

Short Communication:**Synthesis, Spectroscopic, and Photophysical Studies of Phosphorescent Bis(2-(2,4-difluorophenyl)pyridine)Iridium(III) Complex Containing Derivative of 1H-1,2,4-Triazole Anchillary Ligand**

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Abstract: A cationic complex of iridium(III), $[\text{Ir}(\text{2,4-F}_2\text{ppy})_2(\text{F}_2\text{bpyta})]\text{PF}_6$ utilizing 1,2,4-triazolepyridyl as an anchillary ligand modified with a 2,6-difluorobenzyl substituent was synthesized and characterized. The aromatic signals of pyridyltriazole and phenylpyridine proton were detected in the ¹H-NMR spectrum between 10.00 and 7.00 ppm. Only one singlet peak was detected at 8.46 ppm H(8) shifted to the upfield, demonstrating that C5 was coordinated to the central iridium metal. The bands exhibited in the range of 1555–1431 cm⁻¹ in the IR spectrum because of the C=C and C=N aromatic rings stretching pyridine, phenyl, and triazole vibrations. The UV-Vis absorption spectrum showed a slight and broad absorbance peak at lower energy at a $\lambda_{\text{max}} = 371 \text{ nm}$ ($\epsilon = 6129 \text{ M}^{-1} \text{ cm}^{-1}$) in the visible range due to ¹MLCT and ³MLCT transitions. Blue emission was observed in the steady-state emission spectral of $[\text{Ir}(\text{2,4-F}_2\text{ppy})_2(\text{F}_2\text{bpyta})]\text{PF}_6$ and the other two previously synthesized iridium(III) complexes in CH₂Cl₂ solutions (air-equilibrated) at room temperature. The spectrum of luminescence for the $[\text{Ir}(\text{2,4-F}_2\text{ppy})_2(\text{F}_2\text{bpyta})]\text{PF}_6$ ($\lambda_{\text{em}} = 461 \text{ nm}$) is blue-shifted when compared to the $[\text{Ir}(\text{2,4-F}_2\text{ppy})_2(\text{hpyta})]\text{PF}_6$ ($\lambda_{\text{em}} = 469 \text{ nm}$), but red-shifted when related to the $[\text{Ir}(\text{2,4-F}_2\text{ppy})_2(\text{mbpyta})]\text{PF}_6$ ($\lambda_{\text{em}} = 454 \text{ nm}$).

Keywords: iridium(III) complex; 1H-1,2,4-triazole; ancillary ligand

■ INTRODUCTION

Iridium(III) complexes incorporating 2-phenylpyridine as cyclometalating (C[^]N) ligands have been thoroughly designed and have become the attention considering their high phosphorescence quantum efficiencies, significantly excellent lifetime, versatile color tunability, and thus regarded as the preferable phosphors used in the various photonic application, especially for organic light-emitting diodes (OLEDs) [1-3]. However, in general, the fluorescence color of iridium(III) complexes is easily affected by the alteration of the ligand bonded to the central metal [4-5]. Up to this point, the design of

phosphorescent green and red emitter displays has been incredibly successful, whereas the development and innovation of highly efficient, long-lived blue emitters have remained a challenge [6-7]. Therefore, numerous strategies have been developed to modify the emission to blue, one of which is the employment of strong σ -donating ligands such as triazole [8-9]. However, the design of 1H-1,2,4-triazole ligands for considerably efficient and sustained blue phosphorescent iridium(III) complexes is still under investigation [10-11]. Notably, 1H-1,2,4-triazole rings were incorporated into ligands and exploited to manipulate the electrochemical and spectroscopic properties of transition metal complexes

[12-14], making related triazolium salts as precursors to *N*-heterocyclic carbenes (NHCs) (Fig. 1).

Nazeeruddin et al. reported the designation of three blue iridium(III) complexes having similar modification strategies, with the dfppy (difluorophenylpyridine) primary cyclometalating ligand and NHC of imidazolium salt as an anchillary ligand. The emission is considerably blue-shifted to 467 and 464 nm when modifying the pyridylimidazole using methoxy, dimethoxy, and methyl substituent but their photoluminescence quantum yields (PLQYs) calculation is still at an average of 0.31–0.66 [7]. In addition, earlier studies on utilizing methyl and phenyl substituent into the imidazole ring also improved iridium(III)-carbene complexes [2]. As many previous studies have shown loopholes in quantum yields efficiency related to imidazole class of iridium(III)-carbene complexes, it becomes crucial to enhance this study by utilizing a 1*H*-1,2,4-triazole type of NHCs.

