

Novel Cationic 2-Phenylpyridine-based Iridium(III) Complexes Bearing an Ancillary Phosphine Ligand: Synthesis, Photophysics and Crystal Structure

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Three novel phosphorescent 2-phenylpyridine-based iridium(III) complexes, [(ppy)₂Ir(P[^]N)]PF₆ (1), [(dfppy)₂Ir(P[^]N)]PF₆ (2), and [(dfmppy)₂Ir(P[^]N)]PF₆ (3), where P[^]N = 2-[(diphenylphosphino)methyl]pyridine (dppmp), were synthesized and characterized. The absorption, photoluminescence, cyclic voltammetry and thermal stability of the complexes were investigated. The complexes showed bright blue luminescences at wavelengths of 448 ~ 500 nm at room temperature in CHCl₃ and revealed that the π -acceptor ability of the phosphorous atom in the ancillary dppmp ligand plays an important role in tuning emission color resulting in a blue-shift emission. The single crystal structure of [(dfmppy)₂Ir(P[^]N)]PF₆ was determined using X-ray crystallography. The iridium metal center adopts a distorted octahedral structure coordinated to two dfmppy and one dppmp ligand, showing *cis* C-C and *trans* N-N chelate dispositions. There is a π - π overlap between π electrons delocalized in the difluorophenyl rings.

Key Words: Iridium complex, Cationic heteroleptic cyclometalated complex, Phosphine ligand, Blue phosphorescence

Introduction

Phosphorescent iridium(III) complexes have been an active research area for application in organic light-emitting diodes (OLEDs) since Baldo *et al.*¹ reported high-efficiency green phosphorescent OLEDs at room temperature based on *fac*-tris(2-phenylpyridine)iridium(III) [Ir(ppy)₃]. Iridium(III) complexes are regarded as the most effective phosphorescent materials given their relatively long-lived excited state and high quantum efficiency resulting from effective utilization of both singlet and triplet excited states for light emission. As such, they are often used as light emitters in electroluminescence displays. Red, green, and blue emissions with good color purity and high efficiencies are required for full-color display applications. Although great successes have been achieved in the development of red² and green³ iridium emitters, pure blue emission materials⁴ are still rare due to the wide gap and relatively low efficiency.

In 2-phenylpyridine (ppy)-based iridium(III) complexes, the emission is believed to originate from mixed triplet states possessing both intraligand (IL) ³ π - π^* and metal-to-ligand charge transfer (³MLCT) characters or states with greater contributions from ³MLCT. From the view point of ligand chromophores, the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) energy levels are mainly located at the pyridyl portion and phenyl segment of the ppy ligand, respectively, which are affected by the electronic state of the ligand. In principle, in order to blue-shift the emission wavelength in iridium(III) complexes, the LUMO-HOMO energy gap should be increased, thereby stabilizing the HOMO and/or destabilizing the LUMO energy levels. Recently, [(dfppy)₂Ir(pic)], where dfppy = 2-(2,4-difluorophenyl)pyridine and pic =

picolate, Irpic⁵, was reported and used as a blue emission phosphor in an electroluminescence device. The electron-withdrawing F atoms were introduced in the phenyl ring in the ppy ligand, resulting in stabilization of the HOMO energy level, and the picolate ligand finely tuned the emission color in the Irpic. The emission wavelength was tuned by modification of the ppy ligand as well as by introducing an adequate ancillary ligand.

