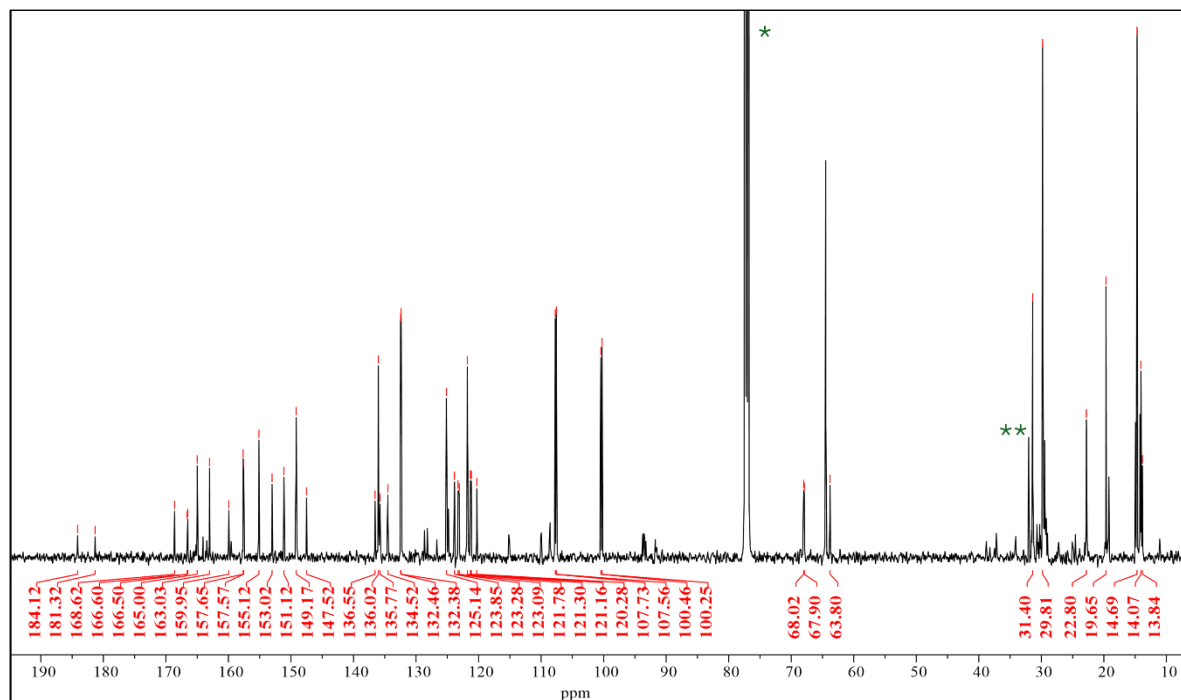


Figure 3. ^{13}C NMR spectrum of $[\text{Ir}(\text{bFppy})_2(\text{eFppy})]$ complex. The residual solvents are labelled accordingly: CDCl_3 is marked with * and n-hexane is marked with **.

Characterisation

NMR Spectra Analysis

The successful synthesis and structural framework of the target complex, $[\text{Ir}(\text{bFppy})_2(\text{eFppy})]$, were unambiguously established by ^1H (Figure 2) and ^{13}C NMR spectroscopy (Figure 3), with all spectra recorded in CDCl_3 . The spectra displayed well-resolved resonances, with integrated intensities in full agreement with the expected number of protons and carbons for each ligand, confirming their successful incorporation into the complex. Proton assignments were made by comparing the ^1H NMR spectrum of the final complex (Figure 2) against those of the free ligands (Figures 4 and 5) and the precursor chloro-bridged dimer, $[\text{Ir}(\text{bFppy})_2(\mu\text{-Cl})_2]$ (Figure 6). Aromatic proton signals attributable to the phenylpyridine moieties were observed in the ^1H NMR spectrum over the range of δ 5.59–8.81 ppm

[19]. The signals detected in the aliphatic region of the spectrum were attributed to the protons of the butoxy and ethoxy substituents incorporated within the complex. The three methyl groups gave rise to triplet peaks at 1.00 ppm and 1.39 ppm, whereas the methylene protons appeared as multiplet resonances at 1.53 ppm, 1.88 ppm, and 4.04 ppm [19]. The ^{13}C NMR spectrum (Figure S4) corroborates the proposed structure, with all observed carbon signals appearing at chemical shifts corresponding to the expected aromatic and aliphatic carbon environments. A total of 44 carbon signals were identified across the spectrum, with aromatic carbons resonating in the range of 109.20–182.53 ppm. The aliphatic region, appearing upfield at 11.09–94.35 ppm, displayed distinct signals corresponding to the methyl and methylene carbons of the butoxy and ethoxy substituents. Taken together, this carbon distribution is fully consistent with the proposed structural framework and provides strong evidence for the successful formation of the target complex.