Interestingly, our research group has discovered that complex of [Ir(2,4-F₂ppy)₂(pyta)Cl] whereas F₂ppy and pyta refer to 2-(2,4-difluorophenyl)pyridine and (1*H*-1,2,4-triazole)pyridine respectively, emitted blue-green light ($\lambda_{em} = 469$ nm) [14]. In addition, we have reported two more iridium(III) complexes incorporating with anchillary ligand-based of pyta: (1*H*-1,2,4-triazole)pyridine, where pyta is modified with 4-methylbenzyl and hexyl, yielding (4-(4-methylbenzyl)-1*H*-1,2,4-triazol-1-yl)pyridine and (4-hexyl-1*H*-1,2,4-triazol-1-yl)pyridine, respectively, (later labeled as mbpyta and hpyta) [15]. Both of these cationic complexes exhibited significant differences in the absorbance spectral data, definable by the existence of electron-withdrawing (EWG) and electron-donating group (EDG), which have tailored the HOMO-LUMO energy gap [15-16]. Due to this significant finding, a further photophysical study of the

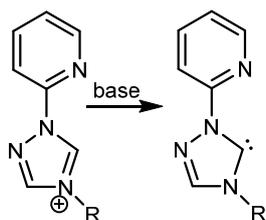


Fig 1. NHCs prepared *via* deprotonation of the corresponding triazolium salts

previously synthesized [Ir(2,4-F₂ppy)₂(mbpyta)]PF₆ and [Ir(2,4-F₂ppy)₂(hpyta)]PF₆ cationic complexes were reported herein. We also made a new cationic complex by adding an EWG benzyl group to the pyta and labeled it as [Ir(2,4-F₂ppy)₂(F₂bpyta)]PF₆.

■ EXPERIMENTAL SECTION

Materials

The industrial organic solvents and chemicals were reagent grade and utilized as received without any purification tests. Our group made pyta by arylating 1*H*-1,2,4-triazole and 2-bromopyridine in the catalyst under Ullman procedures [14]. The chloro-bridged iridium(III) dimer, [Ir(2,4-F₂ppy)₂(μ -Cl)]₂, was synthesized following the report by Nonoyama [16].

Instrumentation

The CHNS-O model Flash EA 1112 Series Elemental analyzer was employed to conduct carbon (C), hydrogen (H), and nitrogen (N) elemental analysis. JNM-ECX-500, JEOL NMR analyzed ¹H and ¹³C-NMR spectra using deuterated chloroform (CDCl₃), deuterated dichloromethane (CD₂Cl₂), and deuterated dimethyl sulfoxide (CD₃)₂SO as solvents. In addition, IR spectra from the Thermo Nicolet 6700 were acquired in the 4000–500 cm⁻¹ region. In air equilibrated dichloromethane solutions, the UV-Vis absorption absorbance data were examined using the Cary 60 UV-Vis spectrophotometer from Agilent Technologies. The steady-state luminescence spectra were obtained from Cary Eclipse (Agilent Technologies) fluorescence spectrophotometer.

Procedure

Synthesis of ligand (2-(2,6-difluorobenzyl)-1*H*-1,2,4-triazol-1-yl)pyridine, (F₂bpyta)

2-(1*H*-1,2,4-triazol-1-yl)pyridine (0.610 g, 0.004 mol) and 2,6-difluorobenzylbromide (1.860 g, 0.009 mol) were refluxed at a mole ratio equivalent to 1:2.1 respectively, for 19 h under N₂ atmosphere in 80 mL of acetonitrile. The brown oil crude was treated following modified method from the literature [17] before purified by *n*-hexane trituration. Yield: 89%. ¹H-NMR (500 MHz, (CD₃)₂SO) δ 11.15 (s, 1H), 9.53 (s, 1H), 8.65 (d, 1H), 8.19

