



# Deep-blue phosphorescent iridium(III) dyes based on fluorine-functionalized bis(2,3'-bipyridyl) ligand for efficient organic light-emitting diodes



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## ABSTRACT

Four blue phosphorescent complexes with the general formula **(4-R-dfppy)<sub>2</sub>Ir(L<sup>+</sup>X)**, where **4-R-dfppy** = 4-alkyl-2',6'-difluoro-2,3'-bipyridine and **L<sup>+</sup>X** = picolinate or dipivaloylmethanate, were synthesized, and their photoluminescent properties were systematically investigated. All complexes show bright deep-blue phosphorescence emissions with  $\lambda_{\text{max}} = 440\text{--}450$  nm and quantum efficiencies of 0.25–0.78 in the fluid state. The emission bands of compounds **1–4** are slightly red shifted by 5–10 nm relative to the homoleptic congener, **Ir(dfppy)<sub>3</sub>**. Electroluminescent (EL) devices were fabricated using compound **2** as a dopant, 1,3-bis(N-carbazolyl)benzene (mCP) as the host, and TSP01 (diphenylphosphineoxide-4-(triphenylsilyl)phenyl) as the electron transporting/exciton blocking layer. These EL devices show a deep-blue color (CIE:  $x, y = 0.14, 0.17$ ) with high efficiencies. The EL device of compound **2** at a doping level of 5 wt% has the best performance with an EQE of 14.6% at a brightness of 100 cd/m<sup>2</sup> and a current efficiency of 18.3 cd/A.

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## 1. Introduction

Recently, there has been much focus on cyclometalated iridium(III) compounds bearing a fluorinated bipyridine ligand (**dfppy** = 2',6'-difluoro-2,3'-bipyridine) due to their excellent external quantum efficiencies in blue phosphorescent organic light-emitting diodes (PHOLEDs) [1]. Compared to other iridium compounds with chelating C<sup>+</sup>N ligands, bipyridine-based iridium (III) compounds have displayed significantly blue-shifted emissions, which is attributed to the electronegative pyridine ring [2]. Therefore, significant effort has been directed toward developing blue phosphorescent iridium compounds using bipyridine as a main ligand [3]. The introduction of substituents onto the main chelated ligand is considered an important step to achieving blue to red emission in C<sup>+</sup>N-based Ir(III) compounds [4]. For example,

increasing the HOMO-LUMO energy gap in the Ir(ppy)<sub>3</sub> system, where ppy = phenylpyridine, can be accomplished by introducing electron-withdrawing substituents onto the phenyl-rings and electron-donating substituents onto the pyridyl-rings. In addition, the energy gap can also be adjusted by the simple modification of bidentate ancillary ligands L<sup>+</sup>X (monoanionic chelate ligand). Ha et al. recently reported on a series of iridium compounds with fluorinated bipyridines as the main ligand and the effects of these substituents on the optical and electroluminescent properties [5]. However, the electroluminescent characteristics and structural characterization of these compounds have not been fully evaluated due to their lack of stability. Moreover, the substituents effect on the phosphorescent properties of bipyridine based iridium compounds has so far never been reported. The development of a variety of iridium compounds is still required to understand the origin of this emission, as well as to gain the ability to tune emission energy by adding substituents to the main or ancillary ligands. These facts prompted us to develop new heteroleptic iridium(III) compounds possessing different substituents on one of the pyridine rings in

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the main bipyridine ligand and to investigate the effect of the substituents on the photoluminescent and electroluminescent properties. Here, we describe the results of our investigation including the preparation, crystal structure, and photophysical properties of a series of iridium compounds.

## 2. Result and discussion

### 2.1. Synthesis and crystal structure

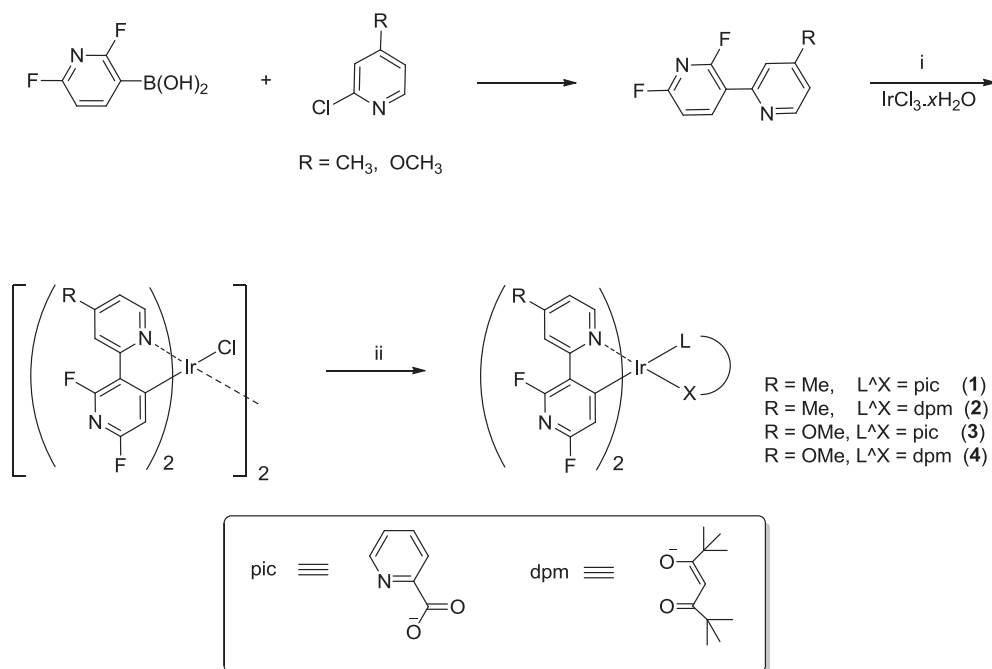
The synthetic route and details for **1–4** are shown in Scheme 1. The cyclometalated dimer  $[(4\text{-alkyl-dfpypy})_2\text{Ir}(\mu\text{-Cl})_2]$  was prepared by the typical procedure reported by Nonoyama [6]. Subsequently, the chloride of this Ir(III) dimer was substituted by  $\beta$ -diketonate or picolinic acid in the presence of sodium carbonate in THF/MeOH at ambient temperature. The yields of compounds **1–4** are moderate to high (60–90%). All compounds are very stable in air and were fully characterized by NMR and elemental analysis. The structure of **1** was established by single-crystal X-ray diffraction analysis and is shown in Fig. 1a.