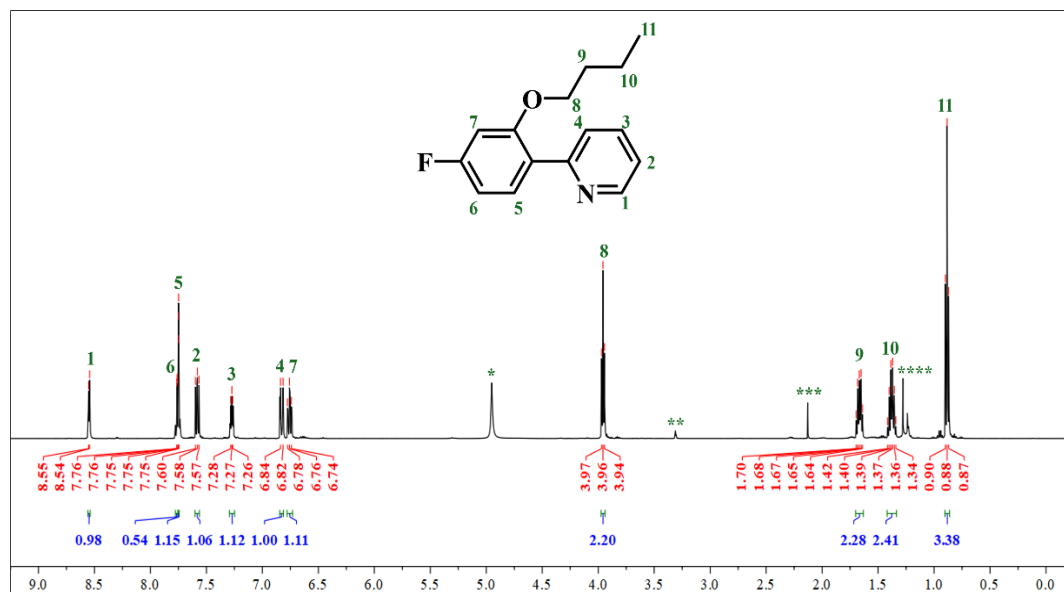


Figure 4. ^1H NMR spectrum of 2-(2-butoxy-4-fluorophenyl)pyridine (**bFppy**). ^1H NMR (500 MHz, CD₃OD) δ 8.55 (d, J = 4.7 Hz, 1H), 7.76 (d, J = 1.7 Hz, 1H), 7.75–7.75 (m, 3H), 7.60–7.56 (m, 1H), 7.29–7.26 (m, 1H), 6.83 (d, J = 11.2 Hz, 1H), 6.76 (t, J = 8.3 Hz, 1H), 1.70–1.63 (m, 2H), 1.38 (h, J = 7.4 Hz, 3H), 0.88 (t, J = 7.4 Hz, 4H). The residual solvents are labelled accordingly: H₂O is marked with *, CD₃OD is marked with **, residual acetone is marked with *** and residual n-hexane is marked with ****. Inset: chemical structure of ligand **bFppy** with its atom numbering scheme.