(t, 1H), 7.99 (d, 1H), 7.69–7.67 (m, 1H), 7.57–7.54 (m, 1H), 7.21 (t, 2H), 5.58 (s, 2H). FTIR (ATR) (ν/cm^{-1}): 3110–3002 (w, $\nu(\text{C-H}_{\text{aromatic}})$), 2985–2936 (s, $\nu(\text{C-H}_{\text{aliphatic}})$), 1564–1498 (s, $\nu(\text{C=C}_{\text{aromatic}})$, $\nu(\text{C=N}_{\text{py}})$). Anal. Calcd. for $\text{C}_{14}\text{H}_{11}\text{N}_4\text{F}_2$: C, 61.53; H, 4.06; N, 20.50%. Found: C, 61.32; H, 4.10; N, 20.31%.

Synthesis of complex $[\text{Ir}(2,4\text{-F}_2\text{ppy})_2(2\text{-}(2,6\text{-difluorobenzyl)-1H-1,2,4-triazol-1-yl)pyridine}]\text{PF}_6$

In 33 mL of 1,2-dichloroethane, F_2bpyta (0.058 g, 2.4 mol equiv.) was reacted with $[\text{Ir}(2,4\text{-F}_2\text{ppy})_2(\mu\text{-Cl})_2]$ (0.103 g, 1.0 mol equiv.) with the addition of Ag_2O (0.049 g, 2.4 mol equiv.). The mixture was refluxed under continuous N_2 for 24 h and prepared following literature report [18]. $[\text{Ir}(2,4\text{-F}_2\text{ppy})_2(\text{F}_2\text{bpyta})]\text{PF}_6$ complex was achieved from the purification using $\text{CH}_2\text{Cl}_2/\text{acetone}$ (4.5:0.5) as eluent of the column chromatography. Yield: 47% (Yellow powder). $^1\text{H-NMR}$ (500 MHz, CD_2Cl_2) δ 8.46 (s, 1H), 8.26 (d, 1H), 8.22 (d, 1H), 7.75 (t, 1H), 7.61–7.58 (m, 1H), 7.46–7.41 (m, 2H), 7.37 (d, 1H), 7.28–7.22 (m, 1H), 6.79–7.04 (m, 5H), 6.67 (t, 1H), 6.45 (t, 1H), 6.31 (t, 1H), 5.70 (d, 1H), 5.63 (d, 1H), 4.77 (d, 1H), 2.09 (s, 2H). FTIR (ATR) (ν/cm^{-1}): 3110–3002, 3079–3029 (w,

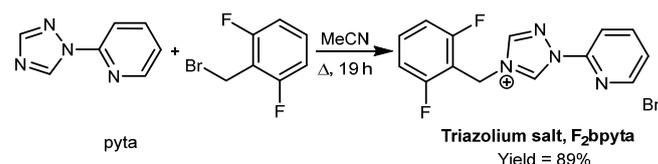
$\nu(\text{C-H}_{\text{aromatic}})$), 2985–2936 (w, $\nu(\text{C-H}_{\text{aliphatic}})$), 1555–1431 (s, $\nu(\text{C=C}_{\text{aromatic}})$, $\nu(\text{C=N}_{\text{py}})$), 830–720 (s, $\nu(\text{C-H})$). Anal. Calcd. for $\text{IrC}_{36}\text{H}_{22}\text{F}_6\text{N}_6$: C, 51.18; H, 2.62; N, 9.95%. Found: C, 50.15; H, 2.57; N, 9.54%.