As expected, compound **1** has a distorted octahedral geometry around the iridium center with an *N,N-trans-mer* structure. The bond lengths of Ir–C, Ir–N and Ir–O for **1** are within the range reported for those of the related compound,  $(\text{dfppy})_2\text{Ir}(\text{pic})$  [7]. Interestingly, the bond lengths of Ir–C and Ir–N between iridium metal and the main dfppy ligand are shorter than those of  $(\text{dfppy})_2\text{Ir}(\text{pic})$  without any substituents in the pyridine ring, which is datively bound to the iridium metal ion. This result may be attributed to the greater electron-donating effect exerted by the methyl substituent of dfppy, compared with the non-substituted dfppy. There are several strong intermolecular interactions including  $\pi$ – $\pi$  interactions and hydrogen bonding via  $\text{C}(\pi)\text{-H}\cdots\text{F}$ ,  $\text{C}(\pi)\text{-H}\cdots\text{O}$  and  $\text{C}(\pi)\text{-H}\cdots\text{N}$  in the crystal lattices of **1**, as shown in Fig. 1b. Such strong intermolecular interactions help stabilize the crystal packing structure. The structural parameters and details for the intermolecular interactions can be found in the Supporting Information.

### 2.2. Photophysical and electrochemical properties

The absorption and emission spectra of **1–4** are presented in Fig. 2. For all compounds, intense absorption bands ( $\epsilon > 30,000 \text{ M}^{-1} \text{ cm}^{-1}$ ) ranging from 250 to 300 nm are observed, indicating that the electronic transitions of **1–4** are mostly spin-allowed  $\pi$ – $\pi^*$  originating from the main ligands. Additional weak absorption at longer wavelengths (360–380 nm) with smaller molar extinction coefficients ( $\epsilon > 5000 \text{ M}^{-1} \text{ cm}^{-1}$ ) can be attributed to singlet metal-to-ligand charge transfer ( $^1\text{MLCT}$ ) transitions. The long tail extending into visible region is assigned to a mixed state involving both spin–orbit coupling enhanced triplet ligand-centered ( $^3\text{LC}$ ) and  $^3\text{MLCT}$  transitions. However, the  $^3\text{MLCT}$  bands above 400 nm can barely be observed in all cases, compared to that of Irpic.

Compounds **1** and **3** show bright deep-blue and well-structured emission bands in solution at room temperature, with  $\lambda_{\text{max}} = 445$  and 442 nm, while compounds **2** and **4** display featureless and red-shifted emissions with weak shoulders at 476 and 477 nm. The highly structured emission bands observed for **1** and **3** mainly originate from the  $^3\pi$ – $\pi^*$  state. However, broad and featureless emissions for **2** and **4** can be mostly attributed to the metal-to-ligand charge transfer ( $^3\text{MLCT}$ ) transition based on previous reports [4b]. The emission characteristics in the range of 400–500 nm for all compounds were examined to investigate substituent effects in the main dfppy ligand. Compounds **3** and **4**, bearing the electron-donating methoxy group at the 4-position in the pyridine ring, showed slightly blue-shifted (*ca.* 1–5 nm) emissions with respect to similar methyl-substituted counterparts. This observation shows that a different electron-donating group, such as methyl or methoxy, at the 4-position in one of the pyridine rings does not significantly affect emission profiles (see the emission profiles of **1** and **3** or **2** and **4** in Fig. 2). However, when a  $\beta$ -ketonate ancillary is replaced by a picolinate, a 10-nm blueshifted emission is observed. Therefore, the phosphorescent emission is strongly dependent on the nature of the ancillary ligand compared to that of the substituent at the 4-position of the pyridine ring.



**Scheme 1.** Reagents and Conditions: i) 2-ethoxyethanol, 140 °C, 24 h ii) Na<sub>2</sub>CO<sub>3</sub>, picolinic acid or 2,2,6,6-tetramethyl-3,5-heptanedione(dpm), RT, overnight.

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