As an effort of a development of blue emission materials, herein we report the synthesis and characterization of three cationic heteroleptic cyclometalated iridium(III) complexes: [(ppy)₂Ir(P[^]N)]PF₆ (1); [(dfppy)₂Ir(P[^]N)]PF₆ (2); [(dfmppy)₂Ir(P[^]N)]PF₆ (3). The electron-donating -CH₃ group in the pyridyl moiety and/or the electron-withdrawing F atom in the phenyl moiety were substituted, varying the electronic state in the ppy ligand; the 2-[(diphenylphosphino)methyl]pyridine (P[^]N) was used as an ancillary ligand. The π -accepting character of the phosphine group is expected to increase the associated MLCT energy level in anticipation of a blue-shift emission.⁶

Experimental

Materials and Synthesis. All reagents and solvents were commercially obtained from Sigma-Aldrich Chemicals or Acros Organics and used without further purification with an exception of tetrahydrofuran (THF), which was distilled from sodium/benzophenone under nitrogen.

2-(2,4-Difluorophenyl)-4-methylpyridine (dfmppy) and 2-(2,4-difluoro)phenylpyridine (dfppy) were prepared from the reaction of 2,4-difluorophenylboronic acid with 2-bromo-4-methylpyridine and 2-bromopyridine, respectively, using tetrakis(triphenylphosphine)palladium(0) as a catalyst in THF.⁷ 2-[(Diphenylphosphino)methyl]pyridine (dppmp) was synthesized

from the reaction of *n*-butyllithium, 2-picoline, and diphenylphosphinochloride using standard Schlenk technique, and the product was directly used for the next step without further purification.

[(C[^]N)₂Ir(dppmp)]PF₆ complexes: General Procedure. Cyclometalated iridium(III) μ -chloro-bridged dimers, [(C[^]N)₂Ir(μ -Cl)]₂, where C[^]N = ppy, dfppy, and dfmppy, were prepared from the reaction of IrCl₃·3H₂O with the main ligand (C[^]N) in a 3:1 mixture of 2-ethoxyethanol and water at 125 °C for 24 h. The dimeric iridium(III) complex, [(C[^]N)₂Ir(μ -Cl)]₂ (0.5 mmol), Na₂CO₃ (5.0 mmol) and dppmp (3.0 eq) were dissolved in 30.0 mL of 2-ethoxyethanol and stirred at 130 °C under nitrogen for 24 h. The cooled mixture was poured into water and extracted with CH₂Cl₂ (50 mL \times 3) and dried over anhydrous magnesium sulfate. The product, [(C[^]N)₂Ir(dppmp)]Cl, was purified by column chromatography on silica gel using *n*-hexane/CH₂Cl₂ as an eluent. The purified chloride salts were reacted with NH₄PF₆ in methanol, refluxing for 1 ~ 2 h. The products were collected by filtration and washed with methanol. The products were characterized by ¹H-NMR and elemental analyses. Elementary analyses were performed at the Korean Basic Science Center.

[(ppy)₂Ir(dppmp)]PF₆ (1). ¹H-NMR (CDCl₃): δ (ppm) 8.55 (d, *J* = 5.4 Hz, 1H); 8.27 (d, *J* = 7.5 Hz, 1H); 7.98 (t, *J* = 7.5 Hz, 1H); 6.80–8.00 (m, 23H); 6.62 (t, *J* = 10.5 Hz, 2H); 6.53 (d, *J* = 6.9 Hz, 1H); 6.11 (dd, *J* = 7.2, 4.8 Hz, 1H); 4.99 (dd, *J* = 18.0, 12.3 Hz, 1H); 4.25 (dd, *J* = 17.4, 6.6 Hz, 1H). Anal. Calcd for C₄₀H₃₂F₆IrN₃P₂: C, 52.06; H, 3.50; N, 4.55. Found: C, 52.72; H, 3.28; N, 4.39.