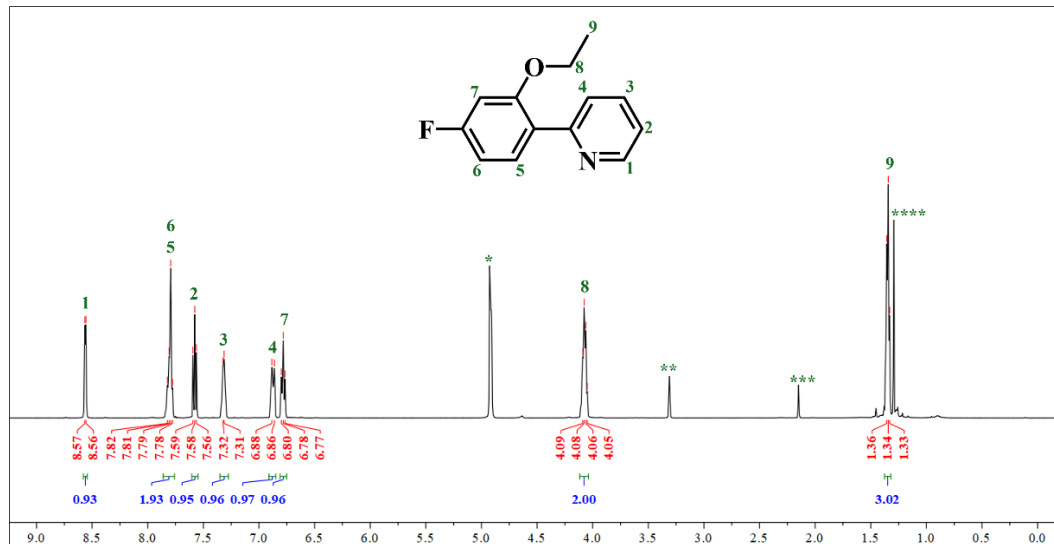


Figure 5. ^1H NMR spectrum of 2-(2-ethoxy-4-fluorophenyl)pyridine (**eFppy**). ^1H NMR (500 MHz, CD₃OD) δ 8.56 (d, J = 4.6 Hz, 1H), 7.80 (q, J = 7.6 Hz, 2H), 7.58 (t, J = 7.7 Hz, 1H), 7.32 (d, J = 5.1 Hz, 1H), 6.87 (d, J = 11.1 Hz, 1H), 6.78 (t, J = 8.3 Hz, 1H), 4.11–4.05 (m, 2H), 1.34 (t, J = 6.6 Hz, 3H). The residual solvents are labelled accordingly: H₂O is marked with *, CD₃OD is marked with **, residual acetone is marked with *** and residual n-hexane is marked with ****. Inset: chemical structure of ligand **eFppy** with its atom labelling scheme.

