



# Phosphorescent cationic iridium complexes with phenyl-imidazole type cyclometalating ligands: A combined experimental and theoretical study on photophysical, electrochemical and electroluminescent properties



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## ABSTRACT

Phosphorescent cationic iridium complexes with phenyl-imidazole type cyclometalating ligands have been synthesized for the first time and their photophysical, electrochemical properties have been comprehensively investigated. By changing the ancillary ligands, the complexes give orange-red or green-blue light. Compared to 2-phenylpyridine (ppy), the phenyl-imidazole ligands destabilize simultaneously the highest occupied molecular orbitals and the lowest unoccupied molecular orbitals of the complexes. Their emitting triplet states show dominant charge-transfer (iridium/cyclometalating ligands → ancillary ligands) character. The complexes have been used to fabricate solid-state light-emitting electrochemical cells (LECs). The orange-red LEC gives a high peak current efficiency of 14.3 cd A<sup>-1</sup>, which is among the highest reported for orange-red LECs; the green-blue LEC gives a peak current efficiency of 6.3 cd A<sup>-1</sup>. It is shown that the phenyl-imidazole cyclometalating ligands hold promise for the invention of iridium-based cationic phosphorescent dyes with tunable energy levels and emission properties.

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## 1. Introduction

Phosphorescent iridium complexes have attracted significant research interest during the past decade, owing to their noteworthy advantages, such as high phosphorescent efficiency, tunable emission color and short-lived emission (~μs), over other small-molecule metal-organic phosphors [1–3]. Depending on the charges carried by them, the complexes can be classified as neutral and ionic ones [2]. In recent years, the ionic complexes, especially the cationic ones, have received growing research interest [4–12], due to their fascinating features such as intrinsic ionic nature, good solubility in polar solvents or even in aqueous media, and facile tuning of photophysical and electrochemical properties through

ligand control. These cationic complexes have been widely applied in biological imaging or sensing [10], photo-catalysis [11] and light-emitting devices such as solid-state light emitting electrochemical cells (LECs) [7,8,12–17].

Most of phosphorescent cationic iridium complexes can be described with the form of [Ir(CAN)<sub>2</sub>(NAN)]<sup>+</sup>A<sup>-</sup>, where CAN is the anionic cyclometalating ligand, NAN is the neutral ancillary ligand and A<sup>-</sup> is the counter anion. The archetype complex, [Ir(ppy)<sub>2</sub>(bpy)]<sup>+</sup>PF<sub>6</sub><sup>-</sup> (ppyH is 2-phenylpyridine, bpy is 2,2'-bipyridine and PF<sub>6</sub><sup>-</sup> is hexafluorophosphate), gives orange-red light (λ<sub>max</sub> ≈ 590 nm) [4,9,18]. Tremendous efforts have been devoted to extending the emission color from red to blue through judicious modification of the ligands [7,8,19,20]. Experimental and theoretical studies have found that the highest occupied molecular orbital (HOMO) resides on iridium and the phenyl rings of ppy, and the lowest unoccupied molecular orbital (LUMO) is delocalized over bpy [9,18]. Thus, attaching electron-donating/electron-withdrawing groups to the ppy or bpy ligands can modulate the

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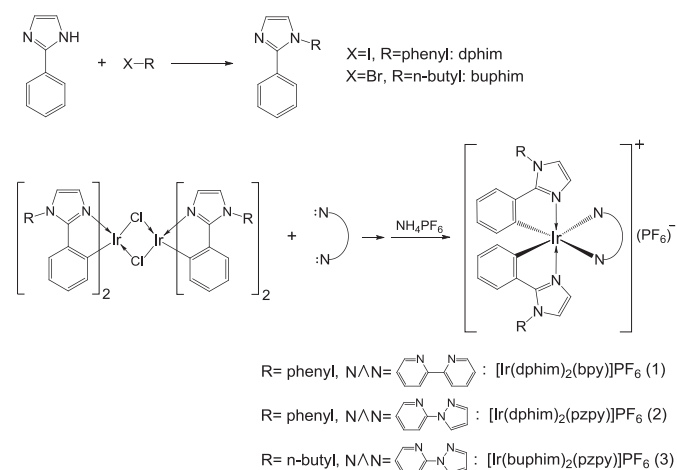
energy levels of frontier molecular orbitals, leading to blue or red-shifted emission [7,8,19,20]. Also, use of  $\Lambda\Lambda\text{N}$  ligands rather than bpy, such as 2-(1*H*-pyrazol-1-yl)pyridine (pzpy) [21], *N*-heterocyclic carbene [22,23] and pyridine-oxidazole [24], allows a large tuning of energy levels and emission properties of the complexes. Recently,  $\text{CAN}$  ligands beyond the ppy skeleton, such as phenyl-pyrazole [25], phenyl-triazole [26,27], phenyl-tetrazole [28], phenyl-oxidazole [29], phenyl-thiazole [30], and phenyl-carbene [31], have been exploited, which opens an important avenue for the tuning of energy levels and emission properties of the complexes.