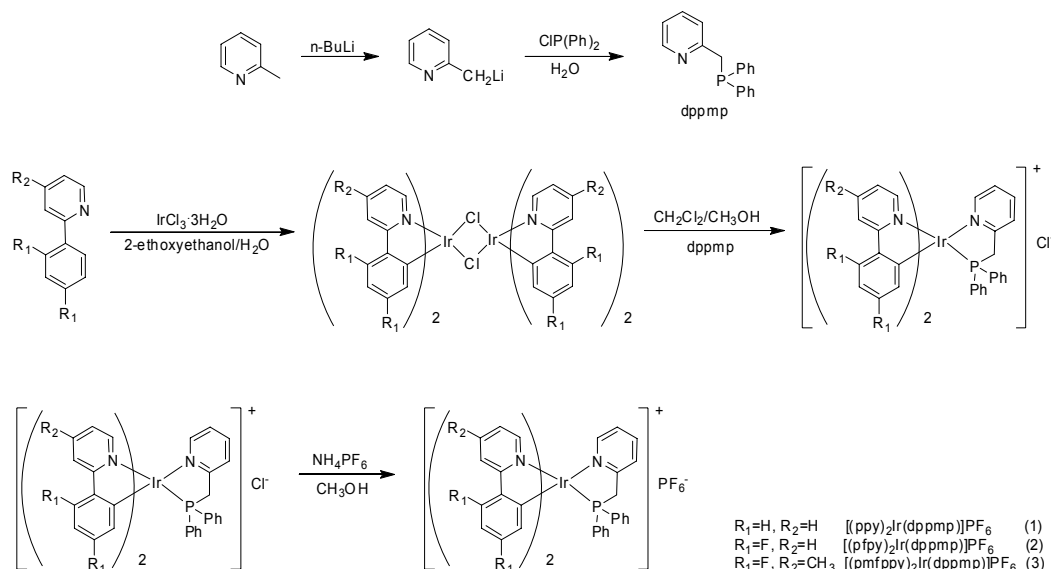
[(dfppy)₂Ir(dppmp)]PF₆ (2). ¹H-NMR (CDCl₃): δ (ppm) 8.53 (d, *J* = 3.9 Hz, 1H); 8.33 (m, 2H); 8.06 (m, 2H); 7.84 (s, 2H); 7.59 (m, 4H); 7.44 (t, *J* = 6.0 Hz, 2H); 7.25 (m, 1H); 7.06 (d, *J* = 6.6 Hz, 1H); 6.97 (s, 4H); 6.62 (m, 5H); 5.93 (dd, *J* = 2.4, 9.6 Hz, 1H); 5.55 (m, 1H); 5.00 (m, 1H); 4.36 (s, 1H). Anal. Calcd for C₄₀H₂₈F₁₀IrN₃P₂: C, 48.29; H, 2.84; N, 4.22. Found: C, 48.56; H, 2.42; N, 4.09.

[(dfmppy)₂Ir(dppmp)]PF₆ (3). ¹H-NMR (CDCl₃): δ (ppm) 8.32 (d, *J* = 6.3 Hz, 1H); 8.28 (d, *J* = 7.5 Hz, 1H); 8.12 (s, 1H);

8.01 (t, *J* = 7.5 Hz, 1H); 7.86 (s, 1H); 7.82 (d, *J* = 5.7 Hz, 1H); 7.60 (t, *J* = 8.1 Hz, 2H); 7.51 (d, *J* = 6.9 Hz, 1H); 7.43 (t, *J* = 5.7 Hz, 2H); 7.20 (t, *J* = 6.0 Hz, 1H); 7.08 (t, *J* = 7.5 Hz, 1H); 6.97 (t, *J* = 5.1 Hz, 2H); 6.80 (d, *J* = 5.7 Hz, 1H); 6.75 (d, *J* = 6.0 Hz, 1H); 6.68–6.54 (m, 4H); 6.39 (d, *J* = 5.7 Hz, 1H); 5.95 (d, *J* = 8.4 Hz, 1H); 5.61 (m, 1H); 4.98 (dd, *J* = 18.6, 12.3 Hz, 1H); 4.27 (dd, *J* = 17.7, 6.6 Hz, 1H); 2.50 (s, 3H); 2.38 (s, 3H). Anal. Calcd for C₄₂H₃₂F₁₀IrN₃P₂: C, 49.32; H, 3.15; N, 4.11. Found: C, 49.31; H, 3.57; N, 4.39.