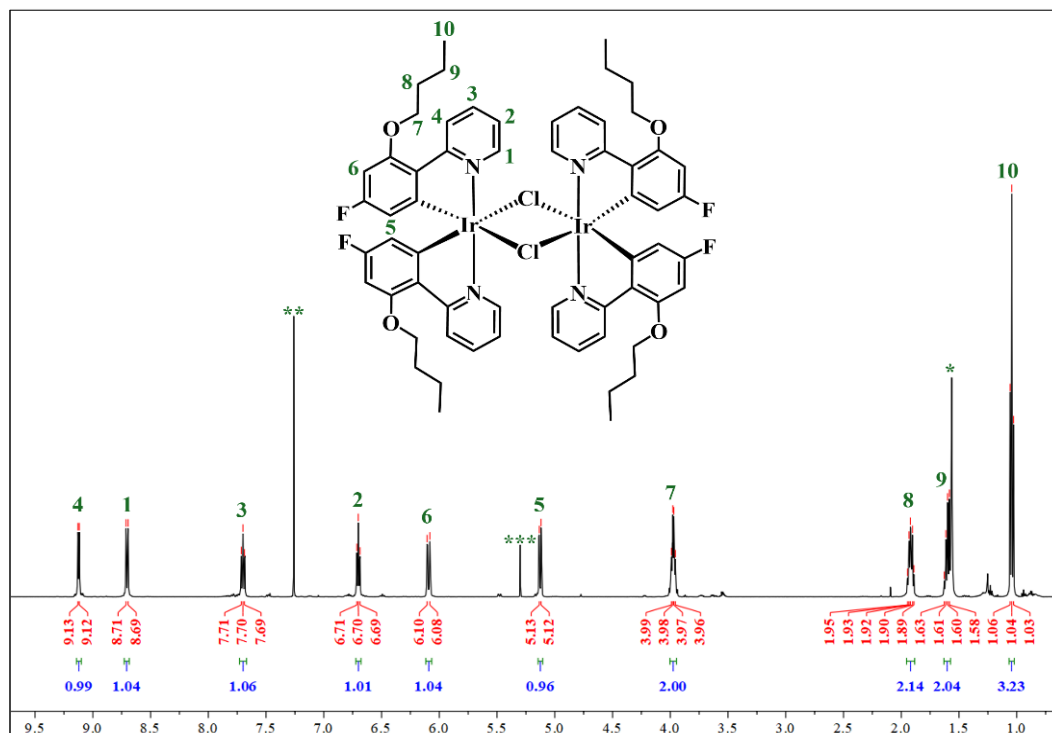


Figure 6. ^1H NMR spectrum of $[\text{Ir}(\text{bFppy})_2(\mu\text{-Cl})_2]$. ^1H NMR (500 MHz, CDCl_3) δ 9.12 (d, $J = 5.7$ Hz, 1H), 8.70 (d, $J = 8.4$ Hz, 1H), 7.70 (t, $J = 7.1$ Hz, 1H), 6.70 (t, $J = 6.6$ Hz, 1H), 6.09 (d, $J = 11.4$ Hz, 1H), 5.13 (d, $J = 7.0$ Hz, 1H), 4.01–3.94 (m, 2H), 1.92 (p, $J = 6.6$ Hz, 3H), 1.61 (dd, $J = 15.0, 7.5$ Hz, 2H), 1.04 (t, $J = 7.4$ Hz, 3H). The residual solvents are labelled accordingly: H_2O is marked with *, CDCl_3 is marked with ** and dichloromethane is marked with ***. Inset: chemical structure of dimer $[\text{Ir}(\text{bFppy})_2(\mu\text{-Cl})_2]$ with its atom labelling scheme.

FTIR Spectrum Analysis

Complementing the NMR data, the FTIR spectrum of the complex (Figure 7) aligns with the proposed structural framework. Characteristic stretching bands corresponding to both aliphatic and aromatic C–H bonds were clearly observed, which were in line with the expected functional groups present within the complex. Of particular note, the aliphatic C–H stretching vibrations were identified at 2925–2853 cm^{-1} , lending further confidence to the presence of the alkoxy substituents in the structure [20, 21], which are attributed to the butoxy and ethoxy substituents. Conversely, Aromatic C–H stretching was identified at 2957 cm^{-1} in the

FTIR spectrum [22], ascribed to the presence of phenyl and pyridine in the complex structure. Infrared spectral bands assignable to C=C, C=N, and C–N stretching modes provided further evidence for the incorporation of aromatic moieties into the molecular framework of the complex. The C=C stretching band was identified at 1571 cm^{-1} , while the coordination of the pyridine nitrogen atoms to the iridium centre was confirmed by the appearance of C=N and C–N stretching vibrations at 1463 cm^{-1} and 1160 cm^{-1} , respectively. Furthermore, a C–O stretching vibration detected at 1042 cm^{-1} corresponds to the presence of oxygen-containing alkoxy substituents, in good agreement with the proposed molecular structure of the complex [23].

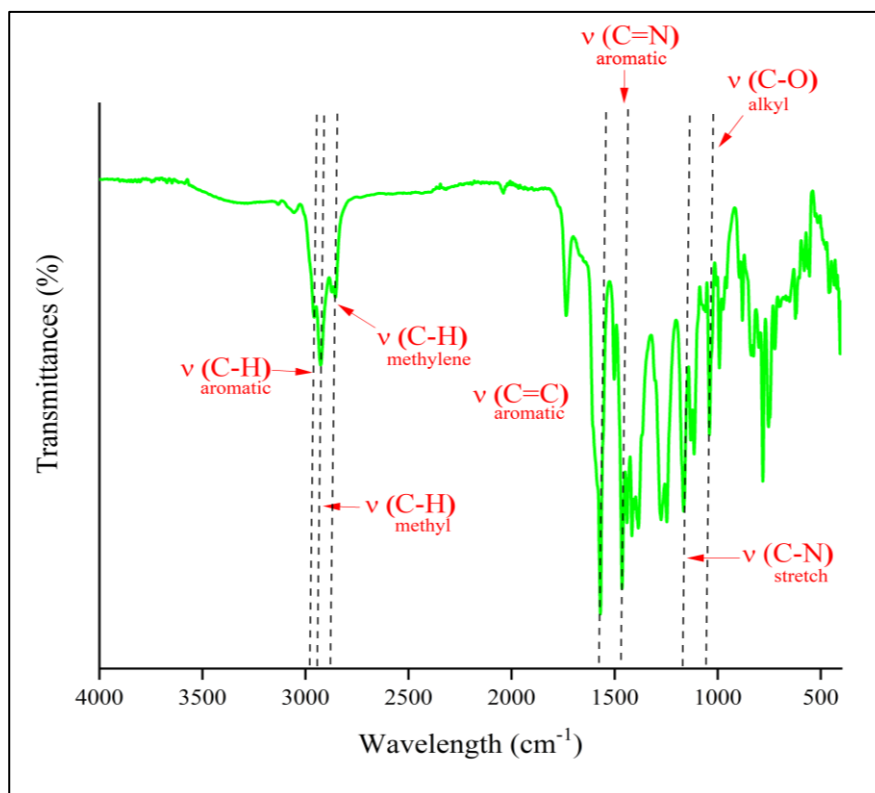


Figure 7. FTIR spectrum of the $[\text{Ir}(\text{bFppy})_2(\text{eFppy})]$ complex.

