



# Design, synthesis, and properties of a series of charged iridium(III) complexes with a neutral bidentate ligand for deep-blue phosphorescent emitter



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## ABSTRACT

We herein report a series of charged iridium(III) complexes with a neutral bidentate ligand for blue phosphorescent emitter. A molecular design bearing a 2-(3,5-dimethyl-1H-pyrazol-1-yl)pyridine ligand proved suitable for efficient blue emission according to the comparison of photoluminescent properties of the complexes. Its Commission Internationale de L'Eclairage  $x,y$ -coordinates (CIE $x,y$ ) in solution was estimated to be (0.17, 0.18), indicating that the complex with the ligand is a promising candidate for deep-blue emitter. We further demonstrated that this complex displays blue electroluminescence by successfully integrating it in a light-emitting device.

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## 1. Introduction

Phosphorescent transition-metal complexes have been extensively studied due to their potential application, particularly in light-emitting devices such as organic light-emitting diodes (OLEDs) and light-emitting electrochemical cells (LECs) [1–3]. Phosphorescent iridium(III) complexes have attracted a great deal of attention because of their higher luminescence efficiency over fluorescent emitter, however, the blue-emitting phosphorescent complexes still have some drawbacks compared to their red and green counterparts. For instance, Flrpic, which is known as the standard blue emitter, has Commission Internationale de L'Eclairage  $x,y$ -coordinates (CIE $x,y$ ) of (0.16, 0.29) (Fig. 1, left) [4]. These coordinates correspond to a sky-blue (typically CIE $y$  > 0.2) and cannot be considered sufficient as deep-blue emission (CIE $y$  < 0.2). Although various types of complexes besides Flrpic have been investigated, the number of studies reporting sufficient deep-blue emitting complexes is limited so far [5]. Among these studies, a

major contribution is attributed to Lee et al. who have reported a new homoleptic iridium(III) complex, (dfppy)<sub>3</sub>Ir, bearing three 2',6'-difluoro-2,3'-bipyridine (dfppy) ligands [6]. Unlike Flrpic and its related complexes based on 2-(2,4-difluorophenyl)pyridine (dfppy) surrogate, the resulting complex exhibited deep-blue emission. The work has introduced a new ligand design, thereby pioneering the intensive investigations on its analogous complexes (Fig. 1, right) [7].

The neutral complexes such as Flrpic and (dfppy)<sub>3</sub>Ir can be used as emitting layers in light-emitting devices but require vacuum deposition process (dry process), which is typically standard in the current manufacturing process. Meanwhile, charged complexes are considered much more promising especially for large-area lighting and display applications due to some of their additional properties: (i) the presence of ionic species should facilitate electric charge injection from electrodes into the emission layers, and (ii) controllable solubility based on the structure of ligands as well as anion moiety enables solution process (wet process) fabrication of the devices. The processability from solution such as by inkjet printing has received broad attention due to its capability for large-area device manufacturing. During our initial studies focused on designing a structural motif for deep-blue emitter, we isolated a charged complex bearing two acetonitrile molecules as ligands, exhibiting bright sky-blue emission under UV irradiation (Scheme 1) [8]. This finding led us to envision a key structural motif of a new series of iridium(III) complexes for efficient blue emission.

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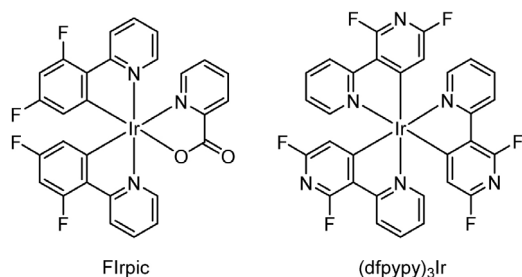


Fig. 1. Irpic and (dfppy)<sub>3</sub>Ir.

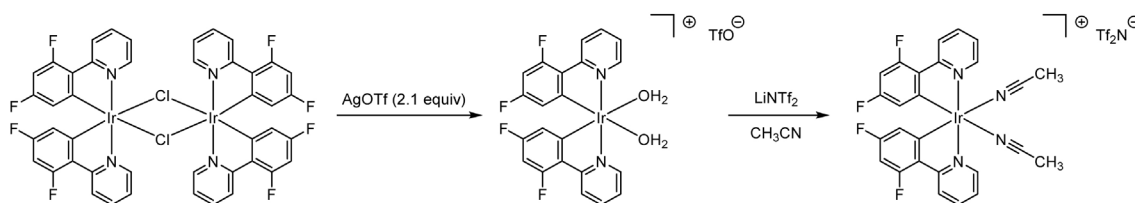
We herein demonstrate the synthesis of a series of charged iridium(III) complexes which have potential as blue phosphorescent emitters. Among them, the complex bearing two dfppy ligands and an *N,N*-bidentate ligand, that is 2-(3,5-dimethyl-1*H*-pyrazol-1-yl)pyridine, efficiently emitted to give an excellent blue color in solution. Although the use of 2-(1*H*-pyrazol-1-yl)pyridine ancillary ligands is previously reported, the emission colors of the corresponding iridium(III) complexes are sky-blue to green [9,10]. Furthermore, we demonstrate that this complex can be successfully integrated into light-emitting devices and therefore, not only exhibit highly efficient photoluminescence but also electroluminescence.