RESULTS AND DISCUSSION

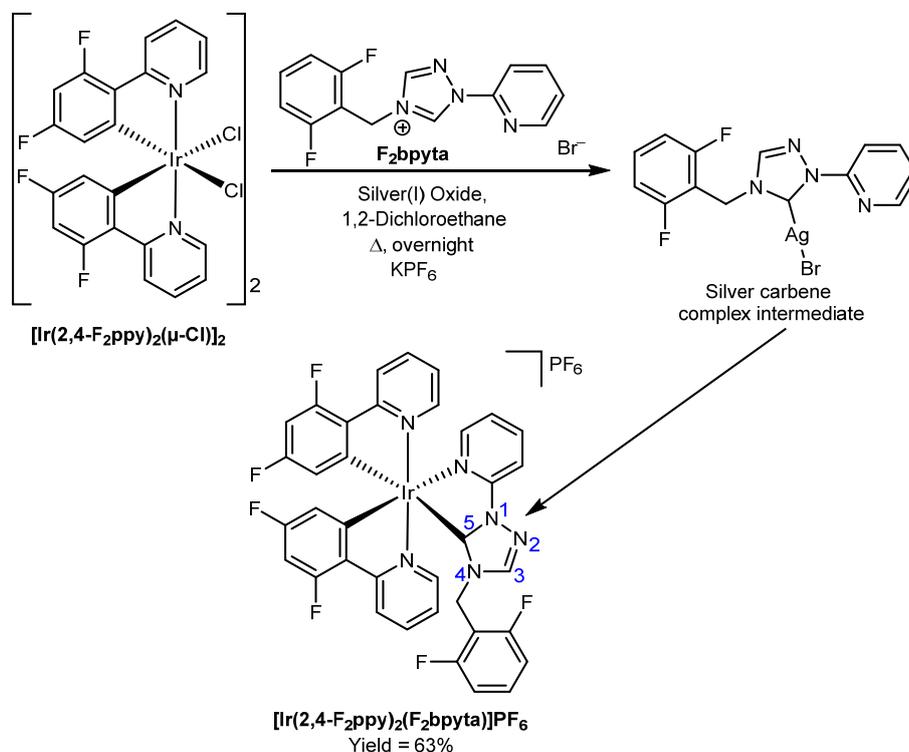
Pyta was further reacted with an alkyl halide, 2,6-difluorobenzylbromide, in acetonitrile, yielding 89% triazolium salt of F_2bpyta . The schematic pathway leading to this triazolium salt was depicted in Scheme 1.

Following the reflux reaction of $[\text{Ir}(2,4\text{-F}_2\text{ppy})_2(\mu\text{-Cl})_2]$ with F_2bpyta , $[\text{Ir}(2,4\text{-F}_2\text{ppy})_2(\text{F}_2\text{bpyta})]\text{PF}_6$ was obtained (47%). The schematic pathway leading to $[\text{Ir}(2,4\text{-F}_2\text{ppy})_2(\text{F}_2\text{bpyta})]\text{PF}_6$ shown in Scheme 2 includes the silver carbene-complex intermediate.

The elemental analysis of F_2bpyta , a derivative of



Scheme 1. Synthesis of a triazolium salt of F_2bpyta



Scheme 2. Schematic pathway to synthesize cationic complex $[\text{Ir}(2,4\text{-F}_2\text{ppy})_2(\text{F}_2\text{bpyta})]\text{PF}_6$

the ligand 1*H*-1,2,4-triazole, and the complex of $[\text{Ir}(2,4\text{-F}_2\text{ppy})_2(\text{F}_2\text{bpyta})]\text{PF}_6$ comply with the suggested chemical formula. The yield of the synthesized ligands successfully exceeds 80%, whereas the resulting product of the complex $[\text{Ir}(2,4\text{-F}_2\text{ppy})_2(\text{F}_2\text{bpyta})]\text{PF}_6$ did not reach 80% due to the complexity and difficulty separating fragments from the pure product during the purification stage. The C=C and C=N stretching for aromatic rings predicted for pyridine, phenyl, and triazole rings appeared at the range of 1564–1498 cm^{-1} and 1555–1431 cm^{-1} in the FTIR transmittance of F_2bpyta and $[\text{Ir}(2,4\text{-F}_2\text{ppy})_2(\text{F}_2\text{bpyta})]\text{PF}_6$ complex respectively (Fig. 2). Besides, the typical stretching bands of $\nu(\text{C-H})$ for aliphatic alkyl, in particular