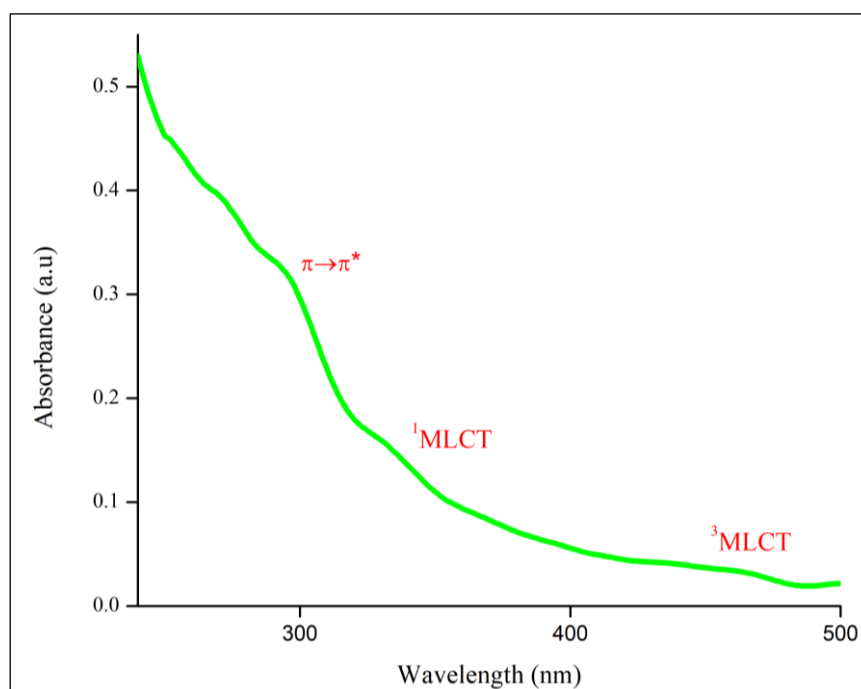


Figure 8. UV-Vis absorption spectrum of the $[\text{Ir}(\text{bFppy})_2(\text{eFppy})]$ complex in a dichloromethane solution (44.6 μM) at 298 K.

Photophysical Properties

UV-Visible Absorption Spectrum Analysis

The photophysical properties of the synthesised complex $[\text{Ir}(\text{bFppy})_2(\text{eFppy})]$ were investigated using UV-Vis absorption spectroscopy, with the spectrum recorded in dichloromethane solution at 298 K (Figure 8). In the higher-energy region spanning 240–320 nm, the spectrum exhibited intense absorption bands attributable to spin-allowed ligand-centred (LC) $\pi\text{-}\pi^*$ transitions, characteristic of the cyclometalating phenylpyridine ligands coordinated to the iridium centre [24]. In the lower energy region spanning 320–450 nm, a series of less intense absorption bands were identified, which were assignable to electronic transitions of predominantly metal-to-ligand charge transfer (MLCT) character [25]. The lowest-energy features appearing between 450 and 500 nm, characterised by low molar extinction coefficients ($\epsilon < 1000 \text{ M}^{-1} \text{ cm}^{-1}$), are ascribed to spin-forbidden transitions of $^3\text{MLCT}$, $^3\text{ILCT}$, and $^3\text{LLCT}$ character [26]. The appearance of these spin-forbidden bands can be rationalised by the strong ligand field environment generated around the iridium(III) centre, a consequence of the heavy-atom effect of iridium and the strong donor character of the cyclometalating

phenylpyridine ligands. These factors collectively facilitate efficient spin-orbit coupling, promoting mixing between the spin-allowed ($^1\text{MLCT}$ and $^1\text{LLCT}$) and spin-forbidden ($^3\text{MLCT}$, $^3\text{LLCT}$, and ^3LC) excited states, thereby enhancing the overall metal-centred contribution to the observed electronic transitions. The resulting absorption profile perfectly correlated with the distinctive spectral behaviour of iridium (III) phenylpyridine complexes [18], confirming the successful coordination of both the cyclometalating ligand bFppy and the ancillary ligand eFppy to the iridium centre.