Instruments. The ¹H-NMR spectra were recorded with a Varian Mercury 300 spectrometer with CDCl₃ (¹H: δ 7.27 ppm) as the solvent. The UV-Vis absorption and photoluminescence (PL) spectra were measured by a Jasco V-570 UV-Vis spectrophotometer and a Hitachi F-4500 fluorescence spectrophotometer, respectively, from 200 to 800 nm. Cyclic voltammetry (CV) experiments were performed on a Bioanalytical Systems CV-50W voltammetric analyzer in a 0.1 M solution of tetrabutylammonium tetrafluoroborate (Bu₄NBF₄) in anhydrous acetonitrile. The Pt disk electrode, Ag/AgNO₃ (0.1 M) electrode and Pt electrode were used as the working, reference and counter electrode, respectively, at a scan rate of 100 mV/s. Thermal analyses were carried out on a Mettler Toledo TGA/DTA 815 analyzer under a nitrogen atmosphere at a heating rate of 10 °C/min.

Crystallography. The X-ray intensity data were obtained using a Bruker SMART APEX-II CCD diffractometer equipped with graphite monochromated Mo K α radiation (λ = 0.71073 Å) at 295 K. Initial unit cell parameters were obtained from SMART software.⁸ Data integration, correction for Lorentz and polarization effects, and final cell refinement were performed by SAINTPLUS.⁹ An empirical absorption correction based on the multiple measurement of equivalent reflections was applied using the program SADABS.¹⁰ Structures were obtained by a combination of the direct methods and difference Fourier syntheses and refined by full matrix least-squares on *F*², using the SHELXTL.¹¹ All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added in calculated positions.



Scheme 1. Synthesis of dppmp and complexes 1, 2 and 3.

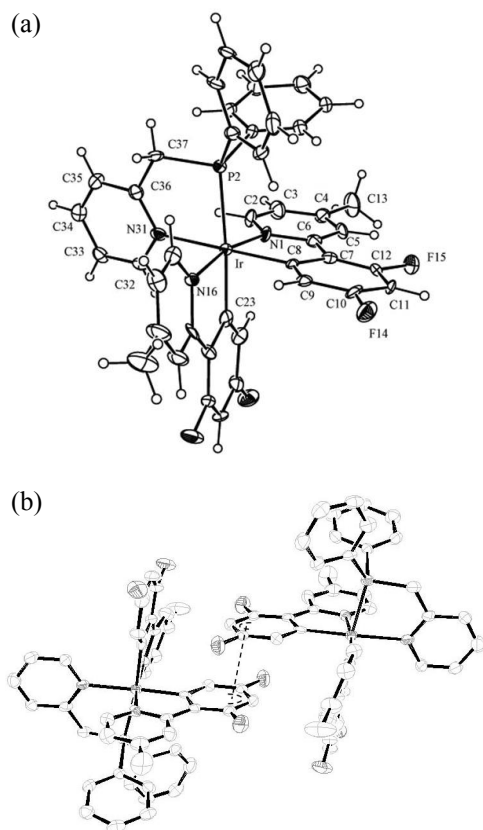


Figure 1. (a) ORTEP drawing of $[(\text{dfmppy})_2\text{Ir}(\text{dppmp})]^+$ showing the atom numbering scheme with 30% probability ellipsoids: Ir-C8 2.021 (7); Ir-N1 2.030(5); Ir-C23 2.044(7); Ir-N16 2.077(6); Ir-N31 2.193(6); Ir-P2 2.348(19); C8-Ir-C23 86.40(3); C23-Ir-N31 93.90(2); C8-Ir-P2 99.38(19); N31-Ir-P2 80.24(16); N1-Ir-N16 167.4(2). (b) Crystal packing diagram between two adjacent molecules showing an intermolecular π - π stacking interaction. The phenyl...phenyl contact distance is 3.254 ~ 3.718 Å.