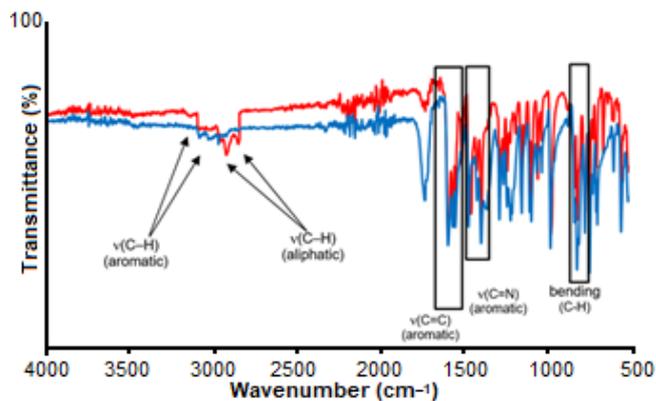


Fig 2. Comparison of FTIR spectral of complexes: $[\text{Ir}(2,4\text{F}_2\text{ppy})_2(\mu\text{-Cl})_2]$ (**blue**) and $[\text{Ir}(2,4\text{-F}_2\text{ppy})_2(\text{F}_2\text{bpyta})]\text{PF}_6$ (**red**)

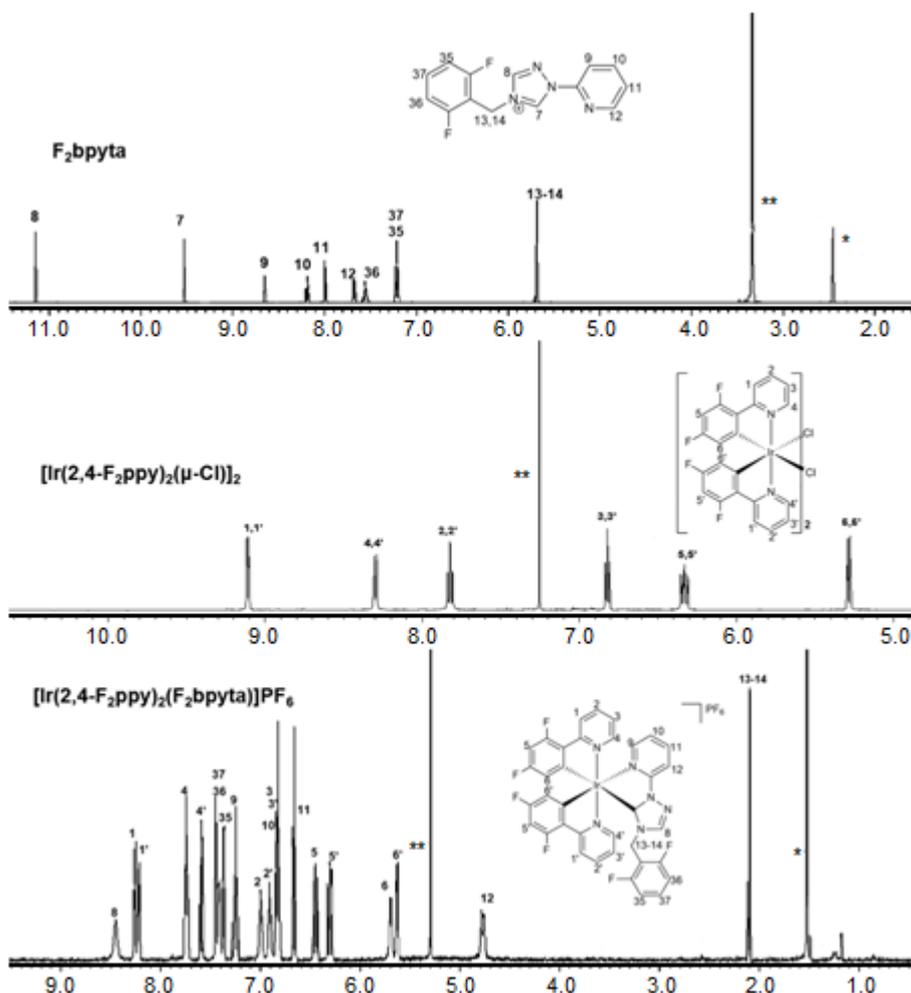


Fig. 3. $^1\text{H-NMR}$ spectra for ligand pyta2FB in deuterated $\text{d}_6\text{-DMSO}$, the dimer of $[\text{Ir}(2,4\text{-F}_2\text{ppy})_2(\mu\text{-Cl})_2]$ in deuterated CDCl_3 and $[\text{Ir}(2,4\text{-F}_2\text{ppy})_2(\text{F}_2\text{bpyta})]\text{PF}_6$ in deuterated CD_2Cl_2 with their labeling scheme, H_2O are marked with * and residual solvent marked with **

