



Synthesis and photophysical properties of bis(phenylpyridine) iridium(III) dicyanide complexes

Noorshida Mohd Ali, Michael D. Ward, Norhayati Hashim & Norlinda Daud

To cite this article: Noorshida Mohd Ali, Michael D. Ward, Norhayati Hashim & Norlinda Daud (2017): Synthesis and photophysical properties of bis(phenylpyridine) iridium(III) dicyanide complexes, Materials Research Innovations, DOI: [10.1080/14328917.2017.1397940](https://doi.org/10.1080/14328917.2017.1397940)

To link to this article: <http://dx.doi.org/10.1080/14328917.2017.1397940>



Published online: 03 Nov 2017.



Submit your article to this journal [↗](#)



Article views: 1



View related articles [↗](#)



View Crossmark data [↗](#)



Synthesis and photophysical properties of bis(phenylpyridine) iridium(III) dicyanide complexes

Noorshida Mohd Ali^a, Michael D. Ward^b, Norhayati Hashim^a and Norlinda Daud^a

^aDepartment of Chemistry, Faculty of Science and Mathematics, Universiti Pendidikan Sultan Idris, Tanjong Malim, Malaysia; ^bDepartment of Chemistry, University of Sheffield, Sheffield, UK

ABSTRACT

Our research group is focusing on luminescence of coordination compounds which based on cyanide bridging interactions. Recently, four cyanometallate complexes based on Ir(III) complex $[\text{Ir}(\text{ppy})_2(\text{CN})_2]^-$, which is one of an extensive family of Ir(III) complexes based on cyclometallating phenylpyridine ligands that have achieved prominence for their desirable photophysical properties, were successfully synthesised. The present study showed that, the introduction of fluorine atoms to the phenyl rings could enhance the triplet excited state energy and thus caused a blue-shift phosphorescence peak ($\lambda_{\text{em}} = 453 \text{ nm}$) as shown by $(\text{PPN})[\text{Ir}(2,4\text{-F}_2\text{ppy})_2(\text{CN})_2]$ (1) compared to that of complex without fluorine atom $(\text{PPN})[\text{Ir}(\text{ppy})_2(\text{CN})_2]$ (4) ($\lambda_{\text{em}} = 474 \text{ nm}$). However, $(\text{PPN})[\text{Ir}(3,5\text{-F}_2\text{ppy})_2(\text{CN})_2]$ (2) shows a negligible hypsochromic shift ($\lambda_{\text{em}} = 473 \text{ nm}$) in the emission. Conversely, $(\text{PPN})[\text{Ir}(4\text{-CF}_3\text{ppy})_2(\text{CN})_2]$ (3) shows a red-shift ($\lambda_{\text{em}} = 479 \text{ nm}$) compared to complex (4). These complexes, like $[\text{Ru}(\text{bipy})(\text{CN})_4]^{2-}$, have a strong emissive and high energy excited state and thus, are potentially good energy donors; and are anionic with cyanide groups, and so can form cyanide-bridged complexes with other metal and lanthanide cations.

ARTICLE HISTORY

Received 20 October 2016
Accepted 24 November 2016

KEYWORDS

Luminescent; cyanometallate iridium(III) complex; energy donor

Introduction

Luminescent complexes of d^6 transition metal ions such as Ru(II), Os(II), Ir(III) and Re(I) have gained much interest in modern materials research due to their rich photophysical and photochemical properties and being attractive for the application in organic light-emitting diode (OLED) device fabrication [1]. However, compared to the ruthenium analogues, the iridium(III) phenylpyridine complexes are particularly highly tunable in the colour of the iridium emission. Generally, iridium(III) complexes containing 2-phenylpyridine are known to exhibit high triplet quantum yields due to mixing of the singlet and the triplet excited states via spin-orbit coupling, leading to high phosphorescence efficiencies [2]. In addition, appropriate substituents on the phenylpyridine ligands can cause shifting of the light emission from the red to the almost blue region of the visible spectrum [3].

The complex $[\text{Ir}(\text{ppy})_2(\text{CN})_2]^-$, which is one of the extensive family of iridium(III) complexes based on cyclometallating phenylpyridine ligands, has achieved prominence recently for its desirable photophysical properties. For instance, (TBA) $[\text{Ir}(\text{ppy})_2(\text{CN})_2]$ (TBA = tetrabutylammonium cation), was first reported by Nazeeruddin et al. [4] possesses an unusually high phosphorescence quantum yield, $97 \pm 3\%$ with an excited-state lifetimes of 1–3 μs in dichloromethane solution at room temperature, due to the presence of CN^- ligands which are known to have a strong ligand field [5]. For that reason, the gap between the lowest unoccupied molecular orbital (LUMO) levels of the phenyl pyridine ligand and the metal empty e_g orbitals is large which prohibits non-radiative deactivation pathways, leading to high or near-unity quantum yields with

long lifetimes. Introducing cyanide ligands also increase the gap between LUMO of the phenyl pyridine ligand and the metal t_{2g} orbitals, resulting in a blue-shift of the lowest MLCT absorption and the emission maximum.

Subsequently, different derivatives of $[\text{Ir}(\text{ppy})_2(\text{CN})_2]^-$ which are (TBA) $[\text{Ir}(2\text{-phenyl}-4\text{-dimethylaminopyridine})_2(\text{CN})_2]$, (TBA) $[\text{Ir}(2\text{-(2,4-difluorophenyl)-pyridine})_2(\text{CN})_2]$, (TBA) $[\text{Ir}(2\text{-(2,4-difluorophenyl)-4-dimethylaminopyridine})_2(\text{CN})_2]$ and (TBA) $[\text{Ir}(2\text{-(3,5-difluorophenyl)-4-dimethylaminopyridine})_2(\text{CN})_2]$ with strong blue phosphorescence have been explored by Di Censo et al. In these complexes, ligands are substituted with donor and acceptor groups on the pyridine and phenyl moieties of 2-phenylpyridine, respectively [6]. The fluorine units on the phenyl ring lower the highest occupied molecular orbital (HOMO) levels and the dimethylamino units on the pyridine raises the LUMO, giving a high energy excited state [7].

