



# Photophysical, electrochemical, and quantum chemical properties of cationic iridium complexes with tunable emission color



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## ABSTRACT

We report the synthesis and characterization of the cationic iridium complexes [Ir(ppy)<sub>2</sub>(mboxd)]PF<sub>6</sub> (**1**), [Ir(dfppy)<sub>2</sub>(mboxd)]PF<sub>6</sub> (**2**), [Ir(piq)<sub>2</sub>(mboxd)]PF<sub>6</sub> (**3**), and [Ir(pq)<sub>2</sub>(mboxd)]PF<sub>6</sub> (**4**) bearing 2-phenylpyridine (Hppy), 2-(2,4-difluorophenyl)pyridine (Hdfppy), 1-phenylisoquinoline (Hpiq), and 2-phenylquinoline (Hppq) as cyclometalating ligands and 5-methyl-3-(2-pyridyl)-1,2,4-oxadiazole (mboxd) as an ancillary ligand. UV-visible absorption spectra, photoluminescence (PL) emission spectra, and cyclic voltammetric measurements were obtained to explore the photophysical and electrochemical properties of **1–4**. Depending on the nature of the cyclometalating ligands, the complexes emit yellow-orange to blue light in acetonitrile solution at room temperature. The significant blue shift in the emission spectrum of **2** is due to the presence of electron-withdrawing fluorine atoms on Hdfppy, which stabilizes the highest occupied molecular orbital (HOMO) to a greater extent than in the other complexes. The electrochemical and photophysical properties of the complexes were also calculated using density functional theory (DFT) and time-dependent DFT simulations. The results indicate that the optical properties of the complexes can be effectively tuned by selective design of the cyclometalating and ancillary ligands.

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## 1. Introduction

Ionic transition metal complexes (iTMCs) have attracted extensive interest due to their unique photophysical properties [1,2]. These materials have found application in photocatalysis [3], bioimaging [4], solar cells [5], light-emitting electrochemical cells (LECs) [6–9], and organic light-emitting diodes (OLEDs) [10]. Recently, LECs incorporating iTMCs have emerged as promising lighting devices and constitute an alternative to sophisticated organic light-emitting diodes (OLEDs) due to their low cost of production [11]. LECs are simpler devices than OLEDs and consist of a single ionic light-emitting layer processed from solution and placed between two metal electrodes by facile spin coating or printing processes [1]. LECs are also insensitive to the electrode work function and do not require air-sensitive charge injection layers, which allows non-rigorous encapsulation of the devices [12]. These benefits make LECs a favorable electroluminescent device for next-generation, flat-panel displays and solid-state lighting applications.

iTMCs, which emit light by phosphorescence, exhibit outstanding photoluminescent quantum yields (PLQYs) in comparison to polymer-based materials, which emit photons from singlet states and thus have

a maximum internal quantum efficiency of only 25% [13,14]. The ionic nature of iTMCs leads to solubility in most polar organic solvents or even aqueous media [15,16]. Moreover, iTMCs possess attractive excited state properties and show multiple stable oxidation states [17]. iTMCs with superior redox reversibility is required in LEC devices to transport holes and electrons. During device operation, mobile ions in the active layer of the LEC move toward the corresponding electrode under an external bias and assist the injection of holes and electrons from the anode and cathode, respectively. The transport and recombination of these charge carriers results in the emission of light at low operating voltages and leads to better power conversion efficiencies [11, 12,18].

Among the reported phosphorescent iTMCs, cyclometalated iridium(III) complexes are considered the most efficient and versatile triplet emitters for LECs, because of their excellent thermal stability, tunable emission color, and relatively short excited state lifetime [19–26]. Cationic iridium complexes can be easily synthesized and purified with very high yields, even close to the theoretical yield. Their large ligand field splitting and strong spin-orbit coupling produces efficient intersystem crossing from the singlet excited state to the triplet manifold, which enhances quantum efficiency. Cationic iridium complexes have the general formula [Ir(C<sup>−</sup>N)<sub>2</sub>(N<sup>−</sup>N)]<sup>+</sup>, where C<sup>−</sup>N is an anionic cyclometalating ligand and N<sup>−</sup>N is a neutral ancillary ligand. By tailoring

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the structures of the C<sup>^</sup>N and N<sup>^</sup>N ligands, the emission color of iridium complexes can be controlled over the visible spectrum from blue to red [26–28]. In the archetypical complex, [Ir(ppy)<sub>2</sub>(bpy)]PF<sub>6</sub>, the highest occupied molecular orbital (HOMO) is located on the phenyl rings of ppy and the iridium ion, whereas the lowest unoccupied molecular orbital (LUMO) is centered on the ancillary bpy ligand [9]. Thus, color tuning can be achieved by changing substituents on the cyclometalating ligand, which alters the HOMO energy, whereas changes on the ancillary ligand alter the LUMO energy [9].