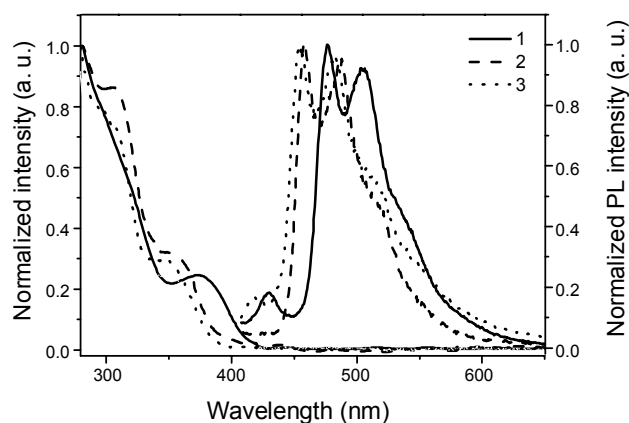


Figure 2. Absorption and photoluminescence spectra of complexes 1, 2 and 3 in CHCl_3 .

Results and Discussion

Synthesis and Structural Characterization. The reaction of 2-picoline and *n*-butyllithium with diphenylphosphinochloride yielded 2-[(diphenylphosphino)methyl]pyridine (dppmp), and

the phenylpyridine derivatives were made from the Suzuki coupling method.⁷ The chloro-bridged dimers, $[(\text{N}^{\wedge}\text{C})_2\text{Ir}(\mu\text{-Cl})]_2$, were prepared through a modified Nonoyama method.¹² The chloro-bridged dimer was used as starting material to yield cationic heteroleptic iridium(III) chloride salts. The PF_6^- salt was made from the chloride salt, using NH_4PF_6 in methanol. The synthetic procedure is shown in Scheme 1. The properties of the chloride salts are nearly consistent with those of the PF_6^- salts discussed herein.

The structure was determined from the single crystal of complex 3 obtained from a mixed solvent system ($\text{Me-OH}/\text{CHCl}_3$). The ORTEP diagram, including the atomic numbering scheme and packing diagram, are shown in Figure 1. The crystallographic data follows: $\text{C}_{30}\text{H}_{32}\text{Cl}_2\text{N}_4\text{Ir}$, $M_w = 584.87$, Monoclinic, $P2_1/c$, $a = 14.108(2)$ Å, $b = 9.4890(16)$ Å, $c = 21.606(4)$ Å, $\alpha = 90.00^\circ$, $\beta = 99.930(3)^\circ$, $\gamma = 90.00^\circ$, $V = 2849.1(8)$ Å³, $Z = 4$, $D_{\text{calc}} = 1.363$ Mg m⁻³, $\mu = 1.075$ mm⁻¹, $\theta_{\text{max}} = 27.50^\circ$, 23572 reflections ($R_{\text{int}} = 0.0667$), 6544 unique reflections, 333 parameters refined. Good of Fit = 1.061, Final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0561$, $wR_2 = 0.1411$, all data: $R_1 = 0.1202$, $wR_2 = 0.1844$.

The iridium metal center adopts a distorted octahedral structure with the *trans* angles of $167 \sim 176^\circ$ coordinated to two dfmppy and one dppma ligand, showing a *cis* C-C and *trans* N-N chelate disposition, which is a coincident mode of the chloride-bridged precursor dimer.¹³ This result indicates that the ancillary ligand (dppma) replaces the chloride ions in the precursor dimer complex in the synthetic reaction.