Our research group is focusing on luminescence of coordination compounds based on cyanide bridging interactions. Fascinatingly, fluorinated phenylpyridine iridium(III) dicyanide complex, likewise $[\text{Ru}(\text{bipy})(\text{CN})_4]^{2-}$ [8] has a strongly emissive and high energy excited state and thus, are potentially good energy donors; and are anionic with externally-directed cyanide groups, and so can form cyanide-bridged complexes with lanthanide cations other transition metal cations [9]. Since $[\text{Ir}(\text{ppy})_2(\text{CN})_2]^-$ and its derivatives offer strong potential to act both as a crucial structural element and an antenna or energy donor group in polynuclear complexes, in this paper we report a structural and photophysical study of various types of fluorinated phenylpyridine iridium(III) dicyanide complexes in

order to examine the effects of F-atom substituents on their luminescence properties.

Experimental

Apparatus

Electrospray mass spectra were recorded using a Micromass LCT instrument. ^1H NMR spectra were recorded on Bruker AV1–250 or AV3–400 spectrometers. UV/Vis absorption spectra were measured on a Varian Cary 50 spectrophotometer and steady-state luminescence spectra on a Jobin-Yvon Fluoromax 4 fluorimeter using air-equilibrated dichloromethane solutions at room temperature. Elemental analysis for C, H, N was carried out by using a CHNS-O (Perkin Elmer 2400 Series II) analyser. IR spectra were measured by a Perkin Elmer Spectrum 100 spectrophotometer using a diamond ATR (Attenuated Total Reflectance) accessory in the 4000–600 cm^{-1} regions. X-ray crystallographic analyses were carried out by using Bruker APEX-2CCD Diffractometer. The structures were solved by direct methods and refined by full-matrix least squares on weighted F^2 values for all reflections using the SHELX suite of programs [10].

Reagents

Organic reagents and metal salts were purchased from Aldrich and used as received. The dimers $[\text{Ir}(2,4\text{-F}_2\text{ppy})_2(\mu\text{-Cl})_2]$, $[\text{Ir}(3,5\text{-F}_2\text{ppy})_2(\mu\text{-Cl})_2]$, $[\text{Ir}(4\text{-CF}_3\text{ppy})_2(\mu\text{-Cl})_2]$ and $[\text{Ir}(\text{ppy})_2(\mu\text{-Cl})_2]$ were prepared according to the literature methods [11–13]. $(\text{PPN})[\text{Ir}(\text{ppy})_2(\text{CN})_2]$ (**4**) was prepared using the method in Ref. [9] followed by cation metathesis with PPNCl as described below for the other PPN^+ salts.

Synthesis

Synthesis of $(\text{PPN})[\text{Ir}(2,4\text{-F}_2\text{ppy})_2(\text{CN})_2]$ (**1**)

$[\text{Ir}(2,4\text{-F}_2\text{ppy})_2(\mu\text{-Cl})_2]$ (0.50 g, 0.41 mmol) was heated to reflux with KCN (0.11 g, 1.69 mmol, 4.1 equiv) in a methanol solution (100 ml) for overnight. The reaction mixture was then allowed to cool to room temperature and evaporated to dryness. The crude solid was dissolved in the minimum amount of water and heated until completely dissolved. After cooling to room temperature, the organic impurities were extracted using dichloromethane. The yellow aqueous solution was evaporated to dryness and redissolved in a minimum amount of hot water. Meanwhile, an aqueous solution of $(\text{PPN})\text{Cl}$ (0.53 g, 0.93 mmol, 1.2 equiv) was heated to 80 °C. The solution containing the Ir(III) complex was pipetted into the hot $(\text{PPN})\text{Cl}$ solution immediately forming a precipitate of $(\text{PPN})[\text{Ir}(2,4\text{-F}_2\text{ppy})_2(\text{CN})_2]$ (**1**) which was isolated by gravity filtration. The solid was washed with hot water to remove any impurities and dried *in vacuo*. Yield: 90%. ^1H NMR (400 MHz, CDCl_3): δ /ppm 9.81 (2H, d), 8.18 (2H, d), 7.66–7.72 (2H, m and 6H, m; PPN cation), 7.42–7.54 (24H, m; PPN cation), 6.95 (2H, t), 6.25 (2H, t), 5.75 (2H, d). Negative ion ESMS: m/z 625 $[\text{Ir}(2,4\text{-F}_2\text{ppy})_2(\text{CN})_2]^-$. IR: ν/cm^{-1} (ATR) 2106 (s, $\text{C}\equiv\text{N}$ stretch). Anal. Calcd. for $\text{C}_{60}\text{H}_{42}\text{IrF}_4\text{N}_5\text{P}_2\cdot\text{CH}_2\text{Cl}_2$: C, 58.7; H, 3.6; N, 5.6%. Found: C, 58.5; H, 3.3; N, 5.8%.