Recently, iridium complexes have been modified to emit light in the blue region, because few blue emitters based on charged iridium complexes have been reported so far [6]. Moreover, white LEDs can be constructed from a combination of blue- with green- and red-emitting iridium complexes [23]. Thus, the design of blue-emitting heteroleptic iridium complexes is highly desirable. One strategy is to attach electron withdrawing substituents such as —F, —CF<sub>3</sub>, and —SO<sub>2</sub>R to the phenyl groups of cyclometalating ligands, which stabilizes the HOMO. The second tactic is to attach electron donating groups (—NR<sub>2</sub>) to the ancillary ligands, which destabilizes the LUMO. Both approaches widen the HOMO-LUMO gap resulting in light emission in the blue region.

In this paper, we report the synthesis and photophysical and electrochemical properties of a series of cationic iridium complexes, [Ir(ppy)<sub>2</sub>(mplexd)]PF<sub>6</sub> (**1**), [Ir(dfppy)<sub>2</sub>(mplexd)]PF<sub>6</sub> (**2**), [Ir(piq)<sub>2</sub>(mplexd)]PF<sub>6</sub> (**3**), and [Ir(pq)<sub>2</sub>(mplexd)]PF<sub>6</sub> (**4**) by incorporating the ancillary 5-methyl-3-(2-pyridyl)-1,2,4-oxadiazole (mplexd) ligand into dichloro-bridged iridium dimers containing the cyclometalating 2-phenylpyridine (Hppy), 2-(2,4-difluorophenyl)pyridine (Hdfppy), 1-phenylisoquinoline (Hpiq), and 2-phenylquinoline (Hpq) ligands, respectively. Photoluminescence (PL) emission spectra demonstrate that the emission color of the complexes can be systematically tuned from yellow-orange to blue by selective design of the organic ligands. We performed density functional theory (DFT) and time-dependent DFT (TDDFT) calculations on complexes **1**, **2**, **3**, and **4**. The experimental photophysical and electrochemical properties were confirmed by the computations.

## 2. Experimental section

### 2.1. Materials and methods

All reactants and solvents were purchased from commercial sources and used without further purification unless otherwise stated. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded with a Varian Unity Inova 500 MHz FT-NMR spectrometer in CD<sub>2</sub>Cl<sub>2</sub> with tetramethylsilane (TMS) as internal standard. Elemental analyses were performed with an Elemental Vario EL CHN elemental analyzer. Electrospray ionization mass spectrometry (ESI-MS) analyses were obtained on an Agilent Q-TOF 6530 MS/MS system using dichloromethane as matrix solvent. Absorption and photoluminescence (PL) emission spectra of the complexes (10<sup>-5</sup> M) were measured in deaerated acetonitrile solution at room temperature using an Agilent 8453 spectrophotometer and an F-7000 FL spectrophotometer, respectively. The PLQYs were calculated in acetonitrile solutions with quinine sulfate (Φ<sub>p</sub> = 0.545 in 1 M H<sub>2</sub>SO<sub>4</sub>) as the standard. The PL decay lifetimes were measured in acetonitrile solution using a compact photoluminescence lifetime spectrometer. The thin film PL spectra were made on quartz substrates by spin coating the complexes in acetonitrile solution (10<sup>-3</sup> M) with a thickness of about 100 nm. The PL quantum yields of thin films were also calculated using 9,10-diphenylanthracene (Φ<sub>p</sub> = 0.90 in cyclohexane) as the external reference. Cyclic voltammetry (CV) was performed using an Ivium potentiostat/galvanostat in acetonitrile solution (10<sup>-3</sup> M). A 0.1 M solution of tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) served as supporting electrolyte. Potentials were referenced internally to the ferrocenium/ferrocene (Fc<sup>+</sup>/Fc) couple at a scan rate of 100 mV s<sup>-1</sup>. The electrolytic cell consisted of a glassy carbon working electrode, platinum wire counter electrode, and Ag/AgCl reference electrode. The