The Ir-N bond lengths [2.030(5) Å and 2.077(6) Å] were within the normal range reported for analogous cyclometalated iridium complexes.¹⁴ The Ir-C23 bond [2.044(7) Å] was found to be longer than the Ir-C8 bond [2.021(7) Å], ascribed to the stronger *trans* influence of the phosphorous atom in the phosphine than the nitrogen atom in the pyridine ring. This *trans* influence was reported in the $\text{Ir}(\text{tpy})_3$ [$\text{tpy} = 2\text{-tolypyridyl}$], in which the Ir-N bond in facial isomer was longer than that in the meridional isomer of the $\text{Ir}(\text{tpy})_3$, resulting from the weaker *trans* influence of the pyridyl group relative to the phenyl group.¹⁵

The dihedral angle between the difluorophenyl and methylpyridine ring, C5-C8-C7-C12, was 4.14° , being almost coplanar. This small distortion is explained by the fact that the π electron density of the difluorophenyl group is smaller than that of phenyl ring. Furthermore, there is an interaction between the C5 hydrogen and F15 fluorine atom (C5...F15; 2.223 Å), therefore the fluoro-substituted groups contribute less to the steric hindrance.¹⁶

The crystal packing diagram [Figure 1-(b)] shows a π - π overlap between the π electrons delocalized on the C10, C11, C12 atoms in the difluorophenyl ring and the similarly distributed π electrons in an adjacent molecule. The distance between the part of the difluorophenyl rings was 3.254 ~ 3.718 Å, suggesting a favorable, shared interaction.¹⁷

Photophysical Properties. The absorption (UV/Vis) and photoluminescence (PL) spectra in aerated chloroform at room temperature are shown in Figure 2, and the results summarized in Table 1.

The absorption bands below 300 nm were tentatively assigned as $^1(\pi \rightarrow \pi^*)$ transitions of the phenylpyridyl-based ligands and the peaks near 350 ~ 375 nm ascribed as spin-allowed metal-

Table 1. Photophysical, electrochemical and thermal properties for complexes 1, 2 and 3.

Complex	λ_{abs} [nm]	λ_{em} [nm]	Φ_{PL}	$E_{1/2}$ (V)	HOMO (eV)	$E_{\text{g}}^{\text{opt}}$ (eV)	LUMO (eV)	T_{d} [°C]
1	281,306,375	470,500	0.004	0.90	-5.70	2.86	-2.84	370
2	281,303,352	452,481	0.007	1.19	-5.99	3.09	-2.90	385
3	277,300,348	448,478	0.016	1.15	-5.95	3.12	-2.83	370

^aAbsorption spectra and PL were tested in aerated chloroform solution at 298 K. ^bPL quantum efficiency was determined using Ir(ppy)₃(bpy), PF₆ ($\Phi = 0.06$) as a standard,^{18a} and calculated with a published method.^{18b} ^cHOMO values were acquired from cyclic voltammetry data, using the onset method.^{18c} ^dEnergy band gaps were obtained from the absorption peaks in the film state.^{18d} ^eHOMO = $-(E_{1/2} + 4.8 \text{ eV})$, LUMO = HOMO + E_{g} . ^f T_{d} indicates the decomposition temperature at a 5 wt% decrease.

Table 2. Photoluminescence properties of complexes 1, 2 and 3 in different solvents and film states.

Complex		λ_{em} [nm]			
		^a C ₂ H ₅ OH	^a CH ₂ Cl ₂	^b Film	^b Film (in PMMA)
1	λ_{max}	470, 500	472, 501	470, 500	470, 499
	Φ	0.003	0.006	0.01	0.17
2	λ_{max}	452, 481	452, 481	455, 483	451, 480
	Φ	0.002	0.013	0.01	0.18
3	λ_{max}	450, 477	449, 476	450, 451	469, 444
	Φ	0.012	0.009	0.01	0.09

^aSame as annotation a and b in Table 1. ^bIridium complexes were 5 wt% doped in PMMA; a thin film of $\sim 10^{-3}$ M 9,10-diphenylanthracene in poly (methyl methacrylate) (PMMA) was used as the standard ($\Phi = 83\%$) for calculating Φ of the films.^{18d}

to-ligand charge transfer (¹MLCT) transitions.¹⁹ The ¹MLCT transition in complex 1 was ~ 20 nm longer than those of complex 2 and 3, indicating that fluorination on the phenyl ring lowered the HOMO energy level of the iridium metal as a result of decreasing the electron density of the phenyl group.