## 2. Results and discussion

### 2.1. Design and synthesis of charged iridium(III) complexes

We employed a structural motif of a heteroleptic Ir(III) complex composed of two monoanionic C,N-bidentate (C<sup>−</sup>N) ligands and another neutral X,Y-bidentate (X<sup>+</sup>Y) ligand according to our finding described above (Fig. 2).

Six new complexes shown in Fig. 2 were straightforwardly synthesized according to modified literature procedures (Scheme 2)



Scheme 1. Formation of a sky-blue emitting iridium(III) complex bearing two acetonitriles as ligands. Tf = trifluoromethanesulfonyl (triflyl), TfO<sup>−</sup> = trifluoromethanesulfonate (triflate).

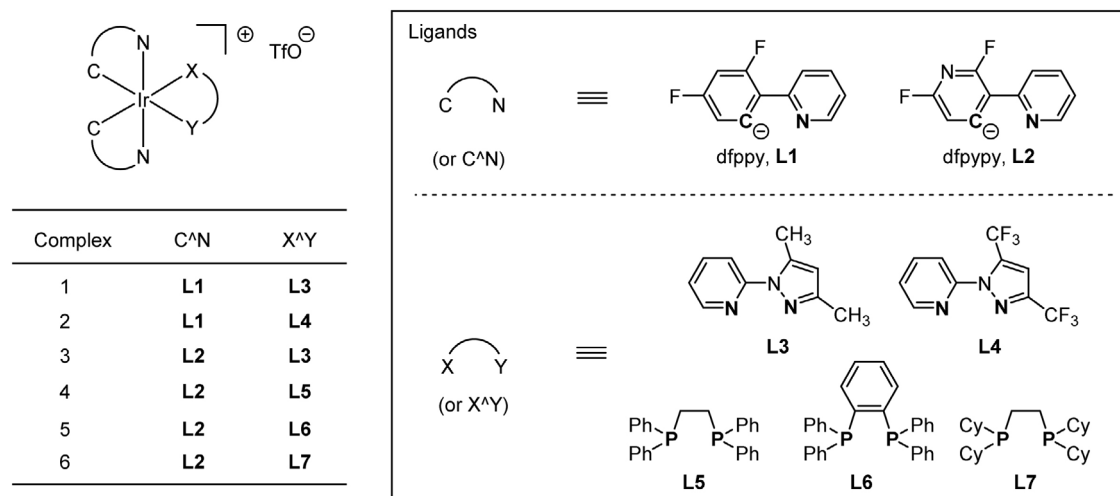


Fig. 2. Structure of charged iridium(III) complexes. Cy = cyclohexyl, Ph = phenyl. Emboldened atoms in L1–L7 would coordinate the iridium center.

[11,12]. Iridium(III) chloride trihydrate reacted with two equivalents of 2-(2,4-difluorophenyl)pyridine (dfppy, L1) or 2',6'-difluoro-2,3'-bipyridine (dfppy, L2) to afford chloro-bridged cyclometalated iridium(III) dimer [L<sub>2</sub>Ir(μ-Cl)]<sub>2</sub> (L = L1 or L2). Subsequent treatment with silver(I) trifluoromethanesulfonate followed by another X<sup>+</sup>Y ligand (L3–L7) yielded the charged complexes in moderate to good yields (28–80%) (See Section 4). For complexes 3 and 6, additional chromatographic procedures on their purification steps were needed to obtain spectroscopically pure sample and this might result in lower isolated yields (see Section 4 for details). These synthetic procedures are scalable, and we thereby readily prepared complex 3 in multi-gram quantities for the following studies.

All complexes showed certain moisture, air, and sunlight tolerances, enabling the storage under ambient conditions without any detectable decomposition. Complex 3, for example, was well soluble in the high boiling solvents such as *N,N*-dimethylformamide, *N*-methyl-2-pyrrolidone, and 1,2-dichloroethane whereas toluene, xylene, cyclopentanone, and anisole have poor to moderate solubility. On the basis of HPLC/MS analysis, we have concluded that complex 3 used in this study contained no detectable impurities.

### 2.2. Properties of charged iridium(III) complexes

Studies on photoluminescent properties of *N,N*-coordinated complexes have revealed that 3 composed of two L2 and one L3 ligands is a promising candidate for deep-blue emitter. Comparison of complexes 1 and 2 bearing different X<sup>+</sup>Y ligands indicated that the emission wavelengths of 1 was much bluer than that of 2, emphasizing that the electron-rich L3 would contribute to bluer emission compared to the electron-deficient L4 (Fig. 3).

Another study featuring the effect of C<sup>−</sup>N ligands highlighted the superior contribution of L2 over L1 in regard to both bluer color emission and enhanced photoluminescent quantum yield (PLQY).

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