Bearing high-triplet energy, phenyl-imidazole  $\text{CAN}$  ligands have been utilized in neutral blue-emitting iridium complexes [32–34], but so far they have not been examined for cationic iridium complexes. Herein we report cationic iridium complexes using phenyl-imidazole type  $\text{CAN}$  ligands (complexes 1–3, Scheme 1), with a combined experimental and theoretical investigation on their photophysical and electrochemical properties. Two phenyl-imidazole  $\text{CAN}$  ligands: 1,2-diphenyl-1*H*-imidazole (dphim) and 1-butyl-2-phenyl-1*H*-imidazole (buphim) (Scheme 1), were developed. The complex  $[\text{Ir}(\text{dphim})_2(\text{bpy})]\text{PF}_6$  (1) uses typical bpy as the  $\Lambda\Lambda\text{N}$  ligand, while  $[\text{Ir}(\text{dphim})_2(\text{pzpy})]\text{PF}_6$  (2) and  $[\text{Ir}(\text{buphim})_2(\text{pzpy})]\text{PF}_6$  (3) employ pzpy as the  $\Lambda\Lambda\text{N}$  ligand. The use of electron-rich pzpy ancillary ligand aims to destabilize the LUMO levels and blue-shift the emission of the complexes [21]. In solution and neat film, complex 1 shows orange-red emission ( $\lambda_{\text{max}} \approx 590$  nm) similar to that of  $[\text{Ir}(\text{ppy})_2(\text{bpy})]\text{PF}_6$ , while complexes 2 and 3 give green-blue emission ( $\lambda_{\text{max}} \approx 500$  nm). The phenyl-imidazole  $\text{CAN}$  ligands destabilizes simultaneously the HOMO and LUMO levels of the complexes as compared to the ppy  $\text{CAN}$  ligand. Experimental results and theoretical calculations confirm that the lowest emitting triplet states of complexes 1–3 possess dominant metal-to-ligand ( $\text{Ir} \rightarrow \Lambda\Lambda\text{N}$ ) and ligand-to-ligand ( $\text{CAN} \rightarrow \Lambda\Lambda\text{N}$ ) charge-transfer character. As used in LECs, complex 1 gives orange-red emission with a high peak current efficiency of  $14.3 \text{ cd A}^{-1}$ , which is among the highest reported for orange-red LECs [7,8]; complexes 2 and 3 give green-blue emission with a lower efficiency of  $6.3 \text{ cd A}^{-1}$ , presumably due to more difficult electron-injection caused by their high LUMO levels.

## 2. Experimental

### 2.1. General information

All reactants and solvents were obtained from commercial sources and, unless otherwise mentioned, used as received. Mass



**Scheme 1.** Synthesis of the phenyl-imidazole-type  $\text{CAN}$  ligands and complexes 1–3.

spectrometry was performed using a LTQ-ORBITRAP-ETD mass spectrometer. NMR spectra were recorded on a BRUKER 400/500 NMR spectrometer. Elemental analysis was determined with an EA3000 elemental analyzer (Eurovector, Italy). Absorption and photoluminescence (PL) spectra were collected using a Shimadzu UV-2450 spectrophotometer and a HITACHI F-4600 spectrometer, respectively. The PL transient lifetimes were measured on a transient spectrofluorimeter (Edinburgh Instruments, FLSP920). The photoluminescent quantum yields (PLQYs) were measured in degassed  $\text{CH}_3\text{CN}$  solution referred to  $\text{Ru}(\text{bpy})_3\text{Cl}_2$  ( $\Phi_{\text{p}} = 0.028$  in water; for complex 1) or quinine sulfate ( $\Phi_{\text{p}} = 0.545$  in 1 M  $\text{H}_2\text{SO}_4$ ; for complexes 2–3) [35,36]. Cyclic voltammetry was performed with a RST5200 voltammetric analyzer in dichloromethane solution ( $10^{-3}$  M) at a scan rate of 100 mV/s, using a glass-carbon working electrode, a silver wire pseudo-reference electrode and a platinum wire counter electrode. Tetrabutylammonium hexafluorophosphate (0.1 M) and ferrocene (Fc) were used as the supporting electrolyte and the internal standard, respectively. All solutions were degassed with argon before measurements.