methylene, are shown in the region 2985–2936 cm^{-1} , while $\nu(\text{C-H})$ in aromatic pyridine and phenyl rings in the spectral region of 3110–3002 cm^{-1} . Both spectra patterns were typical of the previous report on the 1,2,4-triazole compound [9,19-20]. In addition, strong bending bands of (C-H) in the range of 830–720 cm^{-1} of ortho/para substituents on the aromatic ring [10] are shown in the synthesized complexes. When comparing the FTIR transmittance of both complexes, $[\text{Ir}(2,4\text{-F}_2\text{ppy})_2(\mu\text{-Cl})_2]$ and $[\text{Ir}(2,4\text{-F}_2\text{ppy})_2(\text{F}_2\text{bpyta})]\text{PF}_6$, a similar pattern was seen in general (Fig. 2).

The $^1\text{H-NMR}$ assignment peak for ligand F_2bpyta was arranged by comparing it to that of the starting pyta [14] and the reference deuterated DMSO residual peak. Proton signals of the complex $[\text{Ir}(2,4\text{-F}_2\text{ppy})_2(\text{F}_2\text{bpyta})]\text{PF}_6$ were identified by comparing them to the $^1\text{H-NMR}$ spectral of its iridium(III) dimer and ligand F_2bpyta (Fig. 3), as well as our previously synthesized $[\text{Ir}(2,4\text{-F}_2\text{ppy})_2(\text{mbpyta})]\text{PF}_6$ and $[\text{Ir}(2,4\text{-F}_2\text{ppy})_2(\text{hpyta})]\text{PF}_6$ [15]. The aromatic signals of pyridyltriazole and phenylpyridine [18] protons were detected between 10.00 and 7.00 ppm [18]. F_2bpyta showed two singlet peaks at 11.15 ppm H(8) and 9.53 ppm H(7), which were akin to the pyta [14] and were utilized as reference peaks in numerous studies [17]. However, due to the electron-withdrawing capabilities of fluorine substituents, both protons were strongly deshielded and shifted to the downfield with greater ppm.

In comparison to F_2bpyta , only one singlet peak was observed at 8.46 ppm H(8) shifted to upfield for $[\text{Ir}(2,4\text{-F}_2\text{ppy})_2(\text{F}_2\text{bpyta})]\text{PF}_6$, confirming that C5 was coordinated to the central iridium metal (Scheme 2). Besides, the $^1\text{H-NMR}$ spectrum of $[\text{Ir}(2,4\text{-F}_2\text{ppy})_2(\text{F}_2\text{bpyta})]\text{PF}_6$ shows methylene protons at H(13) and H(14), indicating cleavage between triazolepyridyl and the weak electron-donating group of the 4-2,6-difluorobenzyl substituent. In addition, the spectral pattern exhibits trivial change between dimer of $[\text{Ir}(2,4\text{-F}_2\text{ppy})_2(\mu\text{-Cl})_2]$ and complex $[\text{Ir}(2,4\text{-F}_2\text{ppy})_2(\text{F}_2\text{bpyta})]\text{PF}_6$, proved that separating the chloro bridge and inserting it with F_2bpyta ligand did not influence the whole geometrical structure of the iridium(III) complex [21].

Furthermore, the $^{13}\text{C-NMR}$ spectrum of the $[\text{Ir}(2,4\text{-F}_2\text{ppy})_2(\text{F}_2\text{bpyta})]\text{PF}_6$ (Fig. S2) confirmed the structural characterization, which included carbon assignment types and a residual peak for CDCl_3 at 77.2 ppm. Significant carbon signals were divided into aromatic and aliphatic carbon at 80–150 ppm and 0–50 ppm, respectively, matching the respective number of carbon atoms in the synthesized complex. The aromatic ring area has enlarged to 70–200 ppm due to fluorine atoms and heterocyclic groups. It has been stated that aromatic carbon attached to a nitrogen atom (ArCN) can be observed at an area higher than 150 ppm, while aromatic carbon attached to a fluorine atom (ArCF) is in the region of 90–100 ppm [22].