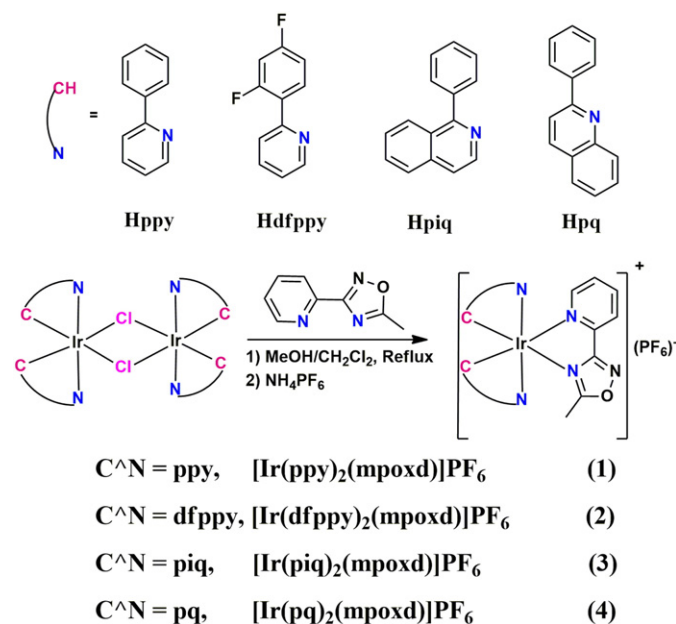
HOMO ( $E_{\text{HOMO}}$ ) and LUMO ( $E_{\text{LUMO}}$ ) energy levels and energy gaps ( $E_{\text{gap}}$ ) of the iridium complexes were calculated from the oxidation ( $E_{\text{ox}}$ ) and reduction ( $E_{\text{red}}$ ) potentials using the empirical formulae [29, 30]:  $E_{\text{HOMO}} = [-e(E_{\text{ox}}(\text{vs. Ag/AgCl}) - E_{1/2}(\text{Fc}^+/\text{Fc vs. Ag/AgCl}))] - 4.8 \text{ eV}$ ,  $E_{\text{LUMO}} = [-e(E_{\text{red}} - E_{1/2})] - 4.8 \text{ eV}$ , and  $E_{\text{gap}} = E_{\text{HOMO}} - E_{\text{LUMO}}$ , where  $E_{1/2}(\text{Fc}^+/\text{Fc vs. Ag/AgCl})$  is the redox potential of ferrocene (0.43 V).

### 2.2. Synthesis of cationic iridium complexes

The iridium complexes were prepared by first isolating the μ-dichloro iridium (III) dimers described by Nonoyama by refluxing 1.0 eq of IrCl<sub>3</sub>·xH<sub>2</sub>O with 2.3 eq of the cyclometalating Hppy, Hdfppy, Hpiq, or Hpq ligands in a mixture of 2-ethoxyethanol and water (3:1 v/v) for 24 h [31]. The [Ir(C<sup>^</sup>N)<sub>2</sub>(μ-Cl)]<sub>2</sub> dimers were then cleaved with mplexd at 60 °C under argon for 18 h to form the monomeric complexes as chloride salts followed by anion metathesis using ammonium hexafluorophosphate, NH<sub>4</sub>PF<sub>6</sub>. The cationic [Ir(C<sup>^</sup>N)<sub>2</sub>(N<sup>^</sup>N)]PF<sub>6</sub> complexes were obtained in good yield and characterized by <sup>1</sup>H NMR spectroscopy (ESI Fig. S1), elemental analysis, and mass spectrometry (ESI, Fig. S2). The synthetic steps with structures of the cyclometalating ligands and cationic complexes are shown in Scheme 1.

#### 2.2.1. Synthesis of [Ir(ppy)<sub>2</sub>(mplexd)]PF<sub>6</sub> (**1**)

[Ir(ppy)<sub>2</sub>Cl]<sub>2</sub> (108 mg, 0.1 mmol) and mplexd (37 mg, 0.23 mmol) were dissolved in dichloromethane (15 mL) and methanol (15 mL). The mixture was heated to reflux at 60 °C under argon for 18 h. The chloride solution of the complex was cooled to room temperature and subjected to ion exchange with solid NH<sub>4</sub>PF<sub>6</sub> (65 mg, 0.4 mmol). The solvent was removed under reduced pressure after stirring for 1 h at room temperature. The residue was dissolved in dichloromethane and filtered to remove insoluble inorganic impurities. The complex was precipitated by the addition of diethyl ether to the filtrate, which was then filtered and dried in a vacuum oven for 24 h. The crude material was crystallized from an acetonitrile/diethyl ether mixture. Yield: 137 mg, 0.17 mmol, 85%. <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ (ppm): 8.50 (d, *J* = 7.75 Hz, 1H), 8.21–8.14 (m, 1H), 8.01–7.95 (m, 4H), 7.88–7.83 (m, 2H), 7.76–7.70 (m, 2H), 7.60–7.56 (m, 1H), 7.52 (d, *J* = 5.11 Hz, 1H), 7.22–7.18 (m, 1H), 7.10–7.03 (m, 3H), 6.95–6.89 (m, 2H), 6.34 (d, *J* = 7.72 Hz, 1H), 6.26 (d, *J* = 7.62 Hz, 1H), 2.01 (s, 3H). <sup>13</sup>C NMR (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ (ppm): 168.3, 167.6, 151.9, 149.9, 146.6, 144.3.



**Scheme 1.** Chemical structures of cyclometalating ligands and synthetic routes to complexes **1–4**.

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