Photoluminescence (PL) Spectrum Analysis

The photoluminescence properties of $[\text{Ir}(\text{bFppy})_2(\text{eFppy})]$ were evaluated in a dichloromethane solution at room temperature, and the resulting emission spectrum is presented in Figure 9. Upon excitation at 378 nm, the complex exhibited a broad, featureless emission in the visible region centred at $\lambda_{\text{em}} = 503 \text{ nm}$. This spectral profile indicates an emissive process with predominant $^3\text{MLCT}$ character, aligning with the well-established photophysical behaviour of cyclometalated iridium(III) complexes [24]. These observations collectively suggest that the emissive properties of the complex are largely governed by the $^3\text{MLCT}$ character.

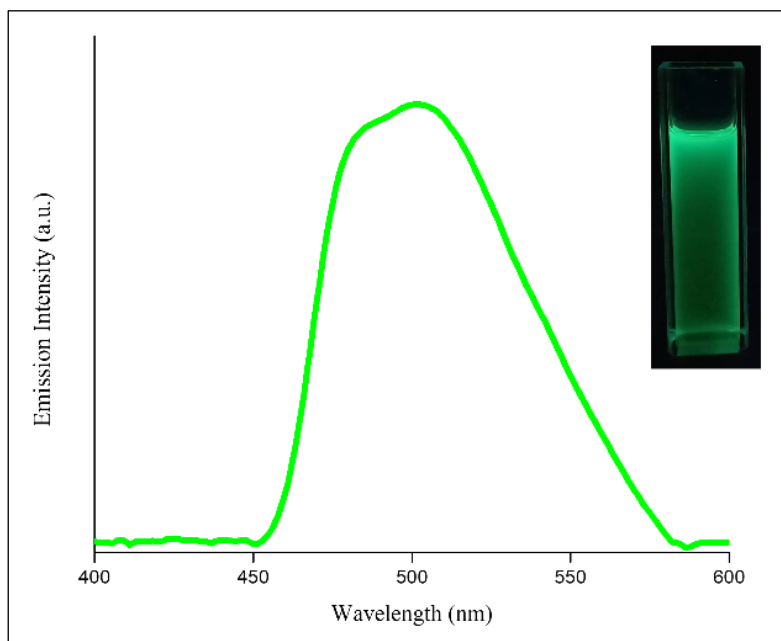


Figure 9. Room-temperature emission spectrum of the cyclometalated iridium(III) complex $[\text{Ir}(\text{bFppy})_2(\text{eFppy})]$ obtained in CH_2Cl_2 solution at a concentration of $44.6 \mu\text{M}$. Inset: Photoluminescence image of the complex in CH_2Cl_2 under UV light irradiation.

CONCLUSION

In conclusion, the successful preparation of a novel neutral cyclometalated iridium(III) complex, $[\text{Ir}(\text{bFppy})_2(\text{eFppy})]$, was accomplished, with comprehensive structural and photophysical characterisation achieved through NMR, IR, HRMS, UV-Vis absorption, and photoluminescence spectroscopic techniques. The proposed molecular structure and successful coordination of both cyclometalating and ancillary ligands were unambiguously confirmed through comprehensive spectroscopic analyses. UV-Vis and emission studies revealed the characteristic presence of $^1\text{MLCT}/^3\text{MLCT}$ and intraligand $\pi-\pi^*$ transitions, while the broad, featureless emission observed in the visible region was consistent with an emissive process predominantly governed by the $^3\text{MLCT}$ excited state. The strong spin-orbit coupling arising from the iridium(III) centre, in conjunction with the electronic perturbations imposed by the alkoxy-substituted phenylpyridine ligands, collectively governs the overall photophysical behaviour of the complex. Collectively, these findings demonstrate that $[\text{Ir}(\text{bFppy})_2(\text{eFppy})]$ exhibits efficient triplet-state emission, highlighting its potential as a promising candidate for application in optoelectronic devices, such as organic light-emitting diodes (OLEDs).

ACKNOWLEDGEMENTS

This research was conducted under the Fundamental Research Grant Scheme (FRGS/1/2019/STG01/UPSI/02/1) awarded by the Ministry of Higher Education (MoHE), Malaysia. The authors further extend their gratitude to Faezatul Alwani Mohd Rahim, Maebed Ahmed Badreldin Ahmed, and Dr. Abubakar Siddiq Salihu for their technical assistance and support throughout the study.

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