Synthesis of $(\text{PPN})[\text{Ir}(3,5\text{-F}_2\text{ppy})_2(\text{CN})_2]$ (**2**)

This was synthesised according to the same procedure as $(\text{PPN})[\text{Ir}(2,4\text{-F}_2\text{ppy})_2(\text{CN})_2]$ (**1**), using $[\text{Ir}(3,5\text{-F}_2\text{ppy})_2(\mu\text{-Cl})_2]$ (0.11 g, 0.09 mmol) and KCN followed by cation metathesis with (PPN)

Cl. Yield: 65%. ^1H NMR (400 MHz, CDCl_3): δ /ppm 9.98 (2H, d), 7.66–7.72 (2H, m and 6H, m; PPN cation), 7.42–7.54 (2H, m and 24H, m; PPN cation), 7.15 (2H, d), 6.95 (2H, t), 6.15 (2H, t). Negative ion ESMS: m/z 625 $[\text{Ir}(3,5\text{-F}_2\text{ppy})_2(\text{CN})_2]^-$. IR: ν/cm^{-1} (ATR) 2103 (s, $\text{C}\equiv\text{N}$ stretch). Anal. Calcd. for $\text{C}_{60}\text{H}_{42}\text{IrF}_4\text{N}_5\text{P}_2\cdot\text{H}_2\text{O}$: C, 61.0; H, 3.7; N, 5.9%. Found: C, 61.3; H, 3.9; N, 6.1%.

Synthesis of $(\text{PPN})[\text{Ir}(4\text{-CF}_3\text{ppy})_2(\text{CN})_2]$ (**3**)

This was prepared in exactly the same way as $(\text{PPN})[\text{Ir}(2,4\text{-F}_2\text{ppy})_2(\text{CN})_2]$ (**1**), using $[\text{Ir}(4\text{-CF}_3\text{ppy})_2(\mu\text{-Cl})_2]$ (0.09 g, 68.9 μmol) and KCN followed by cation metathesis with $(\text{PPN})\text{Cl}$.

Yield: 85%. ^1H NMR (400 MHz, CDCl_3): δ /ppm 9.99 (2H, d), 7.84 (2H, d), 7.66–7.72 (2H, m and 6H, m; PPN cation), 7.57 (2H, d), 7.42–7.54 (24H, m; PPN cation), 7.18 (2H, t), 6.98 (2H, d), 6.15 (2H, s). Negative ion ESMS: m/z 689 $[\text{Ir}(4\text{-CF}_3\text{ppy})_2(\text{CN})_2]^-$. IR: ν/cm^{-1} (ATR) 2104 (s, $\text{C}\equiv\text{N}$ stretch). Anal. Calcd. for $\text{C}_{62}\text{H}_{44}\text{IrF}_6\text{N}_5\text{P}_2\cdot\text{H}_2\text{O}$: C, 59.7; H, 3.7; N, 5.6%. Found: C, 60.0; H, 3.4; N, 5.5%.

Results and discussion

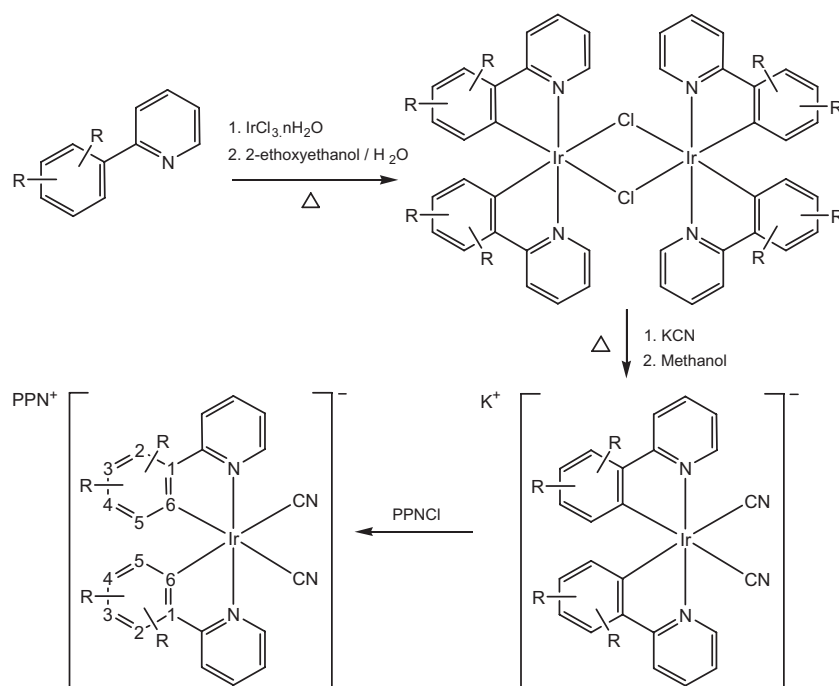
Structural characterisation of Bis(phenylpyridine) Iridium(III) Dicyanide Complexes

Bis(phenylpyridine) iridium(III) dicyanide complexes were successfully synthesised by reacting the dichloro-bridged iridium(III) dimers: $[\text{Ir}(2,4\text{-F}_2\text{ppy})_2(\mu\text{-Cl})_2]$, $[\text{Ir}(3,5\text{-F}_2\text{ppy})_2(\mu\text{-Cl})_2]$, $[\text{Ir}(4\text{-CF}_3\text{ppy})_2(\mu\text{-Cl})_2]$, and $[\text{Ir}(\text{ppy})_2(\mu\text{-Cl})_2]$ in methanol solvent with an excess of potassium cyanide, which gave $\text{K}[\text{Ir}(2,4\text{-F}_2\text{ppy})_2(\text{CN})_2]$, $\text{K}[\text{Ir}(3,5\text{-F}_2\text{ppy})_2(\text{CN})_2]$, $\text{K}[\text{Ir}(4\text{-CF}_3\text{ppy})_2(\text{CN})_2]$ and $\text{K}[\text{Ir}(\text{ppy})_2(\text{CN})_2]$, respectively. The synthetic pathway leading to the phenylpyridine iridium(III) dicyanide complexes is depicted in Scheme 1. According to Nazeeruddin *et al.* [4] reaction of the dimer $[\text{Ir}(\text{ppy})_2(\mu\text{-Cl})_2]$ with more than two equivalents of a cyanide salt generates $[\text{Ir}(\text{ppy})_2(\text{CN})_2]^-$. Subsequently, these complexes were converted to their $(\text{PPN})^+$ salts (bis(triphenylphosphino)iminium cation) to improve solubility in less polar organic solvents such as dichloromethane and acetonitrile [14–16]. In particular, K^+ salts of anionic iridium(III) complexes were reacted with $(\text{PPN})\text{Cl}$ in hot water to give an immediate yellow precipitate, which gave over 60% yields of the complexes.