The absorption spectrum of the complex $[\text{Ir}(2,4\text{-F}_2\text{ppy})_2(\text{F}_2\text{bpyta})]\text{PF}_6$ in a CH_2Cl_2 solution at 298 K is demonstrated in Fig. 4. To the best of our knowledge, the spectral absorbance pattern of the most cyclometalating iridium(III) complexes are subdivided into two; the weak intensity absorbance at the longer wavelength assigned to the metal-to-ligand charge-transfer (MLCT) transitions $[\text{d}\pi(\text{M})-\pi^*(\text{L-ligand})]$ near the visible region whereas the shorter wavelength was related to ligand-centered, $^1\text{LC}(\pi-\pi^*)$ transitions of the ligands within the range of ultraviolet spectral [21,23-24]. The $[\text{Ir}(2,4\text{-F}_2\text{ppy})_2(\text{F}_2\text{bpyta})]\text{PF}_6$ complex absorbs strongly at 260 nm, indicating the presence of phenylpyridine and triazole ligands [14-15]. The typically weak band ($\lambda_{\text{max}} = 371 \text{ nm}$, $\epsilon = 6129 \text{ M}^{-1} \text{ cm}^{-1}$) assuredly correlated with

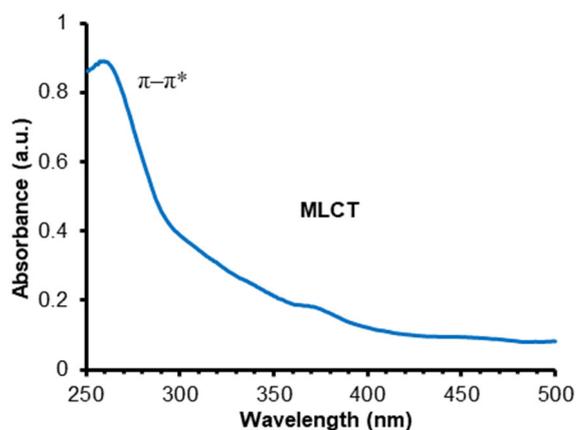


Fig 4. Absorption spectrum of $[\text{Ir}(2,4\text{-F}_2\text{ppy})_2(\text{F}_2\text{bpyta})]\text{PF}_6$ in CH_2Cl_2 solution (31 μM) at 298 K

spin-forbidden $^3\text{MLCT}$ and spin-allowed $^1\text{MLCT}$ transitions as a result of significant intersystem crossing by the triplet (T_1) and singlet (S_1) excited states that are stimulated through a central metal of iridium atom [23-24].

The comparison of the emission spectral data of the $[\text{Ir}(2,4\text{-F}_2\text{ppy})_2(\text{F}_2\text{bpyta})]\text{PF}_6$ to the other two previously synthesized complexes: $[\text{Ir}(2,4\text{-F}_2\text{ppy})_2(\text{mbpyta})]\text{PF}_6$ and $[\text{Ir}(2,4\text{-F}_2\text{ppy})_2(\text{hpyta})]\text{PF}_6$ [15] at room temperature upon excitation at $\lambda_{\text{ex}} = 381$ nm provided an informative discussion on the emission energy, as shown in Fig. 5. The data were compatible with other cyclometalating iridium(III) complexes [24-25], and previous computational investigation came out with the highest occupied molecular orbital (HOMO) is primarily found at the iridium d-orbital and phenyl moieties. In contrast, the pyridyl moieties are dominantly associated with the lowest unoccupied molecular orbital (LUMO) [26]. The EWG effect of a fluorine atom bonded to phenyl ring at 2- and/or 4-carbon position led to stabilizing the HOMO greater than the LUMO and consequently enlarged their energy distances between HOMO and LUMO [27]. Furthermore, adding a pyridyltriazole base anchillary ligand was expected to raise the LUMO energy and

enhance the synthesized complexes' luminescence properties [3,5,18].

