



## Note

## Two new blue-phosphorescent Ir(III) cyclometalated complexes demonstrating the pushing-up effects of amino on levels of Pi-type molecular orbitals



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## ABSTRACT

Orbital interactions between nitrogen's 2p-orbital, 2p(N), and the higher-lying HOMO/LUMO would push-up the latter even higher. This destabilization effect exerted by an amino explains the high-lying LUMO of the 2,2'-dipyridyl amine (HDP A) ancillary ligand, as well as the high-lying LUMO in Ir(ppy)<sub>2</sub>-HDP A<sup>+</sup> (ppy = 2-phenylpyridine). The pi-destabilization effect on MOs exerted by a fluoro must be incorporated into consideration to explain the site-dependent characteristics observed by related color-tuning studies. Two new blue phosphorescent fluorinated Ir(ppy)<sub>2</sub>HDP A<sup>+</sup> complexes have been synthesized by introducing fluoro(s) at suitable phenyl-carbon(s): having small 2p<sub>π</sub>(C) content in HOMO and/or large 2p<sub>π</sub>(C) content in LUMO.

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## 1. Introduction

Color-tuning of luminescent Ir(III) cyclometalated complexes has attracted numerous research efforts made to obtain blue-emission materials [1]. Since the broad tunable emission-range was achieved for Ir(ppy)<sub>3</sub> (ppy = 2-phenylpyridine) by using chemical substitution tactics [2], the fine color-tuning of ppy-based Ir(III) complexes carried out with various substituents/positions has been intensively studied [1–4]. Fluoro is one of the most popular substituents under study. However, the tuning results exhibiting position-dependent nature remain unclearly explained in view of the pushing-up effect on HOMO found for vinyl fluoride [5]. Blue-shifted emission can also be accomplished by changing the ancillary ligands (L<sub>NN</sub>) [1,3] in Ir(ppy)<sub>2</sub>L<sub>NN</sub> complexes. We have been interested in synthetic and photophysical studies using 2,2'-dipyridyl amine (HDP A) as L<sub>NN</sub> [6]. Compared to most other L<sub>NN</sub> under study, such as 2,2'-bipyridine(bpy) [7], the LUMO in Ir(ppy)<sub>2</sub>HDP A<sup>+</sup> (complex 1) had shown higher-energy through electrochemical data, leading to higher luminescent energy (LE) [6].

This advantage of HDP A has recently been further confirmed [8]. In the present study, Density Functional Theory (DFT) calculations have been carried out to search for quantum-mechanical rationalizations of the high-LUMO found for Ir(ppy)<sub>2</sub>HDP A<sup>+</sup> and the position-dependent tuning effects of fluorination. Two fluorinated Ir(ppy)<sub>2</sub>-HDP A<sup>+</sup> have then been synthesized in this work. It is also our goal to clarify the emission type of those complexes through photophysical studies and time-dependent DFT (TD-DFT) calculations.

## 2. Experimental and calculation methodology

Both C4'-fluoro-Ir(ppy)<sub>2</sub>HDP A<sup>+</sup> (complex 2) and C4',C6'-di-fluoro-Ir(ppy)<sub>2</sub>HDP A<sup>+</sup> (complex 3) as shown in Fig. 1 were synthesized and subjected to photophysical and electrochemical studies. Complex 1 was also synthesized to re-measure the quantum yield in order to clarify the emission-type. Detailed synthetic procedures, together with the materials and instruments in use, and computational methods are presented in the [Supplementary Info](#). The spectroscopic data and elemental analysis results are also available therein. The ORTEP drawings of 2 and 3 are given in [Figs. S1 and S2](#), respectively. Detailed crystallographic data and geometry parameters are contained in [Tables S1 and S2](#), respectively. Emission wavelengths measured in two different solvents are given in [Table S3](#).

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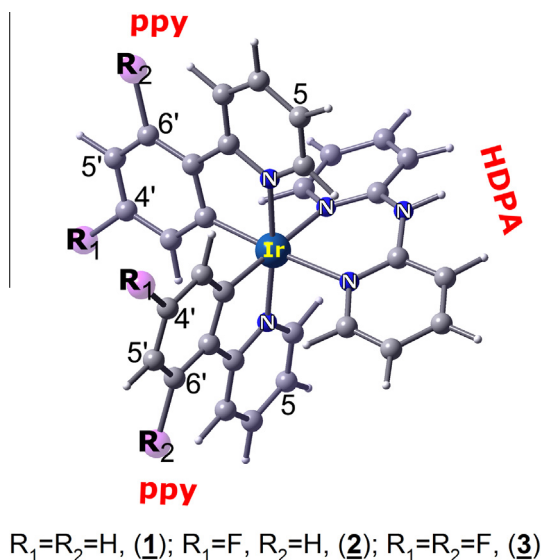


Fig. 1. Numbering of atoms in Ir(ppy)<sub>2</sub>HDPA<sup>+</sup>.