### 2.2. Synthesis

The ligand pzpy was prepared according to a reported procedure [21]. The chloro-bridged iridium dimers,  $[\text{Ir}(\text{dphim})_2\text{Cl}_2]$  or  $[\text{Ir}(\text{buphim})_2\text{Cl}_2]$ , were synthesized by reacting  $\text{IrCl}_3 \cdot n\text{H}_2\text{O}$  with dphim or buphim in refluxed 2-ethoxyethanol/water (3:1) under a nitrogen atmosphere [37], and used for next reactions without further purification.

#### 2.2.1. Synthesis of 1,2-diphenyl-1*H*-imidazole (dphim)

2-phenyl-4*H*-imidazole (3.61 g, 25 mmol), iodobenzene (3.64 mL, 32.5 mmol), 1,10-phenanthroline (1.80 g, 10 mmol), copper iodide (0.95 g, 5 mmol) and cesium carbonate (12.22 g, 37.5 mmol) were dissolved in DMF (80 mL). The mixture was stirred and refluxed overnight under an argon atmosphere. After cooling to room temperature, the solvent was removed under vacuum and the residue was extracted with  $\text{CH}_2\text{Cl}_2$  (200 mL). The organic phase was washed with water, dried with anhydrous  $\text{Na}_2\text{SO}_4$ , and purified by column chromatography on silica gel with petroleum ether: ethyl acetate (2:1) as the eluent, yielding a white solid (3.7 g, 16.8 mmol). Yield: 67%.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ - $d_6$ , 500 MHz,  $\delta$ [ppm]): 7.43–7.38 (m, 5H), 7.31–7.20 (m, 6H), 7.17 (d,  $J = 1.5$  Hz, 1H). HRMS (ESI,  $m/z$ ): 221.1056 [ $\text{M}+\text{H}$ ] $^+$  (calc. 221.1073).

#### 2.2.2. Synthesis of 1-butyl-2-phenyl-1*H*-imidazole (buphim)

2-phenyl-4*H*-imidazole (2.88 g, 20 mmol) and potassium hydroxide (1.68 g, 30 mmol) were suspended in acetone (120 mL). To the suspension, 1-bromobutane (3.22 mL, 33 mmol) was dropped slowly. The mixture was refluxed overnight under an argon atmosphere. After cooling to room temperature, the solvent was removed under vacuum and the residue was extracted with  $\text{CH}_2\text{Cl}_2$  (150 mL). The organic phase was concentrated and purified by column chromatography on silica gel with petroleum ether: ethyl acetate (2:1) as the eluent, yielding a light yellow oil (3.32 g, 16.5 mmol). Yield: 83%.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ - $d_6$ , 500 MHz,  $\delta$ [ppm]): 7.59 (t,  $J = 2.0$  Hz, 1H), 7.57 (t,  $J = 1.5$  Hz, 1H), 7.50–7.40 (m, 3H), 7.16 (d,  $J = 1.5$  Hz, 1H), 7.03 (d,  $J = 1.5$  Hz, 1H), 4.01 (t,  $J = 7.5$  Hz, 2H), 1.77–1.70 (m, 2H), 1.33–1.26 (m, 2H), 0.88 (t,  $J = 7.5$  Hz, 3H). HRMS (ESI,  $m/z$ ): 201.1371 [ $\text{M}+\text{H}$ ] $^+$  (calc. 201.1386).

#### 2.2.3. Synthesis of $[\text{Ir}(\text{dphim})_2(\text{bpy})]\text{PF}_6$ (1)

$[\text{Ir}(\text{dphim})_2\text{Cl}_2]$  (477 mg, 0.357 mmol) and bpy (123 mg, 0.788 mmol) were dissolved in  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$  (25/25 mL). The mixture was refluxed overnight under a nitrogen atmosphere. The solution was cooled to room temperature and evaporated to

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