An insightful finding is shown in Fig. 5, where all the synthesized iridium(III) complexes emitted blue color under ultraviolet light. The emission spectrum of complex $[\text{Ir}(2,4\text{-F}_2\text{ppy})_2(\text{mbpyta})]\text{PF}_6$ with a λ_{em} of 454 nm is blue-shifted in contrary to the complex $[\text{Ir}(2,4\text{-F}_2\text{ppy})_2(\text{F}_2\text{bpyta})]\text{PF}_6$ ($\lambda_{\text{em}} = 461$ nm). Therefore, the addition of methylbenzyl to the phenyl moiety of the triazole ring with a weak EDG effect significantly shifted the electronic properties of the synthesized Ir(III) complex compared to the EWG of fluorine atoms. On the other hand, $[\text{Ir}(2,4\text{-F}_2\text{ppy})_2(\text{hpyta})]\text{PF}_6$ complex exhibited a red-shifted ($\lambda_{\text{em}} = 469$ nm) spectrum due to the addition of hexyl to the phenyl moiety of the triazole ring. It has been shown that simple alkyl weak EDG substituents did not significantly affect the resulting electronic characteristics of the synthesized metal complexes [2]. It is worth noting that triazole-based heteroleptic iridium(III) complexes have been proved to raise the LUMO energy level by widening the energy distance and subsequently raising the T_1 energy level [14]. In the future, further computational studies will be conducted to investigate the reasons for the behavior.

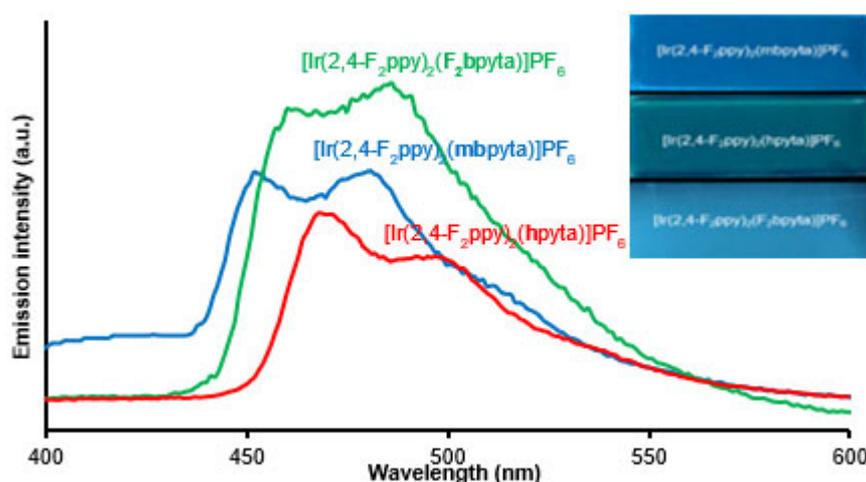


Fig 5. The spectral of luminescence pattern for the iridium(III) complexes **green:** $[\text{Ir}(2,4\text{-F}_2\text{ppy})_2(\text{F}_2\text{bpyta})]\text{PF}_6$ to the other two previously synthesized complexes **blue:** $[\text{Ir}(2,4\text{-F}_2\text{ppy})_2(\text{mbpyta})]\text{PF}_6$, and **red:** $[\text{Ir}(2,4\text{-F}_2\text{ppy})_2(\text{hpyta})]\text{PF}_6$ in CH_2Cl_2 at 298 K. Inset: Luminescence photos of iridium(III) complexes in CH_2Cl_2 under UV light

■ CONCLUSION

In conclusion, a cationic complex of bis(2-(2,4-difluorophenyl)pyridine)iridium(III) containing derivative of 1*H*-1,2,4-triazole anchillary ligand, [Ir(2,4-F₂ppy)₂(F₂bpyta)]⁺, was prepared and characterized by spectroscopic methods. In CH₂Cl₂ solutions (air-equilibrated) at room temperature, [Ir(2,4-F₂ppy)₂(F₂bpyta)]PF₆ and the other two previously synthesized iridium(III) complexes emitted blue color emission in the steady-state luminescence spectra. The emission spectrum of the [Ir(2,4-F₂ppy)₂(F₂bpyta)]PF₆ (λ_{em} = 461 nm) is blue-shifted in comparison to the [Ir(2,4-F₂ppy)₂(hppyta)]PF₆ (λ_{em} = 469 nm), but red-shifted when related to the [Ir(2,4-F₂ppy)₂(mbpyta)]PF₆ (λ_{em} = 454 nm). As a result, this study demonstrated that modification of 1,2,4-triazolepyridyl-based ligands could tailor the electronic properties of iridium(III) complexes, hence contributing to the alternative method of developing novel blue emitters of phosphorescent complexes.

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