In each case, the elemental analysis is consistent with the expected molecular formula. The presence of cyanide groups in complexes (**1**)–(**3**) showed the expected pattern of $\nu(\text{CN})$ stretches [17], displaying strong absorption at 2106, 2103 and 2104 cm^{-1} , respectively in the FT-IR spectra. In contrast, complex (**4**) displays two sharp bands at lower wavenumbers, 2101 and 2092 cm^{-1} , similar to what was observed by Nazeeruddin *et al.* for $\text{TBA}[\text{Ir}(\text{ppy})_2(\text{CN})_2]$ complex [4], due to the lack of fluorine substituents on the phenylpyridine (ppy) unit.

In addition, the electrospray ionisation mass spectrometry (ESMS) spectra of the synthesised phenylpyridine iridium(III) dicyanide complexes (**1**)–(**4**) support the successful preparation of the anionic complexes. For both complexes (**1**) and (**2**), the negative ion ESMS spectrum exhibits a peak at m/z 625, corresponding to the major species $[\text{Ir}(2,4\text{-F}_2\text{ppy})_2(\text{CN})_2]^-$ and $[\text{Ir}(3,5\text{-F}_2\text{ppy})_2(\text{CN})_2]^-$. Similarly, the peaks at m/z 689 and 553 in the negative ion ESMS spectra, also suggest the formation of $[\text{Ir}(4\text{-CF}_3\text{ppy})_2(\text{CN})_2]^-$ (**3**) and $[\text{Ir}(\text{ppy})_2(\text{CN})_2]^-$ (**4**), respectively.

^1H NMR spectroscopy was also used to characterise all four complexes which have C_2 symmetry. ^1H NMR spectra of (**1**)–(**4**) recorded in deuterated CDCl_3 are presented in



Scheme 1. Synthesis of dichloro-bridged cyclometallated iridium(III) complexes and complexes (1)–(4). R (the position of the substituents on the phenyl rings with respect to the coordinating carbon): (1) = 2, 4F; (2) = 3, 5F; (3) = 4CF₃; (4) = H.

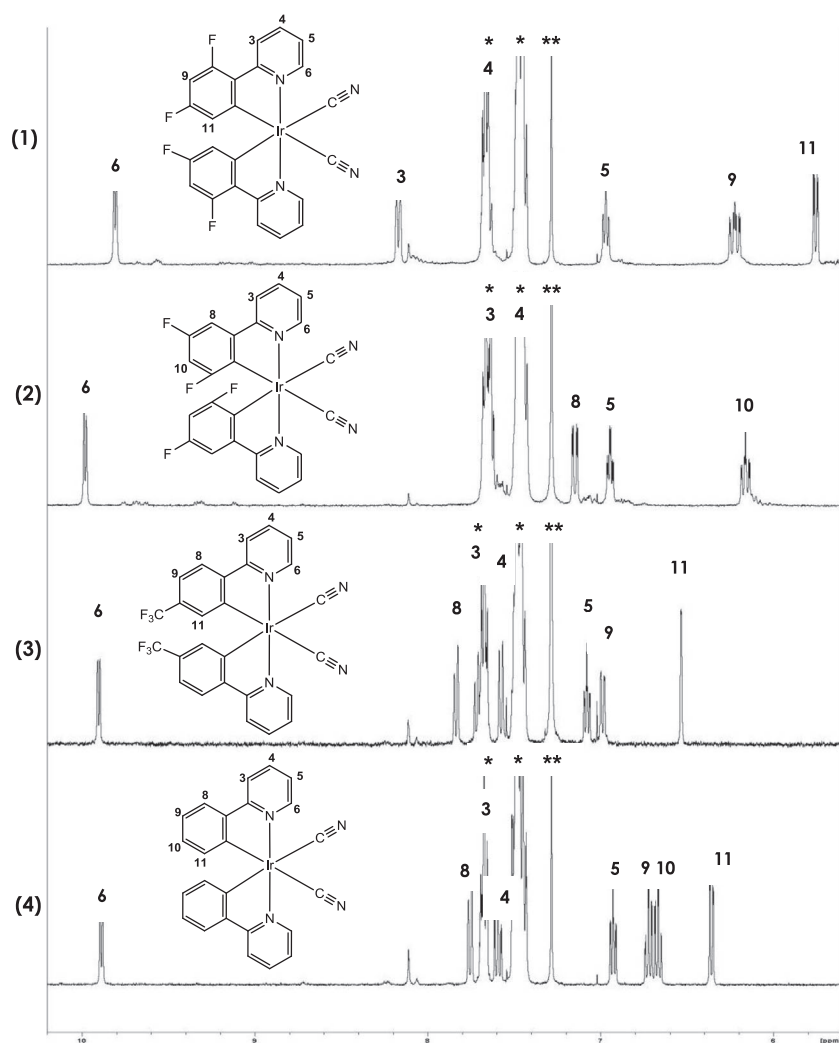


Figure 1. ¹H NMR spectra of aromatic region complexes (1)–(4) in CDCl_3 . The signals marked * are from PPN⁺ and the signals marked ** are from solvent.