### 3. Results and discussion

The oxidation potentials increase from 0.88 V recorded for **1** to 1.07 V for **2**, and further to 1.26 V for **3** (see Table 1), indicating the HOMO-levels drop sequentially due to fluorination. The higher reduction potential of **1** (−1.91 V), compared to the bpy-analogue (−1.77 V) [7], manifests the higher-lying LUMO. The reduction potentials obtained for **2** and **3** reveal that both LUMO-levels are lowered by 0.13 V. These electrochemical data indicate that (1) the HOMO–LUMO gaps increase sequentially on going from **1** to **3** and (2) lowering of HOMO is more responsible for broadening the HOMO–LUMO gaps in **2** and **3**. The latter is well expected by the “composition” analysis, which implies that the phenyl component (subjected to fluorination) is more abundant in HOMO than in LUMO. A more insight look derived from composition analysis is termed as “carbon content” analysis: the contribution of phenyl carbons subjected to fluorination to the MO in consideration (*vide infra*). The phosphorescent profiles of all three complexes are collectively presented in Fig. 2. The phosphorescent energies expressed in the wave-length at maximum intensity ( $\lambda_{em}$  in Table 1) decrease from 482 nm for **1** to 469 nm for **2**, and further to 458 nm for **3**. The value of emission maximum obtained for **1** indicates a higher luminescent energy (LE) than corresponding

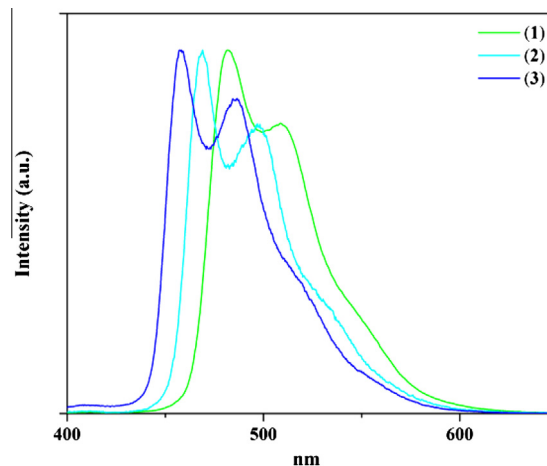


Fig. 2. Normalized emission spectra of complexes **1–3** measured in dichloromethane.

bpy-complex (606 nm) [7], a result in echo with the high-LUMO tactic of changing  $L_{NN}$  employed for color-tuning [1]. In addition to blue emission of **3**, the high quantum yield high (0.72) is noteworthy. The blue-shifted LEs of **2** and **3** are in positive response to the color-tuning technique, stated by “using electron-withdrawing substituent to lower HOMO” [1,4]. For complex **1**, observations of small Stokes shift (see Table 1, as well as Tables 3 and 4 in Ref. [5]) and lacking of solvatochromism (see Table S3) suggest that the triplet ligand-center (<sup>3</sup>LC) emissive process prevails, which is consistent with the structured phosphorescence [3].

TD-DFT results of LE presented in Table 2 (detailed calculational methods are available in Supplementary Info) well predict the experimental data in view of the extents of blue-shift due to fluorination(s). The lowest triplet state ( $T_1$ ) obtained for **1** consists of configurations described by: HOMO → LUMO + 1, HOMO-2 → LUMO + 1, HOMO-1 → LUMO + 2, HOMO-1 → LUMO + 3. Unlike Ir(ppy)<sub>2</sub>bpy<sup>+</sup> [7], LUMO in **1** plays negligible role of optical MO. Since all optical MOs in  $T_1$  are mixed significantly with ppy (see Fig. 3), the <sup>3</sup>LC(ppy)-dominant emission consists with the above-stated photophysical data. The high-lying LUMO is so close in energy to LUMO + 1, as well as to LUMO + 2 and LUMO + 3, that the LC-favor [9] turns out to be more competitive. The <sup>3</sup>LC dominant emissive type can be more explicitly appreciated by examining the drawings of the Electron Density Different Maps (EDDM) [10], a summarized-drawing of the  $T_1$ , shown in Fig. 3. The

Table 1  
Photophysical and electrochemical data of complexes.

Complex	Oxidation $E_{1/2}$ or $E_a/V^a$	Reduction $E_c/V^a$	$\lambda/nm$ ( $10^{-4} \epsilon/M^{-1} \text{cm}^{-1}$ ) <sup>b</sup>	$\lambda_{em}/nm^c$	$\Phi_{em}^d$
[Ir(ppy) <sub>2</sub> (HDPA)](PF <sub>6</sub> ) ( <b>1</b> )	+0.88 <sup>e</sup>	−1.91 <sup>f</sup>	452[sh] (0.02), 422[sh] 0.14, 385[sh] (0.30), 344[sh] (0.48), 316 (1.2), 272[sh] (2.9), 256 (3.5)	482, 509 <sub>sh</sub>	0.70 <sup>g</sup>
[Ir(fppy) <sub>2</sub> (HDPA)](PF <sub>6</sub> ) ( <b>2</b> )	+1.07 <sup>e</sup>	−1.78 <sup>f</sup>	396[sh] (0.48), 370[sh] (0.83), 310[sh] (3.1), 268 (6.1), 254 (6.7)	469, 496 <sub>sh</sub>	0.21 <sup>g</sup>
[Ir(dfppy) <sub>2</sub> (HDPA)](PF <sub>6</sub> ) ( <b>3</b> )	+1.26 <sup>f</sup>	−1.78 <sup>f</sup>	450[sh] (0.12), 368 (0.63), 300 (2.6), 250 (5.3)	458, 486 <sub>sh</sub>	0.72 <sup>g</sup>

<sup>a</sup> Deviations are in hundredth of volt.

<sup>b</sup> Absorption spectra recorded in CH<sub>2</sub>Cl<sub>2</sub> at 298 K.

<sup>c</sup> Emission spectra recorded in CH<sub>2</sub>Cl<sub>2</sub> at 298 K.

<sup>d</sup> fac-Ir(ppy)<sub>3</sub> as referenced standard (0.4).

<sup>e</sup> Reversible wave.

<sup>f</sup> Irreversible wave.

<sup>g</sup> This work. Our earlier value reported for complex **1** (0.43, Ref. [6]) was underestimated.

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