The PL spectra of the complexes showed emission bands in the range of 448 \sim 500 nm, exhibiting vibronic progressions with two maximum peaks. This observation indicated that the intra-ligand (IL) ³ π - π^* contribution was dominant to the luminescent emission.²⁰ The maximum emission wavelengths [$\lambda_{1\text{st.max.}}$, $\lambda_{2\text{nd.max.}}$] were [470, 500 nm], [452, 481 nm] and [449, 476 nm] in the blue region for complex 1, 2 and 3, respectively. The emission maxima of 2 were 13 \sim 18 nm blue-shifted compared to a reported blue light emitter, iridium(III) bis[2-(2,4-difluoro-phenyl)pyridinato](2-picolinate), [FIr(pic)], $\lambda_{\text{max}} = 470, 494 \text{ nm}$ ²¹, reflecting that the π -accepting character of the phosphine group increased the associated MLCT energy levels, resulting in a blue-shift emission.⁶ The substituents in the main ligand showed a hypsochromic shift on the order of ppy \rightarrow dfppy \rightarrow dfmppy, and revealed that difluorination on the 2,4-positions of the phenyl ring led to a significant blue-shift, whereas methylation on the pyridine group caused a small blue-shift of the emission maximum.²²

The emission peaks were next examined in a variety of solvents, but little solvatochromism was observed as shown in Table 2. Although the emission in the film state (5 wt% doped in PMMA) was also similar to those in the solution state, the quantum efficiency (Φ_{pl}) in the film state was enhanced enormously.

For example, Φ_{pl} in chloroform (0.004) increased up to 0.17 in the film state for complex 1. The host materials increased the distance between the guest materials, leading to a decrease in the quenching effect.²³

Electrochemical and Thermal Properties. The electrochemical properties were investigated by cyclic voltammetry (CV) with the resulting data relative to a ferrocenium/ferrocene redox couple²⁴ are in Table 1. All the complexes showed irreversible oxidation potentials in the range of 0.90 to 1.19 V, believed to originate from the iridium metal cationic site together with a contribution from the cyclometalated phenyl fragment.²⁵

From the obtained oxidation potential and the absorption edge of the UV-Vis spectrum, the HOMO and LUMO and the energy gap (E_{g}) were calculated. The results are listed in Table 1. The oxidation potential of complex 2 was 1.19 V, shifted cathodically by 0.29 V compared to the complex 1. Fluorination on the phenyl ring decreased both HOMO and LUMO energy levels, but the significant lowering of the HOMO energy level caused a widening of the energy gap (E_{g}), resulting in a blue-shift of the emission maximum. Methylation on the pyridine ring increased the HOMO energy level by 0.04 V and the LUMO energy level by 0.07 V.

The thermal stability, investigated using thermal gravimetric analysis (TGA), showed that the 5% (wt.) decomposition temperatures were above 370 °C (Table 1), exhibiting the high thermal stability required for an electroluminescent device.

Conclusions

Three blue phosphorescent cationic heteroleptic cyclometalated iridium(III) complexes, containing phenylpyridine derivatives in combination with a newly designed 2-[(diphenylphosphino)methyl]pyridine (dppmp) ligand, were prepared. It was revealed that the ancillary dppmp ligand played an important role in tuning the emission color and led to a blue-shift emission due to the π -acceptor ability of the phosphorous atom in the dppmp. In particular, [(dfmppy)₂Ir(P^{^N})]PF₆ could be a novel candidate for application in optoelectronic devices for blue emission.

Supplementary Data. CCDC No. 633532 contains the supplementary crystallographic data for [(dfmppy)₂Ir(dppmp)]PF₆. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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