Figure 1 with their labeling scheme. Assignments of proton resonances for these complexes were made by comparison to the ¹H NMR spectra of the starting dimer complexes. All the

¹H NMR spectra display well-resolved signals in the aromatic region between 9.90 and 5.70 ppm, corresponding to the phenylpyridine protons [4,18]. Coupling between hydrogen and

fluorine (spin $\frac{1}{2}$) is very strong. Therefore, the proton signals of H9 (**1**) and H10 (**2**) are split into a triplet because of coupling with two fluorine nuclei [19]. The multiplet signals between 7.70 and 7.40 ppm are assigned to the PPN counter-ion [15]. However, there is no significant change in NMR spectral pattern between the starting dimer complexes and the complexes (**1**)–(**4**), indicating that the cleavage of the chloride bridge and the subsequent substitution of the chloride ligands by cyanide group takes place without altering the geometry of the iridium(III) complexes [4]. In addition, the iridium metal with two phenylpyridine ligands forms a configuration in which the two pyridine groups are trans to each other and the phenyl groups are trans to cyanide groups, resulting in two electronically equivalent pyridines and phenyl groups [18].

X-ray crystallography of fluorinated phenylpyridine iridium(III) dicyanide complexes

Single crystals of the fluorinated phenylpyridine iridium(III) dicyanide complexes (**1**)–(**3**) were grown in each case from a slowly evaporating solution of dichloromethane/*n*-hexane. The crystal structure of (**4**) was collected by a previous member of the Ward group and has been published previously [9]. As expected for all the three complexes, the central ion Ir(III) is six coordinated by four carbon atoms and two nitrogen atoms in an octahedral environment. Two carbon atoms and two nitrogen atoms are provided by the two phenylpyridine ligands and the other two carbon atoms are contributed by the cyanide ligands. The phenylpyridine rings are planar. The bond lengths for Ir–N and Ir–C for phenylpyridine ligands are all in the normal

ranges as expected which are (2.05–2.07 Å) and (2.05–2.08 Å), respectively. The Ir–C bonds lengths for the cyanide ligands also are as expected between 2.05 and 2.08 Å. The selected bond lengths and angles are shown in Table 1 and a summary of the refinement details and resulting factors are given in Table 2.

Complexes of (**1**)–(**3**) have a -1 charge and thus, each contains one (PPN)⁺ as counter ion to balance the charge. As can be seen from the selected bond lengths (Table 1), the structures of (**1**)–(**3**) are quite similar and show no significant differences. As expected the N atoms for both phenylpyridine ligands are in a *trans* position with respect to each other, with the angle N(211)–Ir(1)–N(111) being 173.3°(17) (**1**), 174.7°(2) (**2**) and 171.4°(3) (**3**). In addition, the cyanide ligands are perpendicular to each other with the angles between C(127)–Ir(1)–C(227) being 91.2°(2) (**1**), C(117)–Ir(1)–C(217) being 89.8°(3) (**2**) and C(221)–Ir(1)–C(228) being 91.4°(4) (**3**). However, the major difference between the complexes (**1**) and (**2**) is the position of the fluorine atoms at positions C2 and C4 on the phenyl ring in the former and at positions C3 and C5 in the latter. The X-ray crystal structure of (**1**) with the dichloromethane solvent molecule omitted for clarity and crystal structure of (**2**) with the water solvent molecule omitted for clarity are shown in Figure 2(a) and (b), respectively. The molecular structure of complex (**3**) is also similar with the other two complexes, except the phenylpyridine ligands attached to Ir(III) each contain three F atom substituents on the phenyl ring. The X-ray crystal structure of (**3**) is shown in Figure 2(c) with the water solvent molecule omitted for clarity.

Photophysical Properties of Bis(phenylpyridine) Iridium(III) Dicyanide Complexes

Table 3 shows the comparison of UV/Vis absorption data for complexes (**1**)–(**4**) as their PPN⁺ salts in dichloromethane solution at 298 K. As with most iridium(III) complexes, the absorption spectra can be divided into two regions; the short wavelength π – π^* transitions of the ligands in the UV region, and the longer wavelength metal-to-ligand charge-transfer (MLCT) $d\pi(M) \rightarrow \pi^*(L\text{-ligand})$ transitions in the visible region [20,21]. Since the low spin d^6 configuration of the mononuclear complex provides filled orbitals of proper symmetry at the Ir(III) centre, these can interact with low lying π^* orbitals of the ligands.

Table 1. Selected bond distances (Å) for the crystal structures.

| | | | |
|--|-----------|----------|-----------|
| Complex (1) (PPN)[Ir(2,4-F ₂ ppy) ₂ (CN) ₂] \cdot CH ₂ Cl ₂ | | | |
| Ir1–N111 | 2.059(4) | Ir1–C221 | 2.057(5) |
| Ir1–N211 | 2.052(4) | Ir1–C127 | 2.062(5) |
| Ir1–C121 | 2.054(6) | Ir1–C227 | 2.068(5) |
| Complex (2) (PPN)[Ir(3,5-F ₂ ppy) ₂ (CN) ₂] \cdot H ₂ O | | | |
| Ir1–N111 | 2.060(5) | Ir1–C221 | 2.057(7) |
| Ir1–N211 | 2.049(6) | Ir1–C117 | 2.049(7) |
| Ir1–C121 | 2.049(6) | Ir1–C217 | 2.060(7) |
| Complex (3) (PPN)[Ir(4-CF ₃ ppy) ₂ (CN) ₂] \cdot H ₂ O | | | |
| Ir1–N111 | 2.059(9) | Ir1–C221 | 2.065(11) |
| Ir1–N211 | 2.068(9) | Ir1–C128 | 2.074(10) |
| Ir1–C121 | 2.078(12) | Ir1–C228 | 2.076(10) |

Table 2. Crystallographic data for the crystal structures (**1**)–(**3**).

| Complex | (PPN)[Ir(2,4-F ₂ ppy) ₂ (CN) ₂] \cdot CH ₂ Cl ₂ (1) | (PPN)[Ir(3,5-F ₂ ppy) ₂ (CN) ₂] \cdot H ₂ O (2) | (PPN)[Ir(4-CF ₃ ppy) ₂ (CN) ₂] \cdot H ₂ O (3) |
|------------------------------|--|---|--|
| Formula | C ₆₁ H ₄₄ Cl ₂ F ₄ IrN ₅ P ₂ | C ₆₀ H ₄₄ F ₄ IrN ₅ OP ₂ | C ₆₂ H ₄₆ F ₆ IrN ₅ OP ₂ |
| Molecular weight | 1248.05 | 1181.14 | 1245.18 |
| T/K | 150(2) | 150(2) | 150(2) |
| Crystal system | Triclinic | Monoclinic | Triclinic |
| Space group | P-1 | P2(1)/c | P-1 |
| <i>a</i> /Å | 11.7481(3) | 17.8442(7) | 12.0036(10) |
| <i>b</i> /Å | 14.8048(5) | 17.0360(7) | 15.6513(11) |
| <i>c</i> /Å | 16.0460(5) | 16.9942(6) | 15.9262(13) |
| α /° | 97.2590(10) | 90 | 95.010(5) |
| β /° | 108.0570(10) | 107.129(2) | 111.768(5) |
| γ /° | 96.2850(10) | 90 | 98.484(5) |
| <i>V</i> /Å ³ | 2599.24(14) | 4937.0(3) | 2715.3(4) |
| <i>Z</i> | 2 | 4 | 2 |
| ρ /g cm ⁻³ | 1.595 | 1.589 | 1.523 |
| Crystal size/mm ³ | 0.31 \times 0.23 \times 0.23 | 0.60 \times 0.20 \times 0.05 | 0.43 \times 0.32 \times 0.18 |
| μ /mm ⁻¹ | 2.794 | 2.834 | 2.585 |
| Data/restraints/parameters | 11,614 / 0 / 676 | 11,378 / 0 / 658 | 9654 / 876 ^b / 694 |
| Final R1, wR2 ^a | 0.0379, 0.0976 | 0.0513, 0.1279 | 0.0730, 0.1879 |

^aThe value of R1 is based on 'observed' data with $I > 2\sigma(I)$; the value of wR2 is based on all data.

^bStructure showed disorder of solvent molecule and ligand fragments which required application of geometric restraints on Ir–C, C–F and C–N distances to keep refinements reasonable.

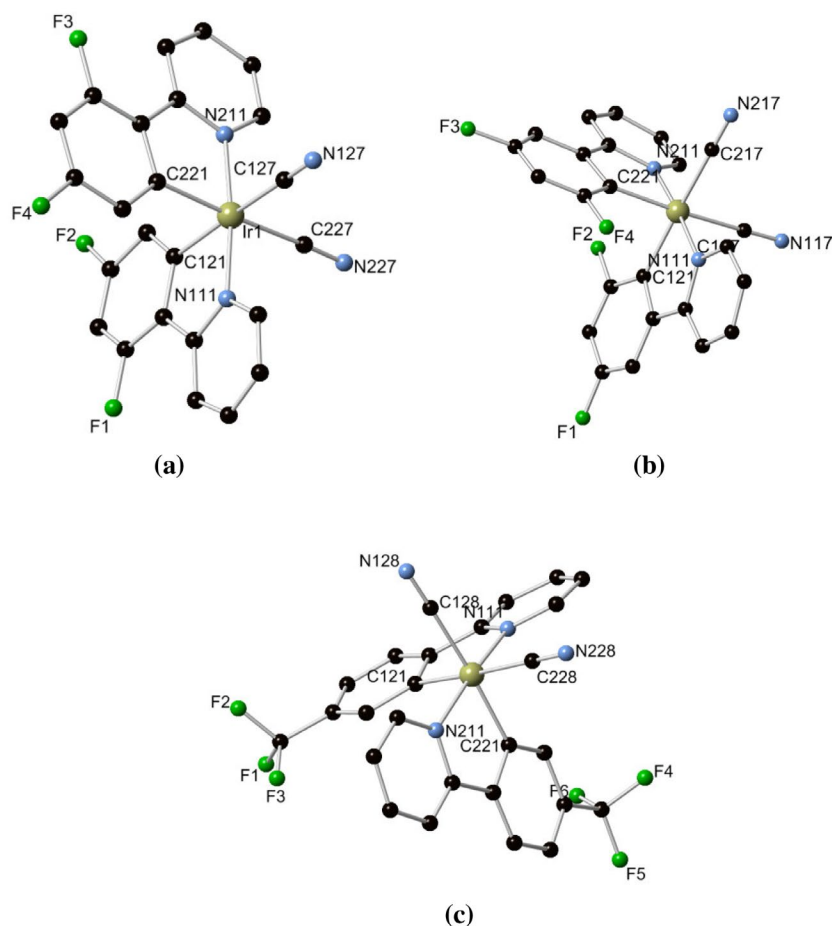


Figure 2. Molecular structures of the complex anions of (a) PPN[Ir(2,4-F₂ppy)₂(CN)₂] (1), (b) PPN[Ir(3,5-F₂ppy)₂(CN)₂] (2) and (c) PPN[Ir(4-CF₃ppy)₂(CN)₂] (3).

Table 3. Summary of UV/Vis spectral data for the bis(phenylpyridine) iridium(III) dicyanide complexes (1)–(4) in dichloromethane.

| Complexes | $\lambda_{\text{max}}/\text{nm}$ ($10^{-3} \epsilon / \text{M}^{-1} \text{cm}^{-1}$) |
|---|--|
| PPN[Ir(2,4-F ₂ ppy) ₂ (CN) ₂] (1) | 251 (52), 300 (18.5), 364 (5.8) |
| PPN[Ir(3,5-F ₂ ppy) ₂ (CN) ₂] (2) | 261 (53), 287 (31), 335 (11), 377 (6.8) |
| PPN[Ir(4-CF ₃ ppy) ₂ (CN) ₂] (3) | 259 (47), 289 (19.5), 345 (7.5), 386 (5.5) |
| PPN[Ir(ppy) ₂ (CN) ₂] (4) | 259 (53), 294 (23), 342 (9), 383 (6) |

These complexes show very similar absorption spectra to each other, in which less intense absorptions at lower energy have a mixture of ligand centred (LC) $\pi-\pi^*$ and metal-to-ligand charge-transfer (MLCT) character (ϵ between 5500 and 6800 $\text{M}^{-1} \text{cm}^{-1}$) in the region 364–382 nm, and the expected strong $\pi-\pi^*$ transitions associated with aromatic ligands occur in the UV region. In particular, the low-energy MLCT band in complex (1) (364 nm) is significantly blue-shifted compared to complex (2) (377 nm), (3) (386 nm) and (4) (383 nm). In 2002, Hay also reported the spectral properties of iridium(III) phenylpyridine complexes, in which all of the low-lying transitions are categorised as MLCT transitions, although the metal orbitals have significant mixture of ligand π character, and the high-energy bands above 280 nm are assigned to the intraligand (IL) $\pi-\pi^*$ transition of 2-phenylpyridine [22]. The absorption spectra of these complexes are shown in Figure 3.

The room temperature luminescence spectra of complexes (1)–(4) in dichloromethane solutions, with maximum ranging from 453 to 479 nm, are shown in Figure 4. The emission is attributed to a transition from the lowest ³MLCT/³LC excited state, to the ground state. It can be seen that complex (1), where the fluorine atoms are at positions C2 and C4 on the phenyl ring, shows an

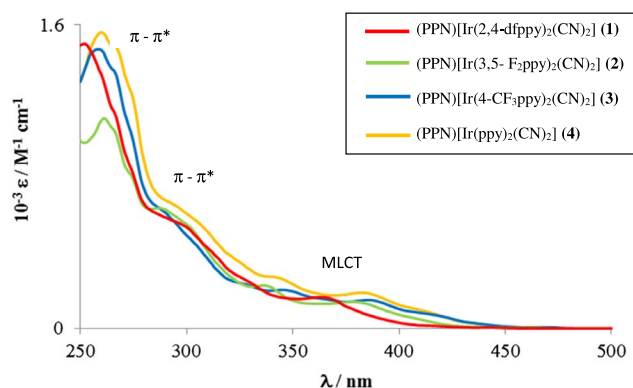


Figure 3. Absorption spectra of complexes (1)–(4) in dichloromethane at 298 K.

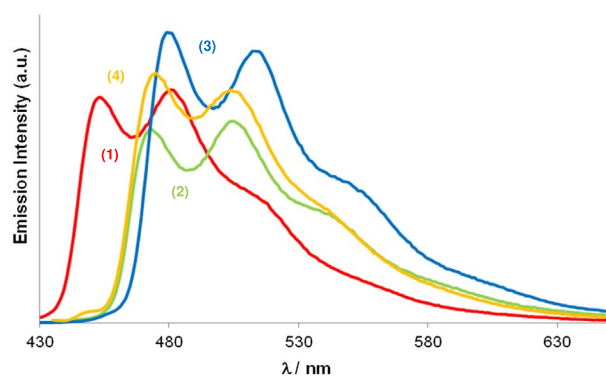


Figure 4. Luminescence spectra of PPN[Ir(2,4-dfppy)₂(CN)₂] (1) (red), PPN[Ir(3,5-F₂ppy)₂(CN)₂] (2) (green), PPN[Ir(4-CF₃ppy)₂(CN)₂] (3) (blue) and PPN[Ir(ppy)₂(CN)₂] (4) (orange), in air-equilibrated dichloromethane at 298 K.

almost blue emission ($\lambda_{\text{em}} = 453 \text{ nm}$), with a blue-shift in the maximum emission of 21 nm, compared to that of non-fluorinated complex (4) ($\lambda_{\text{em}} = 474 \text{ nm}$). Complex (2) with fluorine atoms at positions C3 and C5 on the phenyl ring shows a negligible hypsochromic shift ($\lambda_{\text{em}} = 473 \text{ nm}$) in the emission. The electron-withdrawing effect of a fluorine atom attached on the 2- and/or 4-carbon positions of the phenyl ring gives a large blue shift by the greater HOMO stabilisation than LUMO. However, substitution at the 3- and/or 5-carbon positions offset the electron-withdrawing effect of the fluorine atom by weak π -donation from fluorine into the HOMO, which reduces the HOMO-LUMO gap [7]. Conversely, complex (3) where the CF_3 groups are at position C4 on the phenyl ring, shows a red-shift ($\lambda_{\text{em}} = 479 \text{ nm}$), compared to complex (4). Therefore, the different energies of the luminescence for the different complexes show how the positions of the fluorine atoms on the phenyl ring are essential in determining the photophysical properties of the iridium(III) complexes [6,23].

Conclusions

In conclusion, a series of cyclometallated iridium(III) dicyanide complexes containing various types of fluorinated phenylpyridine ligand were successfully synthesised. The effect of the number and position of the fluorine units has been investigated via UV/Vis absorption and luminescence studies. Addition of fluorine atoms to the phenyl rings, have been used to enhance the triplet excited state energy and thus, blue-shift the phosphorescence for complex (1) ($\lambda_{\text{em}} = 453 \text{ nm}$) compared to that of complex (4) ($\lambda_{\text{em}} = 474 \text{ nm}$). However, complex (2) shows a negligible hypsochromic shift in the emission ($\lambda_{\text{em}} = 473 \text{ nm}$). Conversely, complex (3) shows a red-shift ($\lambda_{\text{em}} = 479 \text{ nm}$) compared to complex (4).

Acknowledgement

The author wishes to thank Universiti Pendidikan Sultan Idris and University of Sheffield for all affords and supports in this research.

Contributors

NMA conceived and designed the study, obtained funded and ethics approval, analysed the data, wrote the article in whole/part, and revised the article. MDW collected and analysed the data. NH collected and analysed the data. ND collected and analysed the data.

Disclosure statement

No potential conflict of interest was reported by the authors.

Funding

This work was supported by the Universiti Pendidikan Sultan Idris of Malaysia [grant number 2014-0070-101-01]; EPSRC of United Kingdom.

References

- [1] Baranoff E, Yum J-H, Graetzel M, et al. Cyclometallated iridium complexes for conversion of light into electricity and electricity into light. *J Organomet Chem.* 2009;694:2661–2670.
- [2] Wang Y, Herron N, Grushin VV, et al. Highly efficient electroluminescent materials based on fluorinated organometallic iridium compounds. *Appl Phys Lett.* 2001;79:449–451.
- [3] Ma A-F, Seo H-J, Jin S-H, et al. Novel cationic 2-phenylpyridine-based Iridium(III) complexes bearing an ancillary phosphine ligand: synthesis, photophysics and crystal structure. *Bull Korean Chem Soc.* 2009;30:2754–2758.
- [4] Nazeeruddin MK, Humphry-Baker R, Berner D, et al. Highly phosphorescence iridium complexes and their application in organic light-emitting devices. *J Am Chem Soc.* 2003;125:8790–8797.
- [5] Mingos DMP. *Essential Trends in Inorganic Chemistry.* New York (NY): Oxford University Press; 1998.
- [6] Di Censo D, Fantacci S, De Angelis F, et al. Synthesis, characterization, and DFT/TD-DFT calculations of highly phosphorescent blue light-emitting anionic iridium complexes. *Inorg Chem.* 2008;47:980–989.
- [7] Kim T, Kim H, Lee KM, et al. Phosphorescence color tuning of cyclometallated iridium complexes by *o*-carborane substitution. *Inorg Chem.* 2013;52:160–168.
- [8] Ward MD. Structural and photophysical properties of luminescent cyanometallates $[\text{M}(\text{diimine})(\text{CN})_4]^{2-}$ and their supramolecular assemblies. *Dalton Trans.* 2010;39:8851–8867.
- [9] Ali NM, MacLeod VL, Jennison P, et al. Luminescent cyanometallates based on phenylpyridine-Ir(III) units: solvatochromism, metallochromism, and energy-transfer in Ir/Ln and Ir/Re complexes. *Dalton Trans.* 2012;41:2408–2419.
- [10] Sheldrick GM. A short history of SHELX. *Acta Crystallogr Sect A Found Crystallogr.* 2007;64:112–122.
- [11] Coppo P, Plummer EA, De Cola L. Tuning iridium(III) phenylpyridine complexes in the ‘almost blue’ region. *Chem Commun.* 2004;1774–1775.
- [12] Nonoyama M. Benzo[*h*]quinolin-10-yl-*N* Iridium(III) Complexes. *Bull Chem Soc Jpn.* 1974;47:767–768.
- [13] Sprouse S, King KA, Spellane PJ, et al. Photophysical effects of metal-carbon σ bonds in ortho-metalated complexes of Ir(III) and Rh(III). *J Am Chem Soc.* 1984;106:6647–6653.
- [14] Baca SG, Adams H, Grange CS, et al. $[\text{Os}(\text{bipy})(\text{CN})_4]^{2-}$ and its relatives as components of polynuclear assemblies: structural and photophysical properties. *Inorg Chem.* 2007;46:9779–9789.
- [15] Evju JK, Mann KR. Synthesis and spectroscopic investigations of a crystalline humidity sensor: bis(triphenylphosphine)iminium 2,2'-bipyridyltetracyanoruthenate. *Chem Mater.* 1999;11:1425–1433.
- [16] Ward MD. Structural and photophysical properties of luminescent cyanometallates $[\text{M}(\text{diimine})(\text{CN})_4]^{2-}$ and their supramolecular assemblies. *Dalton Trans.* 2010;39:8851–8867.
- [17] Watzky MA, Endicott JF, Song X, et al. Red-shifted cyanide stretching frequencies in cyanide-bridged transition metal donor-acceptor complexes. Support for vibronic coupling. *Inorg Chem.* 1996;35:3463–3473.
- [18] Garces FO, Dedeian K, Keder NL, et al. Structures of *Ortho*-Metalated [2-(*p*-Tolyl)pyridine]iridium(III) complexes. *Acta Cryst C.* 1993;49:1117–1120.
- [19] Brisdon AK. *Inorganic spectroscopic methods.* New York (NY): Oxford University Press; 1998.
- [20] Lo S-C, Shipley CP, Bera RN, et al. Blue phosphorescence from Iridium(III) complexes at room temperature. *Chem Mater.* 2006;18:5119–5129.
- [21] Schmid B, Garces FO, Watts RJ. Synthesis and characterizations of cyclometallated iridium(III) solvent complexes. *Inorg Chem.* 1994;33:9–14.
- [22] Hay PJ. Theoretical studies of the ground and excited electronic states in cyclometallated phenylpyridine Ir(III) complexes using density functional theory. *J Phys Chem A.* 2002;106:1634–1641.
- [23] Coppo P, Plummer EA, De Cola L. Tuning iridium(III) phenylpyridine complexes in the ‘almost blue’ region. *Chem Commun.* 2004;